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**Nanomaterial Case Study:  
A Comparison of Multiwalled Carbon Nanotube and  
Decabromodiphenyl Ether Flame-Retardant Coatings  
Applied to Upholstery Textiles (DRAFT)**

*July 2012*

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U.S. Environmental Protection Agency  
Washington, DC

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# Key Terms

Upholstery textiles	Fabric or cloth material that is fixed to furniture (e.g., chairs), mattresses or transportation industry components (e.g., seating, roof linings)
Flame retardant	A chemical or other manufactured material that has the ability to inhibit the combustion process and increase the resistance of textile products to degradation associated with fire and flame.
DecaBDE	The only polybrominated diphenyl ether (PBDE) that is fully brominated (i.e., all available hydrogen atoms in the diphenyl rings have been substituted with bromine atoms) and therefore exists as a single isomer (see BDE-209); commercial formulations of decaBDE may contain trace amounts of lower brominated congeners (e.g., nona- or octaBDEs) as impurities
BDE-209	The single isomer of deca-substituted BDE (see DecaBDE) named as the final of the 209 possible congeners of PBDE (many lower brominated PBDEs [e.g., heptaBDE] are composed of many different congeners based on the exact position of the bromine atoms in the chemical conformation)
Multiwalled carbon nanotube	Hollow nanoscale (i.e., with one or more dimensions in the range of approximately 1–100 nm) tubes composed of multiple concentrically nested graphene sheets

# Abbreviations

ADME	Absorption, Distribution, Metabolism, Excretion
BAF	Bioaccumulation Factor
BDE	Brominated Diphenyl Ether
BFR	Brominated Flame Retardant
BMF	Biomagnification Factor
CEA	Comprehensive Environmental Assessment
CNF	Carbon Nanofiber
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DIN	Deutsches Institut für Normung (Germany)
EC50	Median Effective Concentration
EPA	U.S. Environmental Protection Agency
GD	Gestation Day
$K_{ow}$	Octanol Water Partition Coefficient
LCA	Life-cycle Assessment
LOAEL	Lowest-observed-adverse-effect Level
LRT	Long-range Atmospheric Transport
MRL	Minimal Risk Level
MWCNT	Multiwalled Carbon Nanotube
Nanomaterials	Nanoscale materials
$nC_{60}$	Nanofullerenes
NIOSH	National Institute for Occupational Safety and Health
NMAM	NIOSH Manual of Analytical Methods
NOAEL	No-observed-adverse-effect Level
NOM	Natural Organic Matter
NTP	National Toxicology Program
OEL	Occupational exposure limit
PBDD	Polybrominated Dibenzo-p-dioxin
PBDE	Polybrominated Diphenyl Ether
PBDF	Polybrominated Dibenzofuran
PCB	Polychlorinated Biphenyl
PEC	Predicted Environmental Concentration

PMMA	Polymethyl Methacrylate
PMN	Premanufacturing Notice
PND	Postnatal Day
R&D	Research and Development
REL	Recommended Exposure Limit
RfD	Reference Dose
RfC	Reference Concentration
SWCNT	Single-walled Carbon Nanotube

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# Preface

1           This document is part of continuing efforts by the U.S. Environmental Protection Agency (EPA)  
2 to understand the scientific issues and information gaps associated with nanotechnology, consistent with  
3 recommendations in the U.S. EPA *Nanotechnology White Paper* ([2007](#)) and U.S. EPA *Nanomaterial*  
4 *Research Strategy* ([2009a](#)). While no national or international consensus definition yet exists for  
5 nanomaterials, a current working definition is a material having at least one dimension on the order of  
6 approximately 1 to 100 nm ([NSTC, 2011](#)). Materials are intentionally engineered at the nanoscale to  
7 exploit the unique or novel properties that can arise from their small size.

8           The specific nanomaterials considered in this document are multiwalled carbon nanotubes  
9 (MWCNTs), as incorporated into flame-retardant coatings for upholstery textiles. This case study does  
10 not represent a completed or even preliminary assessment, nor is it intended to serve as a basis for near-  
11 term risk management decisions on possible uses of MWCNTs. Rather, the intent is to describe what is  
12 known and unknown about MWCNTs in this selected application as part of a process to identify and  
13 prioritize scientific and technical information to support future assessment and risk management efforts.  
14 Previous EPA case studies focused on nanoscale titanium dioxide used in drinking water treatment and in  
15 topical sunscreen ([U.S. EPA, 2010d](#)) and nanoscale silver in disinfectant spray ([U.S. EPA, 2010e](#)).

16           Like the previous case studies, this case study of MWCNTs is based on the comprehensive  
17 environmental assessment (CEA) approach, which consists of both a framework and a process. Unlike  
18 previous case studies, however, this case study incorporates information about a traditional (i.e., “non-  
19 nanoenabled”) product, against which the MWCNT flame-retardant upholstery coating (i.e., the “nano-  
20 enabled” product) can be compared. The comparative element serves dual purposes: 1) to provide a more  
21 robust database as a foundation from which to identify data gaps related to the nano-enabled product and  
22 2) to provide a context for identifying key factors and data gaps related to assessing the risk-risk and risk-  
23 benefit trade-offs between a nano-enabled and non-nanoenabled product.

24           The organization of this document reflects the CEA framework, the principle elements of which  
25 are described in Chapter 1 of this document and represented in Chapter 2 through Chapter 5. After a  
26 general introduction to the materials and selected application in this case study (Chapter 1), Chapter 2  
27 highlights stages of the product life cycles (i.e., research and development, feedstock processing,  
28 manufacturing, storage and distribution, use, and reuse and disposal) for both the traditional and nano-  
29 enabled products. Chapter 2 also identifies which stages in each of the product life cycles present

1 opportunities for releases to the environment. Chapter 3 then provides information on the transport,  
2 transformation, and fate processes affecting the behavior of the traditional materials, nanomaterials, by-  
3 products, and transformation products in environmental compartments. Chapter 4 characterizes exposure,  
4 uptake, and dose for the traditional materials, nanomaterials, by-products, and transformation products for  
5 different human populations (e.g., workers, general public, consumers, and susceptible populations), and  
6 ecological receptors, after which Chapter 5 describes the human health, ecological, and other impacts  
7 related to those exposures.

8 Collectively, these chapters represent the assembly of information across the vertical spectrum of  
9 the CEA framework (Figure 1-1); however, as outlined in Chapter 1, this is merely the first step in the  
10 CEA process (Figure 1-2). Next, a group of expert stakeholders representing a variety of technical  
11 backgrounds (e.g., analytical chemistry, toxicology, atmospheric science) and sectors (e.g., industry,  
12 academia, nongovernment organizations) will use this document as a starting point for identifying and  
13 prioritizing research needs to support near-term risk management goals for MWCNTs in flame-retardant  
14 textile coatings. As described in more detail in Chapter 6, this step will result in a prioritized list of  
15 research questions that, if pursued, will inform risk assessments and subsequent risk management  
16 decisions for MWCNTs in flame-retardant textile coatings. This next step supports the subsequent steps  
17 of the CEA process, which involve an iterative communication flow across the continuum of research,  
18 risk assessment, and risk management.

# Executive Summary

1           As part of an ongoing effort to identify research needs and data gaps in assessing the broad  
2 environmental implications of nanomaterials, this case study focuses on a specific nanomaterial in a  
3 particular application, multiwalled carbon nanotubes (MWCNTs) in flame-retardant coatings applied to  
4 upholstery textiles. To facilitate the identification of key data gaps related to assessing MWCNTs in this  
5 application, this case study provides a comparative perspective by also presenting information on a  
6 traditional flame retardant, decabromodiphenyl ether (decaBDE). Like previous case studies of nanoscale  
7 titanium dioxide and nanoscale silver, this case study is built on the comprehensive environmental  
8 assessment (CEA) approach, which consists of both a framework and a process. The CEA framework  
9 (Figure 1-1) starts with the inception of a material and encompasses environmental fate, exposure-dose,  
10 and impacts. In addition, the framework incorporates the variety of factors that can influence each aspect  
11 of the framework, including differences in environmental media and the physical, chemical, biological,  
12 and social conditions in which the material occurs. Here, the framework is used to systematically organize  
13 information about decaBDE and MWCNTs in the case study. This information does not represent a  
14 completed or even preliminary assessment; rather, it will serve as the basis for identifying and prioritizing  
15 data gaps and research needs for MWCNTs and other nanomaterial assessments. The prioritized research  
16 gaps that emerge are intended to inform decision-makers in the U.S. Environmental Protection Agency  
17 (EPA) and the broader scientific community in developing research agendas that support future risk  
18 assessment and risk management goals.

19           Given the purpose of the document, this case study does not purport to be a comprehensive  
20 literature review; rather, available sources were incorporated to specifically support the identification and  
21 prioritization of data gaps, as described above. The most recent literature search for this case study was  
22 conducted on May 11, 2012 using specific criteria to search PubMed, Academic Search Complete,  
23 Environment Complete, and CINAHL for records published since November 2011, and Web of Science  
24 for records published since January 2012. Search terms included carbon nanotube\*, carbon nanofiber\*,  
25 CNT\*, CNF\*, MWNT\*, MWCNT\*, and SWCNT\*.

## Chapter 1: Introduction to this Document

26           Production and importation of decaBDE is currently being phased out in the United States as a  
27 result of voluntary commitments within the industry and EPA actions in response to concerns regarding  
28 potential human health and ecological impacts. As a result, a range of alternative flame-retardant  
29 technologies, including nanotechnologies, are being evaluated as potential replacements for this



1 extensively used material. Thus, this document presents information on a potential alternative flame-  
2 retardant technology, MWCNT, to begin the process of identifying and prioritizing research gaps that  
3 would support future assessments of this product. Information on decaBDE is provided alongside  
4 available information on MWCNT for two purposes: 1) to provide a relatively robust database against  
5 which data gaps for MWCNT may become more clear, and 2) to provide a basis for identifying key  
6 considerations for future efforts to evaluate risk-risk and risk-benefit trade-offs of replacing a traditional  
7 product like decaBDE with an alternative technology like MWCNTs (see Section 1.1). Together these  
8 two objectives support an overarching goal of CEA to effectively link research planning, risk assessment,  
9 and risk management by transparently planning research to support risk assessments that inform risk  
10 management decisions. Given that future evaluations of nano-enabled products such as MWCNT in  
11 flame-retardant textile coatings could involve the consideration of risk-related trade-offs (e.g., thyroid  
12 health effects versus pulmonary health effects, environmental justice considerations versus energy costs),  
13 this document and subsequent steps of the CEA process (see Chapter 6) strive to identify and prioritize  
14 research that would support conducting assessments that can inform risk management decisions about  
15 such trade-offs for MWCNTs in flame-retardant textile coatings.

16 Many manufacturers choose to incorporate flame-retardant materials into textiles to comply with  
17 State, Federal, and industry fire-safety standards (i.e., certain flame test performance criteria that must be  
18 met). Once applied, flame retardants act to inhibit the combustion process through a variety of physical or  
19 chemical means (e.g., producing inert gases that dilute the oxygen supply available to the flame,  
20 producing protective char barriers) (see Section 1.2).

21 Both decaBDE and MWCNTs can be mixed with binding agents and applied as coatings to  
22 increase the flame resistance of upholstery textiles. In this application the two materials are both referred  
23 to as barrier technologies because both exhibit similar mechanisms of flame-retardant action: decaBDE  
24 forms a protective char barrier, and MWCNTs form a network floccules layer (i.e., network of loosely  
25 bound MWCNT bundles). The similar potential applications for decaBDE and MWCNTs support the  
26 justification for the comparison of the two materials as flame-retardant coatings in upholstery textiles and  
27 will inform the identification of data gaps related to assessing possible risks and benefits associated with  
28 MWCNTs. Moreover, the comparison of these materials can provide insight into MWCNT- and nano-  
29 specific factors that might influence future research directions for nanomaterials and nano-enabled  
30 products. For example, unlike decaBDE, the physicochemical properties of MWCNTs are often  
31 intentionally altered during synthesis; thus MWCNTs are not a single material with a defined set of  
32 characteristics, but rather a variety of materials—often present as mixtures—with vastly different  
33 physicochemical characteristics. Such variation in the physicochemical characteristics of MWCNTs

1 presents challenges in describing the releases, behavior, and effects of exposure to MWCNTs as a class of  
2 materials (see Section 1.3).

## Chapter 2: Product Life Cycle

3 Little information is available on the commercial production and use of MWCNT flame-retardant  
4 coatings, as few commercial-scale products currently exist. Although the research and development and  
5 manufacturing stages of decaBDE and MWCNT flame-retardant textile coatings appear to utilize  
6 different processes and production methods (see Sections 2.1 and 2.2), the storage/distribution (see  
7 Section 2.3), use (see Section 2.4), and reuse/recycling/end-of life stages (see Section 2.5) are anticipated  
8 to be very similar for upholstery textiles treated with decaBDE and MWCNT flame retardants.  
9 Upholstery textile products are expected to have a long lifespan and will likely be disposed of in  
10 municipal landfills or incineration facilities.

11 Based on the available data, releases of decaBDE and MWCNTs to the environment throughout  
12 the life cycle of decaBDE and MWCNT flame-retardant upholstery textiles are expected to occur. The  
13 phase out of decaBDE will likely result in smaller releases of decaBDE over time, while the projected  
14 increase in MWCNT production will likely result in increased environmental releases of MWCNTs.  
15 Releases of decaBDE throughout the lifecycle are anticipated to be in the free form, with some releases  
16 later in the life cycle occurring in the polymer or textile matrix-bound form. Most releases of MWCNTs  
17 in the manufacturing stages are anticipated to be in the free or bundled forms (see Footnote 1 in Chapter 2  
18 for an explanation of this terminology), while most releases later in the life cycle are anticipated to be in  
19 the polymer or textile matrix-bound form.

20 Air and water releases of decaBDE and MWCNTs during manufacturing do occur, especially  
21 during mixing, handling, and equipment cleaning, but releases are expected to be fairly well controlled  
22 when proper ventilation and environmental controls are in place. Air releases of both decaBDE and  
23 MWCNTs have been measured during material synthesis. Additionally, MWCNTs typically require  
24 purification and functionalization, which likely will result in further releases due to chemical and physical  
25 processing methods (see Section 2.2). Activities like textile and furniture processing might take place  
26 outside of closed systems and could result in environmental releases of decaBDE and MWCNTs.  
27 Abrasion, washing, unintended use, and accidental exposure to high heat or fire during the use life stage  
28 could result in releases of decaBDE and MWCNTs (see Sections 2.4 and 2.5).

29 Measured environmental concentrations of decaBDE in buildings with products containing  
30 decaBDE suggest that release occurs during the use stage; in fact, some analyses have suggested that  
31 release of decaBDE is expected to be greatest during the use stage. No similar concentration data  
32 resulting from consumer use currently exist for MWCNTs. The physical and chemical processes (e.g.,

1 shredding, milling, chemical treatment) used to recycle textiles could also lead to releases of decaBDE or  
2 MWCNTs. Air releases from land-filling of decaBDE and MWCNT flame-retardant upholstery could  
3 occur due to mixing and compacting, but decaBDE released as leachate may be unlikely due to its  
4 physicochemical properties. No data exist for MWCNTs, but release in leachate is possible if the product  
5 of polymer matrix degrades. Exposure to high heat or fires during incineration or any other stage (except  
6 at the sufficiently high temperatures of municipal incineration) could present the potential for airborne  
7 release of decaBDE and by-products such as polybrominated dibenzo-p-dioxins and polybrominated  
8 dibenzofurans. Incomplete incineration is one of the most likely airborne release scenarios for CNT  
9 textile coatings. However, preliminary experimental data suggest that MWCNTs may not be released to  
10 the environment when exposed to sufficiently high temperatures (see Sections 2.4 and 2.5).

### Chapter 3: Transport, Transformation, and Fate

11 Although decaBDE and MWCNTs are incorporated into polymer matrices after the flame-  
12 retardant production stage, little information exists that describes the environmental behavior of these  
13 polymer matrices. As a result, this chapter focuses on the transport, transformation, and fate of decaBDE  
14 and MWCNTs and not the polymer matrices in which they are incorporated. Studies evaluating decaBDE  
15 often use the single isomer of the material (BDE-209); both terms are therefore used throughout the  
16 document. The environmental behavior of BDE-209 will be dictated by its chemical and physical  
17 properties—including its high molecular weight, hydrophobicity, low vapor pressure, and lipophilicity—  
18 and its likelihood for biotic and abiotic transformation. A key transformation process for BDE-209 in the  
19 environment is debromination—a process by which bromine atoms are lost to form lower brominated  
20 congeners. Biotic debromination (by aerobic and anaerobic microorganisms) has been documented in soil,  
21 sediment, and sewage sludge. Abiotic debromination (by photolysis) has been demonstrated in air,  
22 surficial soils, water, and surficial sediment. These lower brominated degradation products are likely to be  
23 more readily bioavailable in environmental media than BDE-209. The environmental behavior of  
24 MWCNTs will also be dictated by their physical and chemical properties—in this case, surface area,  
25 surface chemistry, morphology (shape), solubility, presence or absence of functionalization and surface  
26 coatings (e.g., engineered coatings or natural organic matter), and hydrophobicity. The nanostructured  
27 morphology, small size, and high surface area-to-volume ratio of MWCNTs can enhance chemical  
28 reactivity and propensity of MWCNTs to form bundles; single MWCNTs, as compared to bundles, will  
29 differ in their behavior in the environment (see Section 3.1).

30 In air, BDE-209 will be primarily attached to particles and either deposit or stay suspended in the  
31 air and experience long-range transport. Recent literature regarding the behavior of airborne MWCNTs is  
32 extremely limited, and dominant fate, transport, and transformation processes for MWCNTs in indoor and

1 outdoor air are unknown. In general, BDE-209 will partition to particulates (e.g., suspended organic  
2 matter) in water and bind strongly to soils, sediments, and sludges, with limited mobility in these media.  
3 In aqueous media, the hydrophobicity and van der Waals interactions of pure MWCNTs suggest they will  
4 bundle together or sorb to particles and settle out onto sediment. However, environmental conditions can  
5 alter this behavior. For example the presence of dissolved organic matter has been shown to debundle  
6 MWCNTs causing to them to remain in solution. In terrestrial systems, MWCNTs have the propensity to  
7 adsorb to soil surfaces, which can make them less mobile. The presence of surface coatings can affect the  
8 sorption behavior of MWCNTs in these systems and influence their mobility, dispersion, and  
9 bioavailability in environmental media (see Sections 3.2, 3.3, and 3.4).

10 Multimedia models have been used to predict environmental fate and transport of BDE-209 and  
11 other polybrominated diphenyl ether (PBDE) congeners in environmental media. Scientists have  
12 demonstrated the use of simple, deterministic models and more complex probabilistic models to simulate  
13 movement of carbon nanotubes through environmental compartments and predict environmental  
14 concentrations in these compartments, but none specifically examined MWCNTs (see Section 3.5).

## Chapter 4: Exposure-Dose

15 Despite challenges in detecting, measuring, and characterizing PBDE mixtures in the  
16 environment, BDE-209 has been detected in ambient air, water, and soil. Different analytical challenges  
17 for nanomaterials combined with the lack of historical use of MWCNTs in consumer products have so far  
18 prevented MWCNTs from being detected in ambient media (see Section 4.1).

19 Human exposures to decaBDE and MWCNTs released throughout the flame-retardant textile  
20 coating life cycle are expected to differ for occupational workers, consumers, and the general public.  
21 Occupational workers can be exposed to various forms of decaBDE or MWCNTs (e.g., adsorbed to dust,  
22 as part of the polymer or textile matrix) via inhalation and ingestion of and dermal contact with these  
23 substances during manufacturing, storage and distribution, and end-of-life activities. In the workplace, the  
24 inhalation route is expected to represent the greatest potential for exposures, and both decaBDE and  
25 MWCNTs are expected to be in the particulate phase when inhaled. Little is reported about consumer  
26 exposures to MWCNTs, especially those incorporated into flame-retardant textiles, but consumers might  
27 be exposed to decaBDE or MWCNTs released from the upholstered product during use, repurposing, or  
28 reuse. The decaBDE and MWCNTs released from finished products are expected also to be in particulate  
29 form, generally adsorbed to dust or constituents of the polymer or textile matrix. For decaBDE the oral  
30 exposure route is expected to represent the greatest potential for exposure through incidental ingestion of  
31 dusts and particles that settle on surfaces in homes, public places, and in vehicles and aircraft. The dermal  
32 exposure route is also of concern for consumers, however, because direct contact of the flame-retardant

1 textile with skin is expected to occur. Whether this is true for MWCNTs is unclear. Finally, because  
2 decaBDE is ubiquitous in the environment, general public exposures to decaBDE in particulate form  
3 through inhalation of ambient air, ingestion of contaminated drinking water, and dermal contact with  
4 contaminated surface water and soil are expected to occur. Whether this is true for MWCNTs is unclear  
5 (see Section 4.2).

6 Human toxicokinetic studies demonstrate that decaBDE is poorly absorbed from the  
7 gastrointestinal tract and is mainly eliminated in the feces. Small amounts of decaBDE accumulate in  
8 adipose tissues following chronic exposure, but due to the low levels partitioned into adipose tissues  
9 during metabolism, accumulation is expected to be a slow process. Human blood and tissue levels of  
10 BDE-209 are usually low, with the highest concentrations of BDE-209 in plasma and blood-rich tissues  
11 such as the liver, kidney, heart, and intestinal wall. Absorbed decaBDE is metabolized in the liver, with a  
12 minor fraction metabolized to lower PBDE congeners. In general, MWCNTs appear to be biopersistent  
13 and may remain in the lung for up to several months after inhalation. Limited studies show that after oral  
14 exposure, most ingested MWCNTs are eliminated with no detectable metabolism or transport into the  
15 blood. However, distribution to the liver, lungs, and spleen has been reported following intravenous  
16 exposure (see Section 4.2).

17 Children are expected to experience higher exposures to decaBDE in flame-retardant upholstery  
18 textiles than the general population because they typically take in more house dust than adults due to  
19 increased hand-to-mouth activity. Occupational exposures might also contribute to increased exposure  
20 levels for those involved in the manufacturing of decaBDE, flame retardants containing decaBDE, and  
21 related products. Like decaBDE, the activity of children and occupational workers might also increase  
22 total exposure levels relative to the general population, but no evidence is currently available to support  
23 conclusions on whether these would indeed be considered highly exposed populations for MWCNTs (see  
24 Section 4.2).

25 The potential for exposure, uptake, and dose depends on several factors, including properties of  
26 the environmental media and physiological and behavioral characteristics of aquatic and terrestrial  
27 organisms. These factors can in turn, influence the bioavailability of decaBDE and MWCNTs. The  
28 potential for decaBDE to bioaccumulate in biota is expected to be limited due to its low bioavailability, a  
29 result of its strong sorption to soils and sediments. However, decaBDE can slowly bioaccumulate in both  
30 aquatic and terrestrial systems following chronic exposures, and it has been found to biomagnify in  
31 aquatic and terrestrial food webs. Observed levels of decaBDE in predators, such as piscivorous fish and  
32 predatory mammals, are typically much higher than in lower-trophic-level prey animals. MWCNTs are  
33 highly persistent in the environment and hydrophobic, properties which may cause them to accumulate in  
34 food webs. Sorption of other hazardous pollutants by MWCNTs may have a protective effect in some

1 environments, decreasing other pollutants' bioavailability; alternatively MWCNTs carrying hazardous  
2 pollutants could present a more concentrated source of these pollutants to environmental receptors (see  
3 Section 4.3).

4         Although aggregate exposures to decaBDE from multiple sources in residential and  
5 nonresidential spaces are likely (see Section 4.4), accumulation in the body is slow and would only be  
6 expected following chronic exposure. Lower brominated congeners are likely to be created through  
7 environmental degradation of decaBDE, and while indoor debromination is not expected to be a  
8 significant source of other PBDE congeners, debromination in the environment or by biota could lead to  
9 increased cumulative exposures of PBDEs in humans (see Section 4.5). The anticipated increase in the  
10 potential applications of MWCNTs and the corresponding market may lead to an increase in the number  
11 and type of exposures experienced by occupational, consumer, and ecological populations. These changes  
12 are expected to increase aggregate and cumulative exposures to MWCNTs, transformation products, and  
13 by-products.

## Chapter 5: Potential Human Health, Ecological, and Other Impacts

14         Toxicology studies conducted on animals comprise much of the identified data on human health  
15 impacts because there is limited human data for decaBDE and MWCNT exposure. All routes of exposure  
16 were examined in this case study because each route (dermal, inhalation, and oral) offers potential for  
17 human exposures (see Section 5.1).

18         Based on the expected exposure scenarios for decaBDE in upholstery textile coatings, the oral  
19 route of exposure appears to be of the primary toxicological concern for decaBDE; subchronic and  
20 chronic studies using this type of dosing caused thyroid and liver changes in rats and mice. Several  
21 studies also reported neonatal effects, including changes in sperm parameters and changes in locomotor  
22 activity or altered expression of proteins in the central nervous system. A reference dose of 0.007  
23 mg/kg/day was calculated in 2008 by EPA based on developmental neurobehavioral effects. With regard  
24 to carcinogenicity, the National Toxicology Program stated that there was “some evidence of  
25 carcinogenicity” for male and female rats, based on significantly increased incidences of neoplastic  
26 nodules of the liver, and “equivocal evidence of carcinogenicity” for male mice, based on a significantly  
27 increased incidence of hepatocellular tumors in only a low-dose group and non-statistically significant  
28 increases in thyroid follicular cell tumors in two dose groups. Additionally, the International Agency for  
29 Research on Cancer determined that decaBDE is not classifiable as a human carcinogen (Group 3) based  
30 on limited evidence in animals. In 2008, EPA, under the Guidelines for Carcinogen Risk Assessment  
31 determined the descriptor “suggestive evidence of carcinogenic potential” is appropriate for decaBDE.  
32 (see Section 5.1).

1 Toxicological effects from MWCNT exposure have predominately been evaluated after dermal  
2 and inhalation exposures, rather than after oral exposure. Effects were predominately localized in nature  
3 and included irritation (skin and ocular), sensitization (respiratory), and inflammation (respiratory).  
4 Exposure to MWCNTs altered immunological function after inhalation for up to 14 days or via intranasal  
5 injection. The carcinogenicity of MWCNTs is unknown. No carcinogenicity studies using the inhalation  
6 route of exposure were identified. However, several studies indicate that some types of MWCNTs behave  
7 in a similar manner to asbestos, potentially inducing mesotheliomas, and might be more toxic than  
8 asbestos when administered using methods such as instillation (see Section 5.1).

9 Considerations for ecological impact of decaBDE and MWCNTs include the toxicity towards  
10 different species, types of effects, and potential for bioaccumulation and biomagnification. While impacts  
11 of decaBDE have been more intensively studied than impacts of MWCNTs, the field has focused on the  
12 potential for bioaccumulation and biomagnification rather than on toxicological endpoints. Very limited  
13 information is currently available on the ecological impact of MWCNTs (see Section 5.2).

14 DecaBDE is expected to partition in sediments; studies evaluating toxicity in benthic organisms  
15 suggest low toxicity at environmentally relevant decaBDE exposure levels. DecaBDE is not acutely toxic  
16 to fish or marine algae up to its limit of water solubility and is not expected to be chronically toxic to  
17 water-dwelling organisms at environmentally relevant levels. However, thyroid hormone impacts have  
18 been observed in laboratory settings in frogs and fish exposed to decaBDE, indicating a potential for  
19 population dynamic impacts due to endocrine disruption. Few studies have been performed investigating  
20 the effects of MWCNTs on aquatic species or aquatic systems; however, those that have been performed  
21 indicate potentially low acute toxicity, with the effect level varying based on size and functionalization  
22 properties of the MWCNTs. Chronic studies show that MWCNTs can elicit immune responses and  
23 produce negative developmental impacts (see Section 5.2).

24 In terrestrial ecosystems, little information is available on the effects of decaBDE or other  
25 PBDEs, but bioaccumulation and biomagnification of both decaBDE and other PBDE congeners as a  
26 result of decaBDE release could lead to potential ecosystem impacts. Studies of MWCNTs in terrestrial  
27 systems focus on soil communities. Laboratory-based studies established acute antimicrobial activity at  
28 low exposure concentrations. However, increased exposure concentrations and durations do not  
29 necessarily increase the intensity of the effect. Species-specific differences in cytotoxicity levels have  
30 been demonstrated. It is unclear whether MWCNT contamination in soils would negatively affect soil  
31 microbe communities. Studies on plants indicate exposure to high levels of MWCNTs might have adverse  
32 effects on seed germination and plant growth, depending on the diameter and bundling state of the  
33 MWCNTs. Plants might be able to tolerate low levels of MWCNTs without major population-level  
34 effects due to a self-defense response (see Section 5.2).

1           Other impacts associated with general production, use, and release of decaBDE and MWCNTs  
2 have been identified, although these are not associated with specific applications. Studies have linked  
3 higher decaBDE body burdens with lower socioeconomic status, indicating that the decaBDE life cycle  
4 has environmental justice implications. No such empirical data exist relating MWCNTs to other impacts,  
5 but the background literature on processes involved in manufacturing similar materials (e.g., carbon  
6 nanofibers, single-walled carbon nanotubes) provides some basis for concerns regarding potential impacts  
7 of MWCNTs on energy demand, resource depletion, climate change, and economics. These related  
8 studies provide a plausible foundation for suggesting that MWCNT manufacturing can be an energy-  
9 intensive process potentially causing the depletion of nonrenewable natural resources like fossil fuels, and  
10 that the synthesis of MWCNTs can result in emissions of other compounds causing adverse  
11 environmental effects (e.g., volatile organic compounds; see Section 5.3).

## **Chapter 6: Identifying and Prioritizing Research Needs to Support Risk Assessment and Risk Management**

12           This case study is a compilation of the available information, as opposed to an assessment of the  
13 information; therefore, this document is not intended to present conclusions or research priorities. Instead,  
14 this document will serve as the foundation from which participants in the CEA process can identify key  
15 data gaps and assign research priorities. The information presented in this case study and the results of the  
16 CEA process will ultimately be used to inform ongoing research planning for nanotechnology in the  
17 general scientific community as well as at the EPA.



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# Chapter 1. Introduction to this Document

## 1.1. Background

1           Nanoscale materials (nanomaterials) have been described as having at least one dimension on the  
2 order of approximately 1–100 nm ([NSTC, 2011](#)). Although this definition is not universally accepted and  
3 continues to evolve, 100 nm is typically used as an upper bound, and this working definition is used as the  
4 size standard in this case study. Engineered nanomaterials are intentionally synthesized at the nanoscale,  
5 rather than being produced as incidental by-products of combustion or a natural process such as erosion,  
6 to exploit the unique or novel properties that can arise from their small size. Like all emerging  
7 technologies, engineered nanomaterials offer the potential for both benefits and risks, the assessments of  
8 which depend on the availability of relevant data and other information.

9           This document is part of an endeavor to identify what is known and, more importantly, what is  
10 not known that could be of value in assessing the broad environmental implications of nanomaterials. As  
11 a case study, this document presents information about a specific nanomaterial in a particular application.  
12 It does not represent completed or even preliminary assessments; rather, it provides a starting point in a  
13 process to identify and prioritize possible research directions to support future assessments of  
14 nanomaterials. As with previous case studies, the prioritized research gaps that emerge are intended to  
15 inform decision-makers in the U.S. Environmental Protection Agency (EPA) and the broader scientific  
16 community in developing research agendas that support future risk assessment and risk management  
17 goals. Such information is expected to be considered in the context of the particular focus, budgetary  
18 constraints, ongoing research, and other considerations of any organization; however, as discussed below,  
19 by using a holistic framework paired with input from a diverse group of expert stakeholders, the priorities  
20 identified through the comprehensive environmental assessment (CEA) approach can provide a unique  
21 perspective on research directions to support future risk management goals.

22           The focus of this document is a specific application of a selected nanomaterial: the use of  
23 engineered multiwalled carbon nanotubes (MWCNTs) as an agent in flame-retardant coatings on  
24 upholstery textiles. <sup>1</sup> The process for selecting MWCNT flame-retardant coatings for upholstery textiles  
25 as a CEA case study involved individuals representing several EPA program offices, regional offices, and

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<sup>1</sup>Although flame retardants are commonly used in both upholstery textiles and furniture foam, this case study focuses only on information relevant to the use of flame retardants as coatings on upholstery textiles. The extent to which the information presented might be relevant to the use of flame retardants in furniture foam is not addressed.

1 Office of Research and Development laboratories and centers. Individuals were appointed by their  
2 organization within EPA to be involved with development of this and the previous nanomaterial case  
3 study documents. They were encouraged to share information on five candidate carbon-based  
4 nanomaterials and applications—carbon nanofibers in cement, MWCNTs in flame-retardant coatings,  
5 single-walled carbon nanotubes in textiles, nanocrystalline cellulose in biodegradable packaging, and  
6 MWCNTs in rubber tires—with colleagues in their organization and represent the views of their  
7 organization in voting for their preferences. Among factors considered for selecting a candidate was the  
8 apparent relevance of the nanomaterial to EPA programmatic interests (see Appendix A). Using a similar  
9 selection process, EPA completed case studies of nanoscale titanium dioxide used for drinking water  
10 treatment and for topical sunscreen ([U.S. EPA, 2010d](#)) and nanoscale silver used as an agent in  
11 disinfectant spray products ([U.S. EPA, 2010e](#)). Unlike previous case studies, the present case study  
12 incorporates information about a traditional (i.e., “non-nanoenabled”) flame-retardant product,  
13 decabromodiphenyl ether (decaBDE), against which the MWCNT flame-retardant coating (i.e., the  
14 “nanoenabled” product) can be compared (see Section 1.1.4).

15 Part of the rationale for compiling a series of nanomaterial case studies is that the properties  
16 associated with different nanomaterials are often complex and vary considerably within, between, or  
17 among specific types of nanomaterial groups, nanomaterials in general, and different applications of  
18 nanomaterials. As a result, applying generalities could result in overlooking key characteristics or  
19 information. Focusing on a single example of an MWCNT application is not intended to represent all  
20 ways in which this nanomaterial could be used or all issues that other applications might raise. By  
21 considering this single application of MWCNTs, however, research directions can be identified that  
22 would support future assessments of this material. Such information might be used more broadly as an  
23 analog for other applications of MWCNTs or types of nanomaterials. For instance, research investigating  
24 the influence of MWCNT surface treatment on potential release from flame-retardant textile coatings and  
25 subsequent behavior in environmental media can also inform efforts to understand the influence of  
26 surface treatment on the environmental behavior of MWCNTs in other applications.

### 1.1.1. Introduction to Comprehensive Environmental Assessment

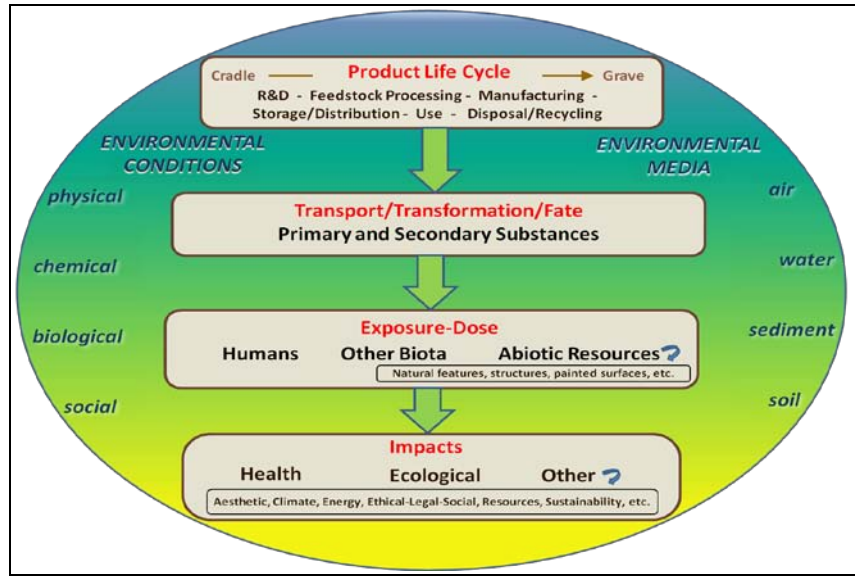
27 This case study of MWCNTs, like the previous case studies of nanoscale titanium dioxide ([U.S.](#)  
28 [EPA, 2010d](#)) and nanoscale silver ([U.S. EPA, 2010e](#)), is built on the CEA approach, which consists of  
29 both a framework and a process, the principal elements of which are illustrated in Figure 1-1 and Figure  
30 1-2, respectively. The uppermost box of Figure 1-1 lists typical stages of a product life cycle: research

1 and development (R&D),  
2 feedstock processing,  
3 manufacturing, storage and  
4 distribution, use, and disposal  
5 (which would include reuse or  
6 recycling, if applicable).

7 Although not  
8 considered a life-cycle stage in  
9 typical life cycle analyses, R&D  
10 is included in business models  
11 of product value chains.

12 Because of the relatively large  
13 portion of resources and  
14 information associated with this  
15 stage for emerging materials,  
16 such as nanomaterials, R&D is  
17 considered in the CEA  
18 framework. The actual volume  
19 of the material used in R&D is  
20 likely small but could represent a significant proportion of the total market, particularly during product  
21 development, given the limited number of full-scale commercial manufacturing efforts early in the life  
22 cycle for emerging materials. For these materials, processes in R&D lend insight to full-scale commercial  
23 processes and might constitute an important source of material release into the environment, as well as  
24 occupational exposures. Other CEA applications focusing on traditional or more mature materials or  
25 technologies might provide minimal or no information on the R&D portion of the product lifecycle, given  
26 that R&D would be less active.

27 Regardless of the material of focus, releases to the environment associated with any stage of the  
28 product life cycle lead to what is depicted in the second box in Figure 1-1, which refers to transport,  
29 transformation, and fate processes. These processes can result in the spatial distribution of both primary  
30 and secondary contaminants in the environment. The chains of events represented in the CEA framework  
31 occur within multiple environmental media (air, water, sediment, soil) and under various conditions  
32 (physical, chemical, biological, social). Also of note are the single arrows connecting one facet of the  
33 CEA framework to the next, which represent a variety of linkages, transfers, and feedback loops. For



Source: [\(Davis, 2011\)](#)

**Figure 1-1. Comprehensive environmental assessment framework.**

The CEA framework is used to systematically organize complex information in evaluations of the environmental implications of selected chemicals, products, or technologies (i.e., materials). The framework starts with the inception of a material and encompasses the environmental fate, exposure-dose, and impacts. Notably, the sequence of events is not always linear when, for example, transfers occur between media or via the food web. In addition, a variety of factors influence each event, including differences in environmental media and the physical, chemical, biological, and social conditions in which the material event occurs. Details on these influential factors are thus included throughout the framework when possible.

1 example, the transfer of material from one organism to another through the food chain would represent a  
2 bidirectional exchange between transport, transformation, and fate and exposure, uptake, and dose.

3 The third box in Figure 1-1, exposure-dose, goes beyond characterizing the occurrence of  
4 contaminants in the environment, as exposure refers to actual contact between a contaminant and a  
5 receptor, whether living or nonliving. Living organisms consist of humans and other biota.<sup>2</sup> Nonliving, or  
6 abiotic, receptors can include features of the natural landscape, structures such as buildings and statues,  
7 and painted surfaces of vehicles and other objects. Exposure can involve aggregate exposure across routes  
8 (e.g., inhalation, ingestion, dermal), cumulative exposure to multiple contaminants (both primary and  
9 secondary), and various spatiotemporal dimensions (e.g., activity patterns, diurnal and seasonal changes).  
10 Dose is the amount of a substance that enters an organism by crossing a biological barrier or deposits on  
11 an inanimate object.

12 As part of a chain of cause-effect events, dose links exposure with potential impacts of various  
13 types, as indicated in the last box of Figure 1-1. Human health effects might result when effective  
14 delivered dose reaches a target cell or organ. In an ecological context, effects might occur when a stressor  
15 is at a level sufficient to cause an adverse outcome in biotic or abiotic receptors. Impacts encompass both  
16 qualitative hazards and quantitative exposure-response relationships and can extend to aesthetic (e.g.,  
17 alterations in visibility, taste, and odor), climate change, energy consumption, resource depletion,  
18 socioeconomic, and other effects. Such effects are considered in the CEA framework, but their ultimate  
19 inclusion would depend on whether the compiled information indicates that such effects could reasonably  
20 be expected to occur. As discussed below, the inclusion of such information in the CEA framework  
21 should influence the selection of the technical experts for the next step of the CEA process.

22 Not reflected in Figure 1-1 is the role of analytical methods that make detecting, measuring, and  
23 characterizing nanomaterials in the environment and in organisms possible. Characterizing a substance of  
24 interest (e.g., determining its chemical identity, reactivity, purity, and other properties) is fundamental to  
25 the assessment of any material. Thus, if adequate analytical techniques have not yet been developed or  
26 need refinement, methods development must be included in research efforts to inform future assessments.  
27 For simplicity, such information is not included in this high-level view of the CEA framework. For the  
28 purpose of this document, analytical methods for the materials in this case study are presented in detail in  
29 Appendix B.

30 As previously mentioned, the CEA approach consists of both a framework and a process.  
31 Compiling the information described above into the CEA framework is the first step of the CEA process  
32 (Figure 1-2). Starting with the holistic perspective of the CEA framework facilitates identifying

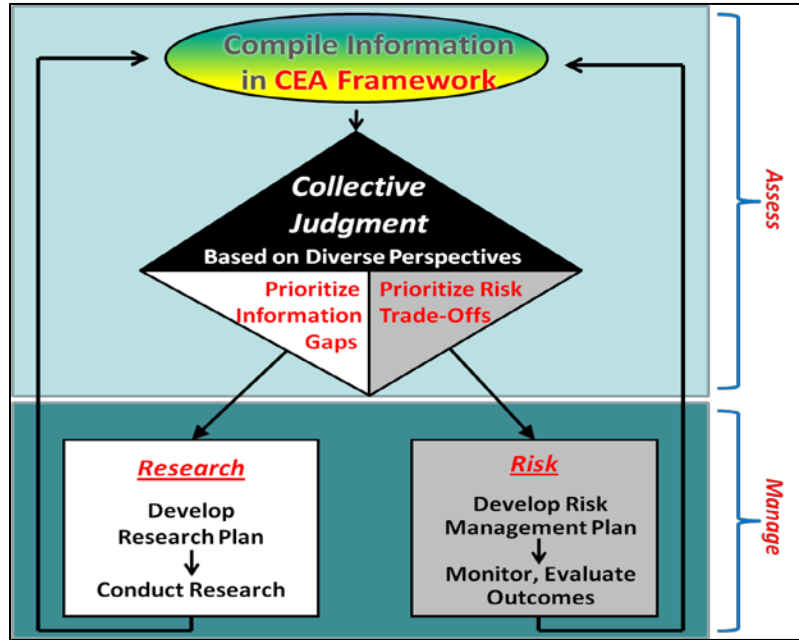
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<sup>2</sup>The term biota is used throughout this document to refer to all living organisms other than humans.

1 information pertinent to consider for  
 2 the material of focus, which in turn  
 3 supports problem formulation and  
 4 scoping for assessment purposes.  
 5 Next, a collective judgment process  
 6 is used to evaluate this information  
 7 and prioritize it. Collective  
 8 judgment, as applied in the CEA  
 9 process to date, refers to a formal,  
 10 structured procedure enabling a  
 11 range of participants to be heard  
 12 individually and to be represented in  
 13 a transparent record of the  
 14 collectively reached outcomes. In  
 15 turn, it supports an essential feature  
 16 of CEA: the inclusion of diverse  
 17 technical and stakeholder  
 18 perspectives to ensure that a holistic  
 19 evaluation is achieved ([U.S. EPA,](#)  
 20 [2010h](#)).

21           Prioritization is a key  
 22 objective in this holistic evaluation

23 within the CEA process. Depending on one's objectives and the state of the science surrounding an issue,  
 24 CEA can be used to prioritize (1) information gaps leading to development of a research plan that will  
 25 support future assessment efforts and (2) risk trade-offs leading to development of an adaptive risk  
 26 management plan. As depicted in Figure 1-2, these uses of CEA cross over from conducting assessments  
 27 into management efforts after the initial identification and prioritization of information. Specifically, this  
 28 transition encompasses the use of prioritized information by research planners and risk assessors in their  
 29 evaluations, which subsequently inform research and risk management decisions. In either instance, CEA  
 30 is meant to be iterative, and thus the results of research and risk management efforts would be used in  
 31 updating the CEA framework after some period of time determined by those conducting the CEA process.  
 32 At present, the CEA framework and process are being applied to help refine research planning for  
 33 nanomaterials, with particular focus on a specific nanomaterial application. As the knowledge base grows  
 34 for nanomaterials, however, and identifying and prioritizing risk-risk and risk-benefit trade-offs with



Source: [Davis, 2011](#)

Figure 1-2. Comprehensive environmental assessment process.

The CEA process involves a series of steps that result in judgments about the implications of information contained in the CEA framework. Compiling information in the CEA framework is fundamental for a given material, but is only a first step in the CEA process. Next, the information in the framework is evaluated using a collective judgment technique (i.e., a structured process that allows the participants representing a variety of technical and stakeholder viewpoints to learn from one another, yet form their own independent judgments). The result of the collective judgment step is a prioritized list of risk trade-offs or information gaps that then can be used in planning research and developing adaptive risk management plans. The knowledge gained from these research and risk management activities feeds back in an iterative process of periodic CEA updates.

1 more complete information becomes feasible, the path leading to risk management (as shown in Figure  
2 1-2) will be pursued. Such prioritized risk-related trade-offs would be only one source of information that  
3 risk managers could consider when making judgments about the risk management options in the context  
4 of relevant legal, political, and other considerations. Yet, the use of the holistic CEA framework and  
5 diverse stakeholder input in the development of such priorities is expected to provide a unique source of  
6 input that is responsive to current recommendations to further refine risk assessment and management  
7 approaches (see Chapter 6).

## 1.1.2. Purpose of this Document

8 This document represents the “Compile Information in CEA framework” step of the CEA process  
9 (Figure 1-2), which supports the next step of the process: identifying and prioritizing information gaps  
10 about MWCNTs that could be relevant to conducting a CEA of nanomaterials. This document attempts to  
11 provide a basis for considering current and future information systematically, which in turn will aid  
12 research planning that supports long-term assessment efforts; it does not, however, purport to present an  
13 exhaustive review of the literature. Thus, this case study is not an actual assessment and does not provide  
14 conclusions on potential ecological or human health impacts related to MWCNTs. Additionally, this  
15 document is focused on identifying data gaps to inform risk assessment and risk management processes  
16 related to MWCNTs, and as such does not discuss benefits. A variety of potential economic, social, and  
17 other benefits likely would need to be considered in future evaluations of risk-related trade-offs for  
18 nanomaterials such as MWCNTs [e.g., Wang and Shapira ([2012](#)), Bonner ([2011](#))].

19 Further, that this case study has been developed without a specific regulatory or policy objective  
20 in mind must be emphasized. Instead, as stated above, the intent is to use this document to identify  
21 scientific and technical information that could be pertinent for future assessment efforts. The results of  
22 future assessments might, of course, provide input to policy and regulatory decision-making at that time.

## 1.1.3. How the CEA Framework Will Be Applied

23 When implemented, a CEA is meant to be comparative, examining the relative risks and benefits  
24 of different products or different formulation options, for example. The focus of a comparative CEA  
25 would be guided by risk management objectives. For example, MWCNT flame-retardant coatings applied  
26 to upholstery textiles might be compared to conventional flame-retardant products, a different  
27 nanoenabled flame-retardant formulation, a flame retardant not applied as a coating, or some other  
28 variable. Although several different options could be of interest to risk managers, considering every

1 potential option in the present case study is not feasible. Therefore, this document focuses solely on a  
2 comparison of MWCNTs and a traditional flame retardant, decaBDE, as they might be used in flame-  
3 retardant coatings for upholstery textiles (e.g., textiles that might be used in homes and nonresidential  
4 areas such as public buildings and automobiles). In each section of this document, information regarding  
5 decaBDE is presented before available information on MWCNTs. The comparative element serves dual  
6 purposes in this case study: (1) to provide a more robust database (i.e., that of a traditional product that  
7 has been relatively well characterized) as a foundation from which to identify data gaps relating to a  
8 nanoenabled product; and (2) to provide a context for identifying key factors and data gaps related to  
9 assessing the risk-risk and risk-benefit trade-offs between a nanoenabled product and a non-nanoenabled  
10 product. Although the specific characteristics, exposure patterns, and effects associated with the use of  
11 MWCNTs and decaBDE can be expected to differ significantly, the data needed to inform risk assessment  
12 and risk management decision-making are comparable; thus, the comparative framework can be used to  
13 help determine whether relevant information (e.g., dominant exposure pathways, sensitive populations) is  
14 available and sufficient to inform future risk decision making, and by extension, identify key data gaps  
15 that could be pursued.

16 The rest of this case study document highlights what is known and not known related to the CEA  
17 of decaBDE and MWCNTs in flame-retardant coatings for upholstery textiles, starting with a general  
18 overview in Chapter 1 of textiles and flame-retardant systems and where decaBDE and MWCNTs fit into  
19 that context. Chapter 2 through Chapter 5 of this case study provide an overview of the information  
20 available to populate the CEA framework, and Chapter 6 describes how this document will support the  
21 subsequent steps in the CEA process to direct research.

#### 1.1.4. Why Compare DecaBDE and MWCNTs?

22 DecaBDE has been used widely in the textile industry to meet fire safety standards (see Section  
23 1.2.1), but because of regulatory, human health, and environmental concerns regarding decaBDE (see  
24 Chapter 5), limitations or bans on its use in the United States and abroad recently have been imposed. As  
25 summarized in Table 1-1, several states have begun to phase out or restrict the use of decaBDE.  
26 In December 2009, the two largest U.S. producers and the largest U.S. importer of decaBDE announced  
27 voluntary commitments to phase out decaBDE in the United States by 2013 in response to concerns  
28 regarding potential adverse impacts on human health and the environment ([U.S. EPA, 2010a](#)). Similarly,  
29 EPA initiated a significant new use rule and Toxic Substances Control Act § 4 test rule for decaBDE in  
30 2012. The significant new use rule would require any entity planning to manufacture or import decaBDE  
31 or articles to which decaBDE has been added to notify EPA at least 90 days in advance, which would



1 provide the Agency an opportunity to review and evaluate data related to the new use and take action to  
 2 limit or prohibit the new use if necessary. The test rule would require laboratory studies to determine the  
 3 effects that decaBDE has on human health and the environment ([U.S. EPA, 2012b](#)). This commitment  
 4 and EPA actions are in response to the growing concern regarding the potential impacts of decaBDE on  
 5 ecological and human health. For example, despite previous assumptions that decaBDE is relatively  
 6 stable and inert in the environment, recent studies have suggested that decaBDE can debrominate, or  
 7 break down into lower congeners, which have been much more widely studied and are known to be  
 8 highly toxic [([Environment Canada, 2010](#); [U.S. EPA, 2010b](#); [Siddiqi et al., 2003](#); [Rahman et al., 2001](#));  
 9 see Section 3.1 and Text Box 3-1].

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**Table 1-1. Existing state regulatory initiatives for decaBDE.**

Regulatory Initiative	State
Implemented studies to assess environmental and human health impacts of decaBDE to inform regulatory action	Illinois, Minnesota, Rhode Island
Restricted the use or sale of products containing decaBDE	Oregon
Prohibited the manufacture, use, or sale of certain products containing decaBDE	Vermont, Maryland, Maine, New York


Source: National Conference of State Legislators ([2011](#)).

10 Although commercial MWCNT flame-retardant products are available, their presence is  
 11 relatively new and they are by no means abundant on the market. Given the projected decline in decaBDE  
 12 use, as described above, investigating these nanoenabled products as a potential emerging alternative is  
 13 relevant. The use of flame retardants in textiles is of interest to EPA and also aligns with the needs of  
 14 other organizations outside of EPA (e.g., Consumer Product Safety Commission, National Institute of  
 15 Standards and Technology). DecaBDE was chosen as the traditional flame-retardant product for  
 16 comparison due to its extensive use since the 1970s and the robust scientific database available for  
 17 decaBDE and the brominated flame retardant (BFR) family in general. The comparison of MWCNTs  
 18 with the larger body of information on decaBDE will help pinpoint data gaps relating to this specific  
 19 MWCNT product. For this reason, available information for decaBDE is generally presented in this case  
 20 study before that for MWCNTs to instruct the reader on how to use the information that is presented.

## 1.2. Introduction to Flame Retardants in Textiles

1 Textiles and fabrics, which are networks of fibers composing flexible woven or nonwoven  
 2 materials, are flammable to varying degrees due to their ignitability and their potential to propagate flame  
 3 and produce burning droplets ([PINFA, 2010](#)). The behavior of various untreated textiles when exposed to  
 4 flame depends on the chemical composition of the raw materials. Table 1-2 lists several common  
 5 categories of textile fibers along with their flammability characteristics. The flammability of these fibers,  
 6 when incorporated in different textile products, has led to the development of numerous fire safety  
 7 standards ([PINFA, 2010](#)), as discussed in Section 1.2.1.

Table 1-2. Common textile fibers and degrees of flammability.

Fiber	Flammability Characteristics of Untreated Fibers	Increasing Fire Hazard
Cotton	Ignite easily, burn heavily; do not melt away from flame <sup>1</sup>	
Flax		
Viscose	Burns rapidly, similar to cotton	
Acetates	Burn heavily; can melt away from flame; form burning droplets <sup>2</sup>	
Acrylics	Burn rapidly; form burning droplets; produce dense black smoke	
Polyesters	Burn slowly and hot; <sup>3</sup> can melt away from flame; form burning droplets	
Polyolefins		
Polyamide		
Other synthetics		
Wool	Difficult to ignite; burns slowly; might self-extinguish	
Modified acrylics	Burn very slowly; tend to melt away from flame; might self-extinguish	
Aramide	Does not burn; strong char formation	

<sup>1</sup>Melting away from the flame refers to the burning characteristic where the fiber essentially melts more quickly than the flame can spread, thereby removing the amount of fiber that is available to the flame to continue burning.

<sup>2</sup>Burning droplets can form if the fiber melts slowly while in contact with the flame.

<sup>3</sup>Burning hot refers to a high peak heat release rate.

Source: PINFA ([2010](#)).

### 1.2.1. Standards for Textiles

8 Upholstery textiles, particularly those used outside of residential settings (e.g., in hospitals,  
 9 airports, airplanes, penal institutions, public transportation, office buildings), are subject to various state,  
 10 federal, and voluntary fire safety standards (see Table 1-3 for examples). Technical standards specify the

1 types of products to which standards apply, methodologies for conducting specific tests, measured  
 2 parameters of interest (e.g., time to ignition, heat release rate), and performance criteria for each test and  
 3 product of interest ([Illinois Environmental Protection Agency, 2007](#)).

**Table 1-3. U.S. and international fire regulations for upholstery textiles.<sup>1</sup>**

Product Category	Standards	Description
Automotive vehicle (bus and car) passenger compartments; curtains or blinds used in automotive vehicles	FMVSS 302/DIN 75200/ISO 3795; DIN 50051	Specimen subjected to Bunsen burner flame for 15 seconds. The rate of flame spread should be <101.6 mm/min (for a 245-mm sample); requires test specimen to have a burning rate <100 mm/min (560-mm sample length) when subjected to a vertical flame test.
Federal flammability standard for mattresses and mattress pads	16 CFR 1632 (2000; updated 2007); 16 CFR 1633 (2006); CA TB 603 (2005); CA TB 129; CA TB 121	Cigarette test for ignition resistance sets requirements for testing of prototype designs of mattresses and mattress pads (based on CA TB 106). Open flame tests: the mattress set must not exceed a peak heat release of 200 kW at any time during a 30-minute test, and the total heat release for the first 10 minutes of the test must not exceed 15 megajoules (25 megajoules in California).
Filling materials used in upholstered furniture	CA TB 117	Furniture that meets the CA TB 117 standard is less likely to ignite rapidly, and if ignited, less likely to burn quickly or to sustain burning.
Passenger equipment in railroad trains	49 CFR Part 238 (2002); ISO 5658-2; ISO 9705	Safety and flammability standards for components of fixed items in passenger cars, seating upholstery, etc. Lateral flame spread test with heat radiator and ignition flame: specimen 800 mm by 155 mm is measured for critical heat flux at extinguishment; flame should not exceed 100 cm above the highest point of the seat surface.
Seating furniture for use in public occupancies	CA TB 133	Requires full-scale flame test <sup>2</sup> for furniture manufactured for use in public buildings in California. Many other states have adopted TB 133.
Cigarette testing of upholstered furniture fabric	Upholstered Furniture Action Council; CA TB 116; NFPA 701	Component standard. All upholstered furniture sold in California must pass this flame test; applies to buildings under NFPA 701 code.

<sup>1</sup>This list is not meant to be definitive or complete; some fire regulations are being re-evaluated and the contents of this table might not be current.

<sup>2</sup>Full-scale flame test refers to the use of a full piece of furniture or mockup (composite)

Note: FMVSS = Federal Motor Vehicle Safety Standards and Regulations; DIN = Deutsches Institut für Normung (Germany); ISO = International Organization for Standardization; CFR = Code of Federal Regulations; CA TB = California Technical Bulletin; NFPA = National Fire Protection Association

Sources: Lowell Center for Sustainable Production ([2005](#)); U.S. EPA ([2012a](#)); PINFA ([2010](#)).

## 1.2.2. Flame-Retardant Materials as Solutions to Flammability

4 The flammability of textiles and the standards described above have created a growing market  
 5 demand for technologies to increase flame resistance and meet fire safety regulations ([Alaee, 2003](#)). Even  
 6 where regulatory standards do not mandate flame resistance, manufacturers often incorporate flame-

1 retardant materials into their products due to market pressures and concerns about brand image ([Illinois](#)  
2 [Environmental Protection Agency, 2007](#)). In fact, the global market for flame-retardant materials, which  
3 are chemicals or other manufactured components that have the quality of resisting or inhibiting the spread  
4 of fire, is estimated to increase 4–5% by 2015 from the base market value of \$3 billion in 2009  
5 ([Grzybowski, 2009](#); [Sullivan, 2009](#)).

6 The most commonly used flame-retardant materials are usually broadly categorized by chemical  
7 structure (e.g., halogenated, phosphorous-based, nitrogen-based, inorganic). Each broad class represents  
8 many possible flame-retardant compounds. Additionally, a variety of inert fillers (e.g., talc),  
9 manufactured components (e.g., glass fibers and microspheres), and more technologically advanced  
10 solutions (e.g., advances in polymer chemistry [see Section 1.2.2.2], nanotechnology) offer flame-  
11 retardant properties to increase the flame resistance of textiles ([PINFA, 2010](#); [U.S. EPA, 2005a](#); [Zhang](#)  
12 [and Horrocks, 2003](#)).

13 The standards and regulations do not specify which flame-retardant materials, if any, must be  
14 used in textiles. Thus, various industry stakeholders must make informed decisions about acceptable use  
15 in textiles based on several key criteria.

### 1.2.2.1. Performance Criteria

16 Performance criteria help determine which flame-retardant materials are appropriate for which  
17 applications and provide a preliminary basis for stakeholders to compare these materials. Such  
18 comparisons are also useful in considering what materials are suitable alternatives to existing  
19 technologies. Some performance criteria proposed by EPA ([U.S. EPA, 2005a](#)) include:

- 20 • **Flame test performance:** a measure of the efficacy of the flame-retardant material included  
21 in specific regulatory standards;<sup>3</sup>
- 22 • **Efficiency:** the degree of flame-retardant action relative to amount of material needed to  
23 obtain result;
- 24 • **Cost:** expense associated with raw materials and downstream production; and
- 25 • **Impacts on textile characteristics:** effect on features such as enhanced strength or reduced  
26 aesthetic appeal that can alter the product's desirability to consumers

27 Another important aspect of performance depends on the intended use of the textile product;  
28 different uses of the material require specific durability standards. Durability is a measure of the ability of  
29 the flame-retardant material to maintain an acceptable level of flame-retardant behavior throughout the

---

<sup>3</sup>For example, the cigarette ignition test and vertical flame test measure aspects such as char length and afterglow of a sample. Flame test parameters and standards are specific to products and end uses [see ([Exponent, 2010](#); [ICL, 2010](#); [Babrauskas and Krasny, 1985](#))].

1 lifetime of the textile as it undergoes abrasion, laundering, weathering, or other expected processes  
 2 ([PINFA, 2010](#); [NRC, 2000](#)). Durability classifications for flame-retardant finishes in textiles are  
 3 presented in Table 1-4.<sup>4</sup> In some cases, durability is a component of flame tests (e.g., both pre- and post-  
 4 wash tests are required for some product uses).<sup>5</sup> Important to note is that these criteria pertain only to the  
 5 performance of a specific flame-retardant material in a specific application.

Table 1-4. Durability classifications of flame-retardant finishes.

Durability Classification	Example Flame-Retardant Materials	Example Application in Textiles
Nondurable – not resistant to washing	Boric acid, aluminum sulfate, ammonium salts, phosphates, some halogenated compounds	Mattresses, draperies, rarely washed textiles
Semidurable – resistant to limited number of washes	Cyanamide and phosphoric acid, phosphorylation of cellulosic fibers, some halogenated compounds	Tents, carpets, curtains (resistant for up to 50 washings)
Durable – resistant to many washes	Organic phosphorous compounds, some brominated compounds	Clothing, other frequently washed fabrics

Sources: GTBL ([1998](#)) and PINFA ([2010](#)).

### 1.2.2.2. Flame-Retardant Application Methods

6 Two principal processes are used for incorporating flame-retardant materials into the textile  
 7 matrix: reactive and additive. Generally, flame retardants *incorporated into* the textile matrix produce  
 8 durable finishes; flame retardants simply *added to* the textile matrix produce nondurable or semidurable  
 9 finishes ([U.S. EPA, 2005a](#); [Rahman et al., 2001](#)).

10 In the reactive process, flame-retardant materials are incorporated directly into polymeric  
 11 materials during the manufacturing process such that they are chemically (i.e., covalently) bound to the  
 12 raw materials of the final product ([U.S. EPA, 2005a](#); [Rahman et al., 2001](#)). Direct incorporation also can  
 13 be accomplished by a chemical reaction between two monomers to form a strong polymer chain, or in a  
 14 post-reaction process such as chemical grafting (functionalization) ([PINFA, 2010](#); [Laoutid et al., 2009](#)).  
 15 Flame-retardant materials produced by the reactive mechanism are often considered to be “inherently”  
 16 flame resistant, as is the case with a variety of polyester blend fabrics.

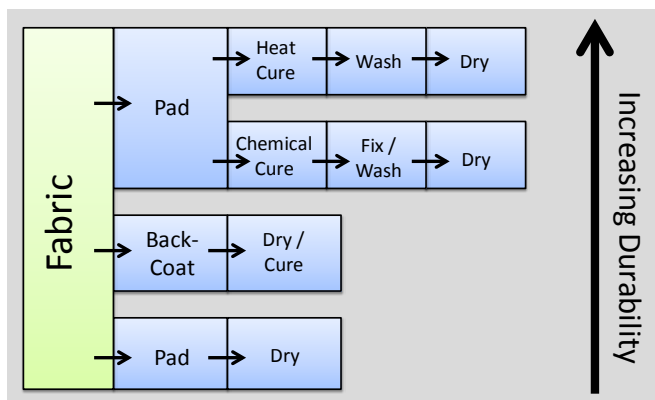
<sup>4</sup>Durability should not be confused with leachability, which refers to the percent removal of flame retardants from the textile matrix ([NRC, 2000](#)). Leachability is a more relevant measure from a risk evaluation perspective, while durability is more important from a product performance perspective. Leachability is discussed further in Section 2.9.5.2.

<sup>5</sup>The *Federal Register* specifies which textile types and products require flame resistance for up to a specific number of washes.

1 In the additive mechanism, flame-retardant materials are applied to the fibers, the finished textile,  
2 or the finished product without the formation of chemical bonds and without a chemical reaction ([Laoutid](#)  
3 [et al., 2009](#); [U.S. EPA, 2005a](#); [Rahman et al., 2001](#)). In some cases, this method requires the use of  
4 binding agents, resins, or copolymers to increase the durability of the flame-retardant properties of the  
5 textile.

6 The particular focus of this case study is the additive application of flame retardants to upholstery  
7 textiles. This method can be distinguished further as illustrated by the schematic in Figure 1-3, which  
8 shows the simple “pad/dry” technique and  
9 variations. In the pad/dry technique, the textile  
10 is immersed in a bath of flame-retardant  
11 solution and then squeezed through rollers at a  
12 specific pressure to remove excess solution.  
13 Back-coating describes several related  
14 application methods where a bonding resin  
15 containing the flame retardant is spread and  
16 smoothed across the reverse surface of a  
17 textile using a knife or blade ([PINFA, 2010](#)).

18 Although additive flame retardants  
19 typically produce a nondurable finish ([NRC,](#)  
20 [2000](#)), Figure 1-3 illustrates methods of  
21 addition that produce more durable finishes  
22 than the simpler pad/dry additive techniques. Thermal or chemical curing, for example, allows for  
23 interaction between the flame-retardant material and the fiber that results in a more durable finish than  
24 those produced using the simpler techniques ([PINFA, 2010](#)). Curing provides the opportunity for cross-  
25 linking (polymerization of the flame retardant onto the substrate), thermal fixation (deposition of the  
26 flame retardant within the fibers), or ionic linkage (negatively charged complexes bind to positively  
27 charged groups). These processes essentially “trap” the flame-retardant material within the polymer  
28 chains, producing a finish that is similar to those the reactive method produces ([PINFA, 2010](#); [NRC,](#)  
29 [2000](#)). After this step, the textile is subjected to other processes (oxidation, neutralizing, or washing) to  
30 remove by-products before the material is dried. Although a more durable finish can be obtained with  
31 heat curing or chemical curing, leaching of flame-retardant material remains of greater concern for  
32 additive flame retardants than for reactive flame retardants (not shown in Figure 1-3) because the material  
33 is not covalently bound to the substrate ([Rahman et al., 2001](#)).



Source: Adapted from NRC ([2000](#)).

Figure 1-3. Durability of additive flame retardants.

This general schematic of the “additive” application method of flame-retardant materials for textiles demonstrates the steps in the additive flame-retardant process that increase durability. The curing process can result in cross-linking, thermal fixation, or ionic linkage between the flame-retardant material and the fibers to increase durability.

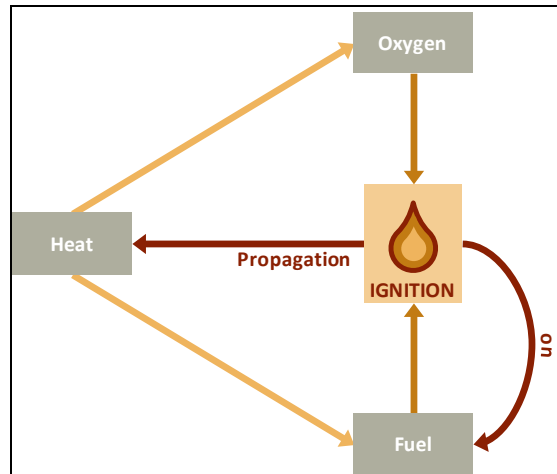
### 1.2.2.3. Mechanism of Flame-Retardant Action

1           Once incorporated into the textile, flame-  
2 retardant materials physically or chemically inhibit the  
3 combustion process. Combustion occurs through a  
4 series of chemical reactions including heating and  
5 ignition, volatilization, and decomposition, which are  
6 self-propagating in the presence of oxygen and a fuel  
7 source (U.S. EPA, 2005a; Alae, 2003) (see Figure 1-4).

8           The mechanism of flame-retardant action can be  
9 categorized generally as follows, although many flame  
10 retardants actually inhibit the combustion process  
11 through a combination of these mechanisms (U.S. EPA,  
12 2005a; Alae, 2003; Rahman et al., 2001):

- 13           • **Physical Dilution:** The flame-retardant  
14 material reduces the fuel content available  
15 for combustion below the concentration  
16 needed to sustain flame propagation or increases the heat capacity of the product and  
17 therefore the amount of heat required for product ignition.
- 18           • **Chemical Interaction/Gas-Phase Radical Quenching:** The flame-retardant material  
19 thermally degrades and releases chemical radicals that are highly reactive with oxygen,  
20 thereby reducing the amount of free oxygen available to supply the combustion process.
- 21           • **Inert Gas Dilution:** The flame-retardant material produces a large volume of  
22 noncombustible gases that dilute the oxygen supply available to propagate the flame.
- 23           • **Thermal Quenching:** The flame-retardant material endothermically degrades, which  
24 removes heat from the substrate and cools the material.
- 25           • **Protective Coatings:** The flame-retardant material forms a liquid or char coating that acts as  
26 an insulation barrier to prevent heat transfer from the flame to unaffected areas of the  
27 product.

28           These five processes act individually or in combination to increase the time to ignition, prevent  
29 spread of the flame, or decrease extinguishing time (Alae, 2003). Table 1-5 provides examples of each  
30 major chemical class of flame retardant described in Section 1.2.2 along with a description of how the  
31 flame retardants are added to textiles, and the general mechanism of flame-retardant action for that class  
32 of flame retardant.



Source: Adapted from Alae et al. (2003) and Laoutid (2009).

Figure 1-4. The combustion process.

The combustion process consists of distinct but overlapping reactions between a fuel source and an oxidant in the presence of heat. Ignition and volatilization in the presence of oxygen produce additional heat, which propagates the cycle.

Table 1-5. Flame retardants summarized by chemical class, method of application, and mechanism of flame-retardant action.

Chemical Class	Examples	Application Method	Flame-Retardant Mechanism
Halogenated	Chlorinated (polychlorinated biphenyls), Brominated (polybrominated diphenyl ethers)	Variations of padding and drying or back-coating	Gas-phase radical quenching/chemical reaction to slow the burning rate; also can form a solid protective layer
	Monomers and copolymers (vinyl bromide), Tetrabromobisphenol A	Combined with copolymeric modifications or grafted onto polymer chains for reactive application	Decreases thermal degradation; reduces extinguishing time
Phosphorous-based	Organophosphorous, Inorganic phosphates	Coatings; chemical bath	Protective coatings or layers; char formation
Nitrogen-based	Melamine, Melamine salts	Intumescent coatings; back-coatings; can be added to polymer melt	Inert gas dilution (inhibits formation of flammable gases); char formation
Inorganic	Metal hydroxides, Minerals	Fillers; back-coating, can be added to polymer melt	Endothermic degradation/thermal quenching or inert gas dilution; forms protective layer; physical dilution; thermal shielding

Sources: U.S. EPA (2005a); GTBL (1998); NRC (2000); Xusen (2010); PINFA (2010); and Laoutid (2009).

## 1.3. DecaBDE and MWCNTs in Flame-Retardant Textiles

1 As noted previously, the focus of this case study is to present available information to conduct a  
 2 comparative CEA in the future of a traditional flame retardant (decaBDE) and a nanoenabled flame-  
 3 retardant technology using MWCNTs, specifically in upholstery textile coatings. The following sections  
 4 provide a general overview of decaBDE and MWCNTs, their use in textiles, and a brief comparison of  
 5 observed flame-retardant action and efficacies.

### 1.3.1. Introduction to DecaBDE

6 DecaBDE is part of a larger group of BFRs called polybrominated diphenyl ethers (PBDEs), a  
 7 group of 209 structurally similar BFRs that differ in the number and location of bromine atoms  
 8 (Table 1-6) (Rahman et al., 2001; NRC, 2000). Although PBDEs are typically categorized into classes by  
 9 number of bromine atoms (e.g., PBDE with two bromine atoms is a diBDE; ten bromine atoms is a  
 10 decaBDE), a single class might contain several different PBDE congeners with the same number of



1 bromine atoms in different locations (i.e., PBDE BFRs can have many isomers). As the only fully  
2 brominated PBDE, decaBDE is the exception, existing only as a single congener (BDE-209).

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**Table 1-6. Major PBDE congeners.**

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PBDE Class	Congeners
DiBDE	BDE-7, BDE-8, BDE-11, BDE-12, BDE-13, BDE-15
TriBDE	BDE-17, BDE-25, BDE-28, BDE-30, BDE-32, BDE-33, BDE-35, BDE-37
TetraBDE	BDE-47, BDE-49, BDE-66, BDE-71, BDE-75, BDE-77
PentaBDE	BDE-85, BDE-99, BDE-100, BDE-105, BDE-116, BDE-118, BDE-119, BDE-126, BDE-138, BDE-140
HexaBDE	BDE-153, BDE-154, BDE-155, BDE-166
HeptaBDE	BDE-181, BDE-183, BDE-190
OctaBDE	BDE-196, BDE-197, BDE-203
NonaBDE	BDE-206, BDE-207, BDE-208
DecaBDE	BDE-209

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Source: U.S. EPA ([2010b](#)).

3 Commercial formulations of decaBDE (see Table 1-7) are generally 97–98% BDE-209 with less  
4 than 3% nonaBDE congeners present as impurities ([Rahman et al., 2001](#); [NRC, 2000](#)) (see Appendix B,  
5 Table B-1 for analytical techniques used to distinguish PBDE congeners in samples). Although the terms  
6 decaBDE and BDE-209 often are used interchangeably, this case study primarily uses the term decaBDE  
7 to refer generally to the flame-retardant formulation and BDE-209 to refer to the specific decaBDE  
8 congener analyzed in scientific studies.

9 DecaBDE is the most widely used of the PBDEs and has been well studied. In 2001, decaBDE  
10 use accounted for 83% of total PBDE production worldwide ([U.S. EPA, 2010b](#)); an estimated 10–20% of  
11 decaBDE use is in the textile industry ([Pure Strategies Inc., 2005](#)). At the end of 2004, both octa- and  
12 pentaBDE were voluntarily withdrawn from the U.S. marketplace due to evidence of environmental  
13 persistence and toxicity, which left decaBDE as the sole PBDE available for commercial products in the  
14 United States ([U.S. EPA, 2010b](#)). Several standard physicochemical properties are used to describe  
15 traditional chemicals: melting point, boiling point, molecular weight, and others. Such values are  
16 presented for decaBDE in Table 1-8.

Table 1-7. Commercial formulations of PBDEs used as flame retardants.

Name	Congener Makeup and Percent Composition	
Penta formulation <sup>1</sup>	Penta	BDE-99 (35–50%), BDE-100 (6–10%)
	Tetra	BDE-47 (25–37%)
	Hexa	BDE-153 (5–10%), BDE-154 (1–5%)
Octa formulation	Hexa	BDE-153 (5–10%), BDE-154 (1–5%)
	Hepta	BDE-183 (40%)
	Octa	BDE-197 (21%), BDE-203 (5–35%), BDE-196 (8%)
	Nona	BDE-208 (10%), BDE-207 (7%)
Deca formulation <sup>2</sup>	Nona	BDE-206 (2.2%), BDE-207 (0.24%), BDE 208 (0.06%)
	Deca	BDE-209 (>97%)

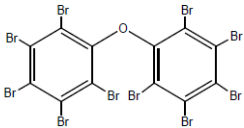
<sup>1</sup>Trace amounts of additional congeners might be present in commercial formulations: <0.2% triBDE congeners.

<sup>2</sup>Trace amounts of additional congeners might be present in commercial formulations: <0.003% heptaBDE congeners; <0.001% hexaBDE congeners; <0.002% pentaBDE congeners; <0.00003% tetraBDE congeners; <0.00001% triBDE congeners.

Source: U.S. EPA (2010b).

1           DecaBDE can be applied to textiles by a variety of mechanisms, but this case study focuses on  
2 the application of decaBDE as a back-coating. This application method is used most frequently for  
3 decaBDE ([Pure Strategies Inc., 2005](#); [NRC, 2000](#)) and is most similar to the application method expected  
4 for MWCNTs used in textiles (see Section 1.3.2). The back-coating process usually involves mixing  
5 decaBDE with a copolymer or resin binder to comply with fire safety standards ([Pure Strategies Inc.,](#)  
6 [2005](#); [NRC, 2000](#)). DecaBDE combines the flame-retardant mechanism of most BFRs (releasing  
7 halogens during combustion to compete with the availability of oxygen for the flame) with formation of a  
8 protective char barrier ([NRC, 2000](#)) that interferes with the spread of the flame and helps the material to  
9 self-extinguish ([Pure Strategies Inc., 2005](#)).

Table 1-8. Physical properties and chemical identity of decaBDE.

	Physical property/chemical identity	Reference
CASRN	1163-19-5	NLM (2011)
Synonyms	2,2',3,3',4,4',5,5',6,6'-decaBDE; BDE-209; benzene, 1,1'-oxybis[2,3,4,5,6,-pentabromo]-; decabromodiphenyl oxide; decabromodiphenyl ether; decabromobiphenyl ether; ether, bis(pentabromophenyl)	NLM (2011); ATSDR (2004)
Physical state	Solid	Hardy (2002b)
Melting point,	300–310 °C	ECB (2003)
Boiling point	Decomposes at >320 °C	ECB (2003)
Vapor pressure	$4.63 \times 10^{-6}$ Pa at 21 °C	Hardy (2002b)
Henry's law constant	$1.93 \times 10^{-8}$ L atm/mol 0.04 Pa m <sup>3</sup> /mol at 25 °C	Hardy (2002b); Cetin and Odabasi (2005)
Density	3.0 g/cm <sup>3</sup>	NRC (2000)
Water solubility	<0.1 µg/L at 25 °C	Hardy (2002b); ECB (2003)
Log K <sub>ow</sub>	6.3–12.6	Hardy (2002b)
Log K <sub>oc</sub>	6.3	Hardy (2002b)
Molecular weight	959.17	NLM (2011); ECB (2003)
Chemical formula	C <sub>12</sub> Br <sub>10</sub> O	NLM (2011)
Chemical structure		

Note: K<sub>ow</sub> = Octanol water partition coefficient, K<sub>oc</sub> = Soil organic carbon-water partition coefficient.

### 1.3.2. Introduction to MWCNTs

1 MWCNTs are carbon nanostructures composed of multiple concentrically nested graphene sheets  
 2 that look similar to nested rolls of chicken wire. Unlike many traditional chemicals, MWCNTs are not a  
 3 homogeneous group of molecules; many of the characteristics of MWCNTs can be intentionally or  
 4 unintentionally altered using different laboratory procedures, treatments, and synthesis methods (see  
 5 Sections 2.1.1 through 2.2.3). As described in Text Box 1-1, altering the physicochemical properties of  
 6 MWCNTs can in turn alter the behavior of MWCNTs during all stages of the life cycle, in environmental  
 7 compartments, and in humans and other biota. As a result, MWCNTs with different physicochemical  
 8 properties might produce different impacts downstream, but which physicochemical properties drive these

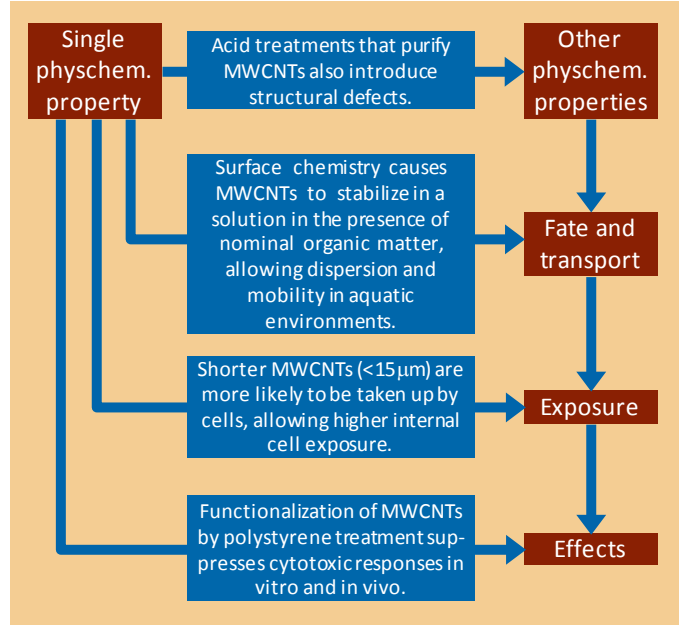
1 differences and to what degree are not fully understood. MWCNTs are not a single homogeneous  
 2 substance; ranges of values describing MWCNT physicochemical properties are provided in Table 1-9 to  
 3 illustrate the array of characteristics recorded for MWCNTs in the literature (see Appendix B, Table B-2  
 4 for analytical techniques used to characterize MWCNTs).

**Text Box 1-1. Physicochemical Properties of Multiwalled Carbon Nanotubes (MWCNTs) Affect Their Release, Behavior in the Environment, and Interaction with Biota**


The environmental fate and transport and potential for release, exposure, and impacts associated with any substance are largely determined by that substance's physicochemical characteristics. The same is true for nanomaterials, but the key characteristics that determine behavior differ between conventional materials and engineered nanomaterials. Driving characteristics for conventional materials like boiling point, melting point, and density are replaced at the nanoscale by size, surface area, surface chemistry, and morphology. Altering just one of these characteristics influences the behavior of nanomaterials. A single nanomaterial, an MWCNT for instance, can be created with dozens of variations of these properties. MWCNTs are generally nested tube-like structures with a very high length-to-diameter ratio, but they can be engineered to have various lengths, surface coatings, and

- Important Physicochemical Properties of Nanomaterials:**
- Size, including agglomeration/aggregation tendencies
  - Morphology, including shape and crystal structure
  - Surface area
  - Chemical composition
  - Surface chemistry and reactivity
  - Solubility and dispersion
  - Conductive, magnetic, and optical properties

functionalizations. Demonstrating and quantifying relationships between individual characteristics and MWCNT behavior is complicated due to the difficulty in altering only one characteristic at a time. For example, oxidizing MWCNTs can shorten them and make them more straight (Johnston et al., 2010). Equally difficult is assigning mechanisms of toxicity to the observed effects. For instance, long, straight MWCNTs injected under the skin of rats can produce more inflammogenic effects than shorter bundles of MWCNTs administered in the same manner (Johnston et al., 2010), but whether the length of the materials, their tendency to bundle and how tightly, or all of these factors directly affect inflammation is unclear. The complex relationships among physicochemical properties, and between these properties and the life cycles of nanomaterials, have not been decoupled, nor have the impacts of these properties on nanomaterial behavior been adequately analyzed, particularly in terms of understanding the potential environmental and health effects of nanomaterials.



**Table 1-9. Physical properties and chemical identity of MWCNTs.<sup>1,2</sup>**

Physical property/chemical identity		Reference
Physical state	Solid	
Morphology	Concentric cylinders	Johnston et al. (2010)
Physical structure		Hirsch and Vostrowsky (2005)
Purity, <sup>4</sup> min. wt% C	Usually >90%; 7.5–40% reported for “multi-wall, powdered cylinder cores” and “multi-wall, as produced” by Sigma-Aldrich	See Appendix F study summaries; Sigma-Aldrich (2011)
Outer diameter	5–170 nm <sup>3</sup>	Aschberger et al. (2010); Li and Huang (2011); Desai et al. (2012); He et al. (2012); Dawson et al. (2011); Golovin et al. (2011); Lu et al. (2011b); Liu et al. (2011a); Ji et al. (2011); Sigma-Aldrich (2011)
Length	20 nm–200 μm	Aschberger et al. (2010); He et al. (2012); Aranberri et al. (2011); Golovin et al. (2011); Lu et al. (2011b); Liu et al. (2011a); Ji et al. (2011); Sigma-Aldrich (2011)
Aspect ratio	Up to 1000	Cipiriano et al. (2007)
Chirality	Varies; chiral angles, described by vectors (n, m), produce different graphene sheet conformations (e.g., “zigzag” [m = 0], armchair [n = m]), and influence other properties (e.g., mechanical, optical, electrical)	Gustavsson et al. (2011)
Axial and radial strength	Axial: rigid; 10 times stronger than steel Radial: flexible; can be bent up to 90 degrees	Gustavsson et al. (2011)
Surface area	253–400 m <sup>2</sup> /g	Aschberger et al. (2010); Aranberri et al. (2011); Lu et al. (2011b);
Bundle size	0.9–100 μm	Li and Huang (2011); Baitinger et al. (2011);
Surface composition	Pristine or modified with various functional groups	Johnston et al. (2010)
Vapor pressure	No information available	
Melting point	3652–3697 °C	Sigma-Aldrich (2011)
Stability	Stable up to 600 °C (CNTs)	Nanoshel (2011)
Density	2.1 g/mL at 25 °C	Sigma-Aldrich (2011)
Zeta potential, mV	–23–0	Li and Huang (2011)
Solubility in water	Insoluble; functionalization treatments result in different degrees of solubility	Lam et al. (2006); Johnston et al. (2010)

<sup>1</sup>Values reported represent total ranges reported in literature.

<sup>2</sup>Values are provided for MWCNTs where available, values for single-walled CNTs or CNTs in general are provided when not.

<sup>3</sup>Depending on the number of walls.

<sup>4</sup>Impurities include cobalt, iron, nickel, and molybdenum (commonly used as catalysts in production; see Sections 2.1.1 through 2.2.3). Percent purity depends on purification methods (see Appendix C).

1 According to the scientific literature, MWCNTs can act as flame retardants in a variety of  
2 textiles, including plastics, polymers, assorted fabrics, and technical materials ([Binetruy and Boussu,](#)  
3 [2010](#); [Kashiwagi et al., 2005b](#); [Kashiwagi et al., 2005a](#)). To date, at least one MWCNT flame-retardant  
4 textile coating is commercially available, but this application does not appear to be widespread ([Nanocyl,](#)  
5 [2009](#)). MWCNTs primarily inhibit flames in a manner similar to that of one of the mechanisms of  
6 decaBDE, that is, by forming a protective layer that seals against combustion. When formed by  
7 MWCNTs, this protective char-like layer often is referred to as a “network-structured layer” that can act  
8 as a thermal shield ([Laoutid et al., 2009](#); [Cipiriano et al., 2007](#); [Kashiwagi et al., 2007](#); [Kashiwagi et al.,](#)  
9 [2005b](#); [Kashiwagi et al., 2005a](#); [Kashiwagi et al., 2004](#)), reduce the peak heat release rate, and increase  
10 thermal conductivity ([Laoutid et al., 2009](#); [Cipiriano et al., 2007](#); [Kashiwagi et al., 2007](#); [Kashiwagi et al.,](#)  
11 [2005b](#); [Kashiwagi et al., 2005a](#); [Beyer, 2004](#); [Kashiwagi et al., 2004](#)).

12 The flame-retardant behavior of MWCNTs depends on the formation of a highly uniform,  
13 network-structured layer of floccules, which are loosely bound MWCNT bundles, with no breaks or  
14 cracks. The formation of the floccules layer, and therefore the flame-retardant behavior, also was found to  
15 vary according to a variety of factors, including dispersion (which can be enhanced with surface  
16 treatments), size, shape, aspect ratio,<sup>6</sup> and loading concentration ([Cipiriano et al., 2007](#); [Kashiwagi et al.,](#)  
17 [2007](#); [Kashiwagi et al., 2005b](#); [Kashiwagi et al., 2005a](#); [Kashiwagi et al., 2004](#)). Cipiriano et al. ([2007](#))  
18 were able to produce a more uniform floccule layer at lower concentration loadings, resulting in enhanced  
19 flame-retardant properties, by using MWCNTs with a higher aspect ratio. In nanoclay the incorporation of  
20 organomodified montmorillonite but not sodium-layered montmorillonite stimulated char formation in  
21 polymer matrices, indicating that surface functional groups can be instrumental in flame-retardant action  
22 ([Laoutid et al., 2009](#)).

### 1.3.3. MWCNTs as Alternative Flame-Retardant Materials in Upholstery Textiles

23 As the use of decaBDE begins to decline, cost-effective and feasible alternatives for replacing  
24 this widely used flame retardant are being evaluated. MWCNTs are one of many possible alternatives to  
25 replace decaBDE. Given the current, albeit limited, availability of an MWCNT product for textile  
26 applications<sup>7</sup> and the projected decline in cost ([Sullivan, 2009](#)), the use of such nanoenabled products is  
27 likely to increase in the future as an emerging application. Table 1-10 provides a comparative summary of

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<sup>6</sup>This dimension refers to the proportional relationship between the length of the nanotube and the width of the nanotube; carbon nanotubes typically are characterized as having large aspect ratios (i.e., greater length than width).

<sup>7</sup>Personal Communication: Nicolas Messin (Nanocyl). 3/2/2012.

1 decaBDE and MWCNTs, which illustrates several similarities in terms of application method, flame-  
 2 retardant action, and relevant uses. Many parallels can also be drawn in the performance criteria that were  
 3 discussed in Section 1.2.2.1, as shown in Table 1-11.

Table 1-10. Overview of decaBDE and MWCNTs for flame-retardant textile application.

	DecaBDE	MWCNTs
Method of incorporation into textile products	Applied as a back-coating to textiles ( <a href="#">NRC, 2000</a> ), often with a binding agent such as latex ( <a href="#">ECB, 2003</a> ), or a copolymer ( <a href="#">NRC, 2000</a> )	Integrated by "melt blending" with polymer ( <a href="#">Cipiriano et al., 2007</a> ; <a href="#">Kashiwagi et al., 2005b</a> ; <a href="#">Kashiwagi et al., 2005a</a> ; <a href="#">Zhang and Horrocks, 2003</a> ); dispersed in resin (e.g., silicon base) and applied as a coating (Nanocyl!) ( <a href="#">Kohler et al., 2008</a> ); applied by "dyeing-like" method to fabrics (e.g., cotton) ( <a href="#">Goncalves et al., 2012</a> ); "layer-by-layer coating" (foam applications) ( <a href="#">Uddin and Nyden, 2011a</a> ; <a href="#">Davis and Kim, 2010</a> )
Mechanism of flame-retardant action	Gas-phase radical quenching; creates a char barrier ( <a href="#">NRC, 2000</a> )	MWCNT network acts as a sealing or shielding agent (i.e., a barrier) ( <a href="#">Berger, 2007</a> ; <a href="#">Cipiriano et al., 2007</a> ; <a href="#">Kashiwagi et al., 2007</a> ; <a href="#">Kashiwagi et al., 2005b</a> ; <a href="#">Kashiwagi et al., 2005a</a> ; <a href="#">Kashiwagi et al., 2004</a> )
Approximate production volume/capacity <sup>2</sup>	Worldwide demand in 2001 reported as 54,000–56,000 tonnes ( <a href="#">Law et al., 2006b</a> ; <a href="#">Pure Strategies Inc., 2005</a> ); >60,000 tonnes reported in 2007 ( <a href="#">Illinois Environmental Protection Agency, 2007</a> ); 10–20% of decaBDE produced is used in textiles <sup>3</sup>	From 2005 to 2009, global annual production capacity increased from 294 tons (approximately 267 tonnes) to more than 1500 tons (approximately 1361 tonnes) ( <a href="#">Kohler et al., 2008</a> ); projected to reach 9400 tons (approximately 8528 tonnes) by 2015 ( <a href="#">Innovative Research and Products Incorporated, 2011</a> ); percent of MWCNTs produced for textile use expected to be very low
Relevant use in textile applications	Used in mattresses, draperies, commercial upholstered furniture, and in transportation industry fabrics ( <a href="#">Pure Strategies Inc., 2005</a> )	Has been tested in "nanocomposites" with polyvinyl acetate, and ethylene vinyl acetate ( <a href="#">Kashiwagi et al., 2005b</a> ; <a href="#">Kashiwagi et al., 2005a</a> ; <a href="#">Kashiwagi et al., 2004</a> ); marketed as coating on cables, metal, foam, and textiles (Nanocyl); marketed as "additives" for flame-retardant textiles or as industrial coatings for fabrics ( <a href="#">Siegfried, 2007</a> )

<sup>1</sup>See ([Nanocyl, 2009](#); [Sullivan, 2009](#)).

<sup>2</sup>Note: not all of the production capacity is relevant for flame retardants or for use in upholstered textiles.

<sup>3</sup>According to U.S. EPA ([2010b](#)), production volumes for PBDEs are not readily available. The most recent industry reporting year for market demand was 2001. At that time, 83% of all PBDE consumed worldwide was decaBDE.

Table 1-11. General qualitative comparisons of performance criteria for decaBDE and MWCNTs.

	DecaBDE	MWCNTs
Flame test performance	Allows textiles to comply with fire safety standards in public places and public buildings. Also used to comply with more stringent fire safety requirements for home upholstered furniture in countries such as Ireland, the United Kingdom, and the United States ( <a href="#">Pure Strategies Inc., 2005</a> )	Reduces peak heat release rate; formation of network-structured protective layer; reduced rate of pyrolysis ( <a href="#">Cipiriano et al., 2007</a> ; <a href="#">Kashiwagi et al., 2005b</a> ; <a href="#">Kashiwagi et al., 2005a</a> ; <a href="#">Kashiwagi et al., 2004</a> )
Efficiency	Very efficient, can be used at relatively low concentrations ( <a href="#">Pure Strategies Inc., 2005</a> ; <a href="#">Rahman et al., 2001</a> ); maximum of approximately 20% w/w added as a back-coating ( <a href="#">NRC, 2000</a> ); <sup>1</sup> applied 10–15% by weight to polymers in conjunction with resin binder ( <a href="#">U.S. EPA, 2010b</a> )	Effective at very low concentrations (0.5–4% by mass) ( <a href="#">Grzybowski, 2009</a> ; <a href="#">Kashiwagi et al., 2005b</a> ; <a href="#">Kashiwagi et al., 2005a</a> ; <a href="#">Kashiwagi et al., 2004</a> ); commercial formulations for textile use are reported to be effective at 100 µg thickness <sup>2</sup>
Cost	Described as “cost effective” ( <a href="#">Pure Strategies Inc., 2005</a> ) and “relatively cheap” ( <a href="#">Posner, 2004</a> ); decaBDE/antimony oxide mixture is roughly \$3.09/kg when used for draperies ( <a href="#">Pure Strategies Inc., 2005</a> )	Relatively low cost of production (\$100/kg) compared to other nanocarbon products, projected to decrease to \$10–\$20/kg ( <a href="#">Sullivan, 2009</a> ); commercial prices vary with purity, size, and functionalization (e.g., \$7000/kg for functionalized, \$2000/kg for 95 wt% <8 nm; \$700/kg for 95 wt% >50 nm) ( <a href="#">Cheap Tubes Inc., 2009</a> )
Impacts on textile characteristics	Must be applied to reverse side of fabric because of negative effect on aesthetics.	Can improve physical and mechanical properties ( <a href="#">Siegfried, 2007</a> ; <a href="#">Hirsch and Vostrowsky, 2005</a> ; <a href="#">Kashiwagi et al., 2005b</a> ), as well as conductivity and optical properties <sup>3</sup> ( <a href="#">Siegfried, 2007</a> ); fatigue resistant; particle embedding can prevent cracks ( <a href="#">Grzybowski, 2009</a> )
Durability	Semidurable ( <a href="#">Rahman et al., 2001</a> ); resin applied with decaBDE bonds to the fiber to increase durability ( <a href="#">Pure Strategies Inc., 2005</a> )	Commercial product has not been tested for durability in laundering, but flame-retardant performance is resistant to other chemical treatments; <sup>2</sup> potential for nanotextiles to release individual nanoparticles or clusters of nanoparticles ( <a href="#">Grebler et al., 2010</a> ) <sup>4</sup>

<sup>1</sup>Depends on the PBDE used (both decaBDE and hexaBDE referenced), the resin binder used, and the fabric to be treated.

<sup>2</sup>Personal Communication: Nicolas Messin Global Sales and Marketing Manager for Thermosets (Nanocyl). 3/2/2012.

<sup>3</sup>Optical properties of textiles include fluorescence or color-changing effects (theoretical; not necessarily relevant for MWCNTs in upholstery).

<sup>4</sup>Based on the fact that textiles are known to lose 5–20% of their weight during use (abrasion, mechanical influence, washing, etc.); authors note that textiles made from fibers with integrated nanoparticles are more likely to have longer lasting functionality compared to those with nanoparticle surface coating or impregnation.

1 A summary of information available from actual flame tests for decaBDE and MWCNTs is  
2 provided in Table 1-12. Note that information available for flame tests for both materials is not  
3 standardized. Some information is qualitative, while other data are quantitative. In both cases, only a few  
4 representative examples are described; in the absence of specific data on MWCNTs used in textiles  
5 relevant to this case study, available information has been provided on a similar MWCNT flame-retardant



1 product used as a coating for a variety of materials. This product is used on foam and other structural  
 2 materials, but might prove useful for comparison to the current application because the product generally  
 3 has been shown to increase flame resistance, increase the heat barrier and charring, and reduce the amount  
 4 of smoke created. Furthermore, the manufacturer advertises that their MWCNT flame-retardant coating is  
 5 appropriate for application to textiles ([Mezzo, 2010](#)).

Table 1-12. Flame test performance of decaBDE and MWCNTs.

	Sample	Without Treatment	With Treatment	Source
DecaBDE	Sofa	Burns quickly (<5 minutes), temperature increases from 20 °C to 800 °C	Burns slowly, increases amount of time to escape by up to 15 times	BSEF ( <a href="#">2012</a> )
	50/50 polyester/cotton twill	Sample burns completely	Char length reduced (<6.3 in.)	ICL Industrial Products ( <a href="#">2010</a> )
MWCNTs <sup>1</sup>	Polyurethane foam	Burns quickly, dense smoke forms, burning droplets fall	Spray coating forms "shell" to keep molten foam contained (no burning or flaming drops)	Mahy ( <a href="#">2009</a> ); Howlett ( <a href="#">2008</a> )
	Polyvinyl chloride	Burns easily, melts, structure destroyed	Does not melt, structure is retained	Mahy ( <a href="#">2009</a> )
	Wires/Cables	Burns completely, releases dense smoke and burning droplets, copper core becomes exposed	No burning droplets; low smoke density; copper core protected; passes UL94, <sup>2</sup> IEC-332-3 <sup>3</sup> tests	Mahy ( <a href="#">2009</a> )
	Polypropylene	Heat release rate = 2800 kW/m <sup>2</sup>	1–2% addition = heat release rate of 800 kW/m <sup>2</sup>	Gryzbowski ( <a href="#">2009</a> )
	Cotton	Burned distance = 77 mm; burning time = 19 sec; burning rate = 243 mm/min	Burned distance = 80 mm; burning time = 21 sec; burning rate = 229 mm/min	Goncalves et al. ( <a href="#">2012</a> )
	Polyester	Burned distance = 66 mm; burning time = 26 sec; burning rate = 152 mm/min	Burned distance = 66 mm; burning time = 53 sec; burning rate = 75 mm/min	Goncalves et al. ( <a href="#">2012</a> )

<sup>1</sup>Due to the limited availability of information relevant to upholstery textiles, data for flame-retardant coatings for foam, polyvinyl chloride, and other materials are included for additional context.

<sup>2</sup>Horizontal and vertical burning tests associated with American Society for Testing and Materials (ASTM) International standards.

<sup>3</sup>Large-scale flammability test for wire bundles under 20.5 kW flame.

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# Chapter 2. Product Life Cycle

1 A product's life cycle encompasses all stages of its existence from "cradle to grave," starting with  
2 the extraction of raw materials from the earth for the manufacture of the product and continuing  
3 downstream until these materials are returned to the environment following disposal ([U.S. EPA, 2006](#)).  
4 The components of the life cycle determine the potential for releases and possible impacts on human  
5 health, ecological populations, and the environment ([Som et al., 2011](#)), which can be evaluated  
6 systematically within the framework of a comprehensive environmental assessment (CEA). Potential  
7 environmental impacts of a product throughout its life cycle can be estimated using a life-cycle  
8 assessment (LCA) approach, which involves four steps: goal definition and scope, inventory analysis,  
9 impact analysis, and interpretation ([U.S. EPA, 2006](#)). The CEA approach incorporates information from  
10 available LCAs in the "product life cycle" and "impacts" portions of the CEA framework to combine this  
11 knowledge with other analyses or qualitative indicators related to transport, transformation, and fate,  
12 exposure-dose, and additional impacts not considered in available LCAs. As discussed in Chapter 1, if a  
13 plausible reason exists to include an impact in the CEA framework, information (qualitative or  
14 quantitative) on that effect can be included from LCAs or other sources (if an LCA has not been  
15 completed) to evaluate that particular impact.

16 A generalized depiction of the life cycle for decabromodiphenyl ether (decaBDE) and  
17 multiwalled carbon nanotube (MWCNT) coatings used to confer flame-retardant properties to upholstery  
18 textiles is presented in Figure 2-1. This figure breaks down the life cycle of these materials into five main  
19 stages: (1) including the acquisition and processing of feedstocks, (2) manufacturing (including research  
20 and development (R&D) processes), (3) storage and distribution, (4) use, and (5) end-of-life processes  
21 (including disposal, reuse, and recycling). These stages correspond roughly to the four primary life-cycle  
22 stages outlined by the U.S. Environmental Protection Agency ([U.S. EPA, 2006](#)), including raw materials  
23 acquisition, manufacturing, use/reuse/maintenance (with storage and distribution discussed as a distinct  
24 stage in this case study), and recycle/waste management. As mentioned in Chapter 1, R&D is included in  
25 the product life-cycle portion of the CEA framework, given its importance regarding emerging materials  
26 such as MWCNTs. For such materials, R&D efforts can elucidate potential risks associated with  
27 commercial-scale manufacturing. In fact, because it often takes place when health and safety information  
28 is being developed for a material, R&D presents an ideal opportunity to gather data on a product's  
29 potential impacts and to make design adjustments if appropriate. Similarly, as discussed below,  
30 differences between R&D activities and the commercial manufacturing process (e.g., use of protective

	<b>Life Cycle</b>	<b>Release Scenarios</b>	<b>DecaBDE Release Form</b>	<b>CNT Release Form<sup>1</sup></b>
<b>Feedstocks</b>	Raw materials from which decaBDE or MWCNTs are synthesized	Extraction Processing	N/A N/A	N/A N/A
	<b>Material Synthesis</b> Production of decaBDEs and MWCNTs	Synthesis	Free	Free, Bundled
Recovery		Free	Free, Bundled	
Handling/packaging		Free	Free, Bundled	
Equipment cleaning		Free	Free, Bundled	
Accidents		Free	Free, Bundled	
<b>Material Processing</b> Purification/modification of decaBDE and MWCNTs	Purification	N/A	Free, Bundled	
	Functionalization	N/A	Free, Bundled	
	Dispersal	N/A	Free, Bundled	
	Handling/packaging	N/A	Free, Bundled	
	Equipment cleaning	N/A	Free, Bundled	
<b>Product Manufacturing</b> Formulation and application of flame retardant to textiles and textile finishing and upholstering	Formulation	Free, Matrix-Bound	Free, Bundled, Matrix-Bound	
	Application	Matrix-Bound	Matrix-Bound	
	Processing	Matrix-Bound	Matrix-Bound	
	Textile/furniture processing	Matrix-Bound	Matrix-Bound	
	Equipment cleaning	Free, Matrix-Bound	Free, Bundled, Matrix-Bound	
	Accidents	Free, Matrix-Bound	Free, Bundled, Matrix-Bound	
	<b>Storage and Distribution</b>	<b>Material</b> Supply of decaBDE and MWCNTs		
<b>Flame Retardant</b> Supply of flame retardant		Accidents	Free, Matrix-Bound	Free, Bundled, Matrix-Bound
<b>Product</b> Supply of flame-retardant upholstery textiles				
<b>Use</b>	Intended and unintended/accidental use of flame-retardant upholstery textiles	Intended (sitting, cleaning, etc.)	Matrix-Bound	Matrix-Bound
		Unintended/accidents	Free, Matrix-Bound	Free, Matrix-Bound
<b>End of Life</b>	<b>Material</b> Reuse, recycling, and disposal of decaBDE and MWCNTs	Reuse/repurposing	Matrix-Bound	Matrix-Bound
		Recycling	Matrix-Bound	Matrix-Bound
	<b>Flame Retardant</b> Reuse, recycling, and disposal of flame retardant	Incomplete incineration	Matrix-Bound	Matrix-Bound
		Landfilling	Matrix-Bound	Matrix-Bound
	<b>Product</b> Reuse, recycling, and disposal of flame-retardant upholstery textile	Wastewater sludge	Matrix-Bound	Matrix-Bound

Sources: Chaudhry et al. (2009); Kohler et al. (2008); Johnson et al. (2010); Zhou and Gong (2008); Som et al. (2011); U.S. EPA (2005a); Lassen et al. (1999); NRC (2000); Palm et al. (2002); Agrell et al. (2004); EU (EU, 2002).

<sup>1</sup>No data available that specifically describe release form of MWCNTs.

N/A = not applicable; CNT = carbon nanotube

Figure 2-1. Life-cycle stages, potential release scenarios, and forms of release for decaBDE and MWCNTs in flame-retardant coatings applied to upholstery textiles

1 equipment, volume of material produced) could be important considerations in mitigating potential risks  
2 to individuals involved in R&D versus commercial manufacturing.

3 To conduct a comparative CEA, relevant information on life-cycle inventories from existing  
4 LCAs would be incorporated into the product life cycle to characterize the inputs (e.g., raw materials,  
5 energy) and outputs (e.g., emissions to air and water, coproducts) associated with each material's  
6 manufacture. Impacts information from existing LCAs also would be considered (see Chapter 5). Other  
7 LCA aspects also might apply, including using an appropriate functional unit, which is a quantitative  
8 measure of a product's function or a process that facilitates comparison ([U.S. EPA, 2006](#)). In the current  
9 case study, a functional unit might correspond to the degree of flame retardancy conveyed by  
10 incorporation of a certain amount of decaBDE or MWCNTs. In general, for this case study, data that  
11 specify appropriate functional units were not identified; the reader might, however, consider how this  
12 aspect of existing or future LCAs could be incorporated into a future CEA when evaluating data gaps and  
13 needs.

14 This chapter outlines important aspects of each of the five life-cycle stages outlined in Figure 2-1  
15 for decaBDE and MWCNTs used in upholstery textiles. This chapter also includes descriptions of the  
16 important environmental release scenarios for decaBDE and MWCNTs across the product life-cycle  
17 stages based on current knowledge. A variety of release scenarios are possible throughout the life-cycle  
18 stages described in this chapter. Figure 2-1 also outlines potential release scenarios for decaBDE and  
19 MWCNT flame-retardant upholstery textile coatings throughout the life cycle along with potential forms  
20 of the released substances (i.e., free, bundled, or matrix bound). The terms free decaBDE or MWCNTs  
21 refer to pure, unbound materials. The term MWCNT bundles refers to clusters of MWCNTs loosely or  
22 tightly bound together.<sup>8,9</sup> The terms matrix-bound decaBDE and MWCNTs refer to these materials as a  
23 part of a polymer matrix (e.g., the flame-retardant formulation).

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<sup>8</sup>The term “bundle” is used to subsume aggregates, agglomerates, and other clusters of MWCNTs reported in the supporting literature because of the inconsistency in usage and, more importantly, the frequent lack of adequate information to determine which specific term might be more appropriately applied to a particular dispersion state observed in a study or report. Where possible, this case study describes the relative characteristics of different dispersion states (e.g., more loosely or tightly bundled, ropier or more entangled) and quantifies the differences between these characteristics if this information is provided by the study authors.

<sup>9</sup>Molecules of decaBDE do not bind with each other and therefore are not present in a form comparable to MWCNT bundles. DecaBDE molecules, however, do adsorb strongly to dust particles (see Section 3.2), as might MWCNTs. Although the ways that adsorption to dust could facilitate release (i.e., offer a transport vector) of pure decaBDE from a product matrix are discussed in this chapter, the dust-decaBDE complex is not considered a “release form” because dust was not included in the original product matrix.

## 2.1. Feedstocks

### 2.1.1. Life-Cycle Processes

#### *Decabromodiphenyl Ether*

1           The raw materials used in commercial synthesis of decaBDE are phenol, bromine, and a catalyst  
2 (e.g., aluminum bromide or iron) ([IPCS, 1994](#)). Phenol is produced from cumene, which is obtained  
3 primarily from the distillation or other processing of petroleum products ([Khanam, 2010](#)). Commercial  
4 production of bromine involves the drying of brine, typically obtained from sea water ([Kesner, 2005](#)). No  
5 data were found on the energy and resource demands of raw material extraction for synthesis of  
6 decaBDE.

#### *Multiwalled Carbon Nanotubes*

7           A wide variety of hydrocarbons and catalysts is used to synthesize MWCNTs. The raw materials  
8 required for MWCNT synthesis include a precursor carbon material, inert gas, and metal catalysts, with  
9 specific materials depending on the particular synthetic pathway used (as described in the next section)  
10 ([Moisala et al., 2003](#)). Support materials such as aluminum, manganese oxide, or silica also are used  
11 during synthesis of MWCNTs ([Gustavsson et al., 2011](#)). No quantitative data were found on total  
12 magnitude of feedstocks that are or might be used in commercial synthesis of MWCNTs. Table 2-1,  
13 however, lists the amounts of inputs required for synthesizing 1 gram of single-walled carbon nanotubes  
14 (SWCNTs) using two of the common forms of carbon nanotube (CNT) synthesis (both of which are  
15 discussed in the next section). According to Healy et al. ([2008](#)), synthesis of SWCNTs requires large  
16 quantities of feedstocks compared to output (see Table 2-2). These inputs were calculated, however,  
17 assuming a very low synthesis reaction yield (2.95–4.50%), or mass of CNTs divided by the mass of  
18 carbon fed into the system. Current synthesis reaction yields can range from 1% to 17,900% depending on  
19 synthesis method and choice of catalyst ([Zhang et al., 2011b](#)). Process optimization has led to  
20 dramatically improved yields of CNTs over the past few years ([Zhang et al., 2011b](#)), which have likely  
21 increased the reaction yield for the CNT synthesis process substantially since Healy et al. ([2008](#)) was  
22 published. Limited information suggests that synthesis of MWCNTs requires larger amounts of precursor  
23 material than SWCNTs ([Tsai et al., 2009](#)).

Table 2-1. Typical inputs for synthesis of 1 gram of single-walled carbon nanotubes (SWCNTs) required for two methods.<sup>1</sup>

Chemical vapor deposition synthesis		Arc-discharge synthesis	
Input	Mass (g)	Input	Mass (g)
Ammonium molybdate tetrahydrate (catalyst precursor)	$2.4 \times 10^{-3}$	Iron powder (catalyst)	13.50
Magnesium nitrate hexahydrate (catalyst precursor)	3.27	Yttrium powder (catalyst)	3.40
Cobalt nitrate hexahydrate (catalyst precursor)	0.02	Sulfur powder (catalyst)	1.82
Citric acid (catalyst precursor)	0.13	Carbon powder (carbon precursor material)	1.70
Methane (carbon-containing gas)	41.85	Helium (process gas)	173.61
Hydrogen (process gas)	42.07	Graphite (anode/carbon precursor material)	169.06
Argon (process gas)	833.67	Graphite (cathode)	0.27

Source: Healy et al. (2008).

<sup>1</sup>These represent the necessary mass inputs assuming a synthesis reaction yield (SRY) of 4.50% for arc-discharge synthesis and 2.95% for chemical vapor deposition synthesis.

## 2.1.2. Potential Releases during the Feedstock Extraction Stage

1 Release of decaBDE and MWCNTs would not occur during this initial phase of the life cycle  
2 given that their synthesis does not occur until the following stage. Release of hazardous raw materials,  
3 however, could occur during the extraction and processing of feedstock materials. Specific materials that  
4 could be released include petroleum-based chemicals for decaBDE. Releases for MWCNT raw materials  
5 would depend on the method of production, but likely would include catalyst metals and carbon precursor  
6 materials. No data were identified quantifying the potential volume of releases during feedstock  
7 extraction for either decaBDE or MWCNTs.

## 2.2. Manufacturing

1           The manufacturing stage for decaBDE and MWCNT flame-retardant upholstery can be viewed as  
2 a sequential process involving synthesis of decaBDE or MWCNTs, material processing (i.e., purification  
3 and modification of MWCNTs), and product manufacture (i.e., formulation of the flame-retardant  
4 mixture, application of the flame-retardant mixture to textiles, and incorporation of the flame-retardant  
5 textile into consumer or commercial goods). R&D also is included in this section, given the similarities to  
6 key aspects of synthesis, processing, and manufacture.

### 2.2.1. Research and Development

#### 2.2.1.1. Life-Cycle Processes

7           Research on decaBDE and MWCNTs and on flame-retardant coatings involving these substances  
8 is principally conducted in specialized laboratory environments. R&D activities are expected to be carried  
9 out by individuals rather than automated mechanisms used in commercial-scale manufacture. The  
10 processes of interest to researchers are similar to those used in commercial-scale manufacture of these  
11 materials: synthesis, purification, modification, dispersion, incorporation into flame-retardant  
12 formulations, and application to textiles. For MWCNTs, current research efforts focus on synthesis and  
13 purification methods to improve CNT quality and purity ([Kohler et al., 2008](#)). Substantially less R&D  
14 related to decaBDE flame retardants is expected to occur at the present time, given that decaBDE flame-  
15 retardant technologies are more mature and the use of decaBDE is decreasing or being phased out due to  
16 health and ecological concerns. The following sections (material synthesis, material processing, and  
17 product manufacturing) provide detailed information on the processes of potential interest for R&D.

#### 2.2.1.2. Potential Releases during the R&D Stage

18           Release scenarios during the R&D stage are expected to be similar to release scenarios from  
19 commercial synthesis described in the following sections, but the quantities released are anticipated to be  
20 much smaller in the R&D stage. The quantities of decaBDE and MWCNTs handled in research  
21 laboratories are much smaller than those handled in commercial-scale manufacturing facilities.  
22 Additionally, R&D activities generally are carried out in laboratories with specialized pollution control  
23 systems in place, including fume hoods, ventilation systems, and environmental control systems. This  
24 practice might not be the case, however, for small start-up operations. Given the experimental and



1 somewhat unpredictable nature of R&D, releases from handling materials during synthesis, processing  
2 and purification, storage, and analysis are possible.

3 No information was found in the literature that describes release of decaBDE from R&D  
4 facilities. One industry report measured airborne release of CNTs ( $0.25 \mu\text{g}/\text{m}^3$ ) in the R&D facilities for a  
5 company that manufactures Thermocyl®, an MWCNT flame-retardant coating application ([Luizi, 2009](#)).  
6 No data were found that describe how releases in academic labs compare with releases in commercial  
7 R&D labs.

## 2.2.2. Material Synthesis

### 2.2.2.1. Life-Cycle Processes

#### *Decabromodiphenyl Ether*

8 Commercial synthesis of decaBDE involves conversion of phenol to diphenyl ether via the  
9 Williamson ether synthesis [Kirk Othmer (2005) as cited in Wright et al. ([2008](#))]. Diphenyl ether is then  
10 brominated in the presence of a catalyst (generally, aluminum bromide or iron) to produce commercial  
11 decaBDE ([EU, 2002](#); [IPCS, 1994](#)). Commercially, decaBDE is synthesized in a batch process in enclosed  
12 vessels during both the reaction and the subsequent drying process ([IPCS, 1994](#)). DecaBDE powder is  
13 collected in bags during the recovery phase following the synthesis process ([EU, 2002](#)). Commercial  
14 formulations of decaBDE typically contain decaBDE, 97–98% weight-for-weight measurement, and other  
15 polybrominated diphenyl ethers (PBDEs) (primarily nonaBDE), 0.3–3.0% weight-for-weight  
16 measurement ([IPCS, 1994](#)). No information was found on by-products of decaBDE synthesis.

#### *Multiwalled Carbon Nanotubes*

17 In 2010, chemical vapor deposition (CVD) synthesis produced approximately 83% of the global  
18 supply of CNTs, followed by arc-discharge synthesis (12%) and laser-ablation synthesis (5%) ([Nanowerk,](#)  
19 [2011](#)) (see Table 1-10 for information on MWCNT global production capacity). What proportion of  
20 MWCNTs is synthesized using each method, however, is unclear. Table 2-2 summarizes some of the  
21 performance characteristics of these three synthesis methods.  
22 CVD synthesis takes place in two furnaces connected by a quartz tube ([Healy et al., 2008](#)). The catalyst  
23 mixture is heated before it is added to the furnace along with a carbon-containing gas ([Karthikeyan et al.,](#)  
24 [2009](#); [Healy et al., 2008](#)). CNTs are recovered once the furnaces cool to room temperature ([Karthikeyan](#)  
25 [et al., 2009](#)). MWCNTs can be grown on a substrate (e.g., Si/SiO<sub>2</sub>) or without a substrate ([Tsai et al.,](#)  
26 [2009](#)). CNTs produced using deposition substrates are recovered by automated or manual mechanical

1 removal ([Kohler et al., 2008](#)); however, specific details regarding the method of recovery were not  
2 identified.

---

Table 2-2. Summary of common CNT synthesis methods.<sup>1</sup>

Characteristic	CVD	Arc discharge	Laser ablation
Growth temperature	600–1100 °C	2500–3000 °C	1200 °C
Production	Continuous	Batch	Batch
Scalability	Scalable	Not currently scalable	Not currently scalable
Product quality	Many structural defects Long tubes Low crystallinity <sup>2</sup>	Few structural defects Short tubes Carbon-containing metal impurities	Few structural defects Diameter control
By-products	Over 45 side products, including polycyclic aromatic hydrocarbons and volatile organic compounds	Black carbon and airborne inorganic compounds	No Data

<sup>1</sup>No data available that specifically describe MWCNTs.

<sup>2</sup>Low degree of structural ordering.

CVD = Chemical vapor deposition

Sources: Li et al. ([2010](#)), Healy et al. ([2008](#)); Karthikeyan et al. ([2009](#)); Rafique and Iqbal ([2011](#)); Plata et al. ([2009](#)).

3            Synthesis by arc discharge involves passing an electric current between two graphite electrodes  
4 ([Healy et al., 2008](#)) in the presence of an inert gas. The anode contains a hole filled with carbon powder  
5 and a catalyst, and the electric current results in the vaporization of the graphite anode and subsequent  
6 condensation on the cathode and the walls of the reaction vessel ([Baddour and Briens, 2005](#)). CNTs  
7 deposits form as black powder in the reaction vessel ([Healy et al., 2008](#)). CNTs are generally recovered  
8 from a receptacle after arc-discharge synthesis ([Kohler et al., 2008](#)), but whether recovery is usually a  
9 manual or automated process is unclear.

10            Laser-ablation synthesis of MWCNTs involves vaporizing a metal-graphite composite block in  
11 the presence of an inert gas and a catalyst ([Karthikeyan et al., 2009](#)). The composite block is placed inside  
12 an oven, a laser is pointed at the block, and argon gas is pumped parallel to the laser beam. As the laser  
13 ablates the target at high temperatures, CNTs form and are carried by the gas flow onto a collector  
14 ([Karthikeyan et al., 2009](#)). See Sections 5.3.2 and 5.3.4 for information on the estimated energy  
15 requirements and costs of CNT synthesis.

## 2.2.2.2. Potential Releases during the Material Synthesis Stage

### *Decabromodiphenyl Ether*

1           Synthesis of decaBDE could result in releases to air or water ([U.S. EPA, 2005a](#)). Fugitive  
2 releases of decaBDE vapor from a reactor vessel have been estimated as  $1.1 \times 10^{-5}$  mg/ton, and release  
3 from the bagging of synthesized PBDEs have been estimated as <70 g/ton PBDE produced [([EU, 2002](#));  
4 EEC (1993) as cited in EU ([2002](#))]. Airborne releases of decaBDE particles likely would sorb to dust (see  
5 Section 3.2), but loose dust likely would be vacuumed and the area would be washed with water, reducing  
6 airborne particles ([EU, 2002](#)). The main source of water release of decaBDE during the synthesis stage  
7 would be due to cleaning of equipment and floors after synthesis. One study found, however, that  
8 wastewater releases of decaBDE are unlikely to exceed 0.5 kg/ton if equipment is washed after every  
9 batch ([EU, 2002](#)). Releases directly to skin could occur through handling of bags containing solid  
10 decaBDE ([U.S. EPA, 2005a](#)). Large manufacturing facilities, however, likely would have exhaust  
11 ventilation in place to minimize air release into the general environment. Engineering controls that  
12 regulate temperature and pressure to minimize the potential for release also would likely be in place ([U.S.](#)  
13 [EPA, 2005a](#)). As a result, air and water releases of decaBDE to the environment during the synthesis  
14 stage are not expected to be large.

15           Accidental releases through fugitive equipment leaks, malfunctioning ventilation systems, and  
16 exposure to fire or high heat could occur at all stages of manufacturing (material synthesis, material  
17 processing, and product manufacture). A fugitive equipment leak or ventilation malfunction could lead to  
18 the airborne releases of decaBDE, as could exposure to fire or high heat. If exposed to high heat,  
19 decaBDE can form polybrominated dibenzofurans (PBDFs), polychlorinated dibenzo-p-dioxins, and  
20 nonhalogenated substances such as polycyclic aromatic compounds, which could be released into the  
21 environment ([EU, 2002](#)). Such accidental events could result in larger releases of decaBDE to the  
22 environment than normal release scenarios due to the lack of control mechanisms compared to those in  
23 place to mitigate anticipated releases.

### *Multiwalled Carbon Nanotubes*

24           The potential release of MWCNTs during synthesis primarily depends on the synthesis and  
25 processing methods and the physical properties of the MWCNTs (e.g., size, bundling, density) ([Kohler et](#)  
26 [al., 2008](#)). Because few data were available that describe releases from commercial-scale manufacture of  
27 MWCNTs, this section also relies on CNT release data from R&D facilities. Although releases of  
28 MWCNTs could occur during the synthesis stage, evidence describing the likelihood and quantity of  
29 release is mixed. In general, MWCNTs grown on substrates are likely to produce fewer airborne releases  
30 than vapor-phase synthesis methods ([Bello et al., 2009](#); [Tsai et al., 2009](#)). Mechanical removal (either

1 automated or manual) of CNTs from the substrate, however, can cause airborne release of CNTs ([Kohler](#)  
2 [et al., 2008](#)). In one study, CVD synthesis, both with and without a substrate, resulted in a concentration  
3 at the source of synthesis of more than  $2$  to  $3 \times 10^6$  particles/cm<sup>3</sup> that measured less than 560 nm in  
4 diameter ([Tsai et al., 2009](#)), but another study found no measurable airborne release of CNTs during  
5 substrate-bound CVD growth of CNTs ([Bello et al., 2009](#)). One study conducted in three commercial  
6 facilities and four research laboratories concluded that during synthesis, processing, and product  
7 manufacturing, nanoparticle releases occurred most frequently when opening the CVD vessel and when  
8 preparing the catalysts ([Lee et al., 2010](#)). No data were found on potential releases from laser-ablation  
9 synthesis of MWCNTs, but low levels of SWCNT clusters were released as aerosols during laser-ablation  
10 synthesis of SWCNTs in laboratory and field conditions ([Maynard et al., 2004](#)). This study intentionally  
11 agitated the SWCNTs, however, which would not be a normal component of the synthesis stage.

12         Synthesis of MWCNTs might release even greater quantities of CNTs, by-products, and  
13 feedstock materials than SWCNTs due to the larger quantities of precursor materials required for  
14 synthesis ([Tsai et al., 2009](#)). CNT powder generally comprises large bundles of CNTs and air release of  
15 these bundles is likely to occur during operations involving agitation (e.g., scraping, shaking) ([Fleury et](#)  
16 [al., 2011](#)), but local exhaust ventilation substantially reduces airborne releases to the environment ([Lee et](#)  
17 [al., 2010](#); [Han et al., 2008](#)). Loose MWCNTs and the equipment used during synthesis are likely to be  
18 cleaned up with a vacuum, which appears to be effective in reducing the airborne concentration of  
19 nanoparticles ([Lee et al., 2010](#)). Vacuuming, rinsing, and changing dust filters and other cleaning and  
20 maintenance activities also could result in subsequent release of MWCNTs to air or wastewater ([Kohler et](#)  
21 [al., 2008](#)).

22         MWCNTs released during synthesis can contain significant impurities (see Section 2.2.3.1). In  
23 addition, by-products from materials used in synthesis can be released at multiple points during the  
24 synthesis process ([Plata et al., 2009](#)). Some by-products, such as phenol, can be formed from general  
25 combustion processes used in CNT synthesis ([Eckelman et al., 2012](#)). Air release of synthesis by-products  
26 including polycyclic aromatic hydrocarbons and volatile organic compounds has been observed during  
27 CVD synthesis of CNTs in the absence of engineering controls ([Plata et al., 2009](#)); if employed, control  
28 technologies would be expected to limit these releases.

29         Accidental releases that could occur during decaBDE synthesis might also occur during MWCNT  
30 synthesis. These accidental scenarios include fugitive equipment leaks, malfunctioning ventilation  
31 systems, and exposure to fire and high heat. MWCNTs will not necessarily be destroyed at high  
32 temperatures (i.e., those possible in accidental fires) ([Kohler et al., 2008](#)), which could lead to airborne  
33 release or creation of ash containing elevated levels of MWCNTs ([Chaudhry et al., 2009](#)). Additionally,  
34 damaged filters that collect MWCNTs could result in airborne release during synthesis ([Kohler et al.,](#)

1 [2008](#)). Such accidental events, while unlikely, could result in potentially large releases of MWCNTs to  
2 the environment.

3 Table 2-3 summarizes the anticipated potential release scenarios from the material synthesis stage  
4 of decaBDE and MWCNTs.

---

Table 2-3. Potential release scenarios during material synthesis.

---

Processes included in material synthesis life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Synthesis and purification	Occurs in closed vessel, but fugitive air emissions could occur	Occurs in closed vessel, but fugitive air emissions could occur; release depends on synthesis method
Recovery of synthesized substance	Air release could occur during bagging	Air release could occur during removal from substrate and bagging
Handling/packageging	Air release could occur	Air release could occur
Equipment cleaning	Air and water release could occur	Air and water release could occur
Accidental releases (equipment malfunction, etc.)	Air release could occur	Air release could occur

---

## 2.2.3. Material Processing

### 2.2.3.1. Life-Cycle Processes

5 Material processing includes any modification of decaBDE or MWCNTs after synthesis and  
6 before incorporation into a flame-retardant formulation. These modifications can include purification,  
7 functionalization, and dispersal in solvents.

#### *Decabromodiphenyl Ether*

8 After synthesis, decaBDE does not require further processing before incorporation into the flame-  
9 retardant formulation.

#### *Multiwalled Carbon Nanotubes*

10 MWCNTs undergo physical and chemical processing before they are incorporated into flame-  
11 retardant applications. Commercial MWCNTs that have not been purified can contain large amounts of  
12 impurities, such as amorphous carbon, graphite, and encapsulated metallic particles ([Hou et al., 2008](#)).  
13 After synthesis, MWCNTs are typically purified using physical (e.g., flocculation, microfiltration,

1 centrifugation) or chemical (e.g., acid treatment) techniques ([Hou et al., 2008](#)). Appendix C presents  
2 various CNT purification methods and their efficacies in removing various classes of impurities.  
3 By-products of purification techniques are expected to differ according to the technique used; one study  
4 reported waste products of sodium hydroxide, ethanol, water, filtrate, and scrap membrane following  
5 general purification of SWCNTs ([Healy et al., 2008](#)).

6 One analysis found that samples of MWCNTs purified by the manufacturer contained metal  
7 impurities ranging from 0.44 to 1.75 (wt%) ([Ge et al., 2011](#)). After further purification with an acid  
8 treatment, significant quantities of catalyst residues (e.g., cobalt, chromium, iron, manganese,  
9 molybdenum, and nickel) remained ([Ge et al., 2011](#)). Additionally, trace noncatalyst impurities (mostly  
10 transition metals such as cerium, gadolinium, holmium, etc.) were also found in purified CNTs, which the  
11 authors theorize can form during production/post-purification processes or might be introduced as catalyst  
12 synergists to improve the quality of synthesized CNTs ([Ge et al., 2011](#)). Additionally, the purification  
13 process itself also can damage the CNTs by introducing structural defects ([Gustavsson et al., 2011](#)).

14 Before application, MWCNTs generally require surface functionalization ([Saeed, 2010](#)).  
15 Functionalization—the modification of materials by covalently or noncovalently attaching new molecular  
16 components—can alter the physicochemical properties of MWCNTs dramatically ([Kohler et al., 2008](#);  
17 [Ma et al., 2008](#); [Hirsch and Vostrowsky, 2005](#)). Often, the goal of functionalization of MWCNTs is to  
18 increase solubility, which facilitates dispersion into solvents and polymers ([Saeed, 2010](#)). One example of  
19 functionalization consists of the covalent grafting of MWCNTs to traditional flame retardants ([Ma et al.,](#)  
20 [2008](#)). Table 2-4 presents examples of MWCNT functionalization. After functionalization, MWCNTs are  
21 often dispersed in water or organic solvents before they are incorporated into products ([Saeed, 2010](#)).  
22 Most dispersion methods use dry mixing or liquid-phase sonication (agitation of particles with ultrasound  
23 energy) to break up clumps and disperse MWCNTs in water or organic solvents.

### 2.2.3.2. Potential Releases from the Material Processing Stage

24 During the recovery, processing, handling, and packaging stages, CNTs are more likely to be  
25 released as bundles from bulk powder than as individual CNTs ([Kohler et al., 2008](#)) (see Table 2-1). In  
26 general, releases resulting from liquid-phase processing of CNTs will be lower relative to those resulting  
27 from dry handling, which can result in greater nanoparticle release ([Kohler et al., 2008](#)). What proportion  
28 of MWCNT processing occurs in the liquid versus the dry phase, however, is unclear. Handling of  
29 MWCNTs can cause airborne release of particles ([Methner et al., 2010](#)). Dispersal of MWCNTs in  
30 suspensions can reduce the likelihood of aerosolization ([Johnson et al., 2010](#)), but mixing and sonicating  
31 (common processes used to disperse MWCNTs in solution) might also result in airborne release of raw  
32 and functionalized MWCNTs ([Johnson et al., 2010](#); [Lee et al., 2010](#); [Methner et al., 2010](#)). Environmental

Table 2-4. Examples of functionalization of MWCNTs.

Functionalization technique	Goal of functionalization	Additional reagents	Reference
Amidation – Formation of carbon nanotube-acyl amides	Creation of anchor groups for further modification	thionyl chloride, dicyclohexylcarbodiimide	Hirsch and Vostrowsky (2005)
Fluorination	Solubility in polar solvents	elemental fluorine	Hirsch and Vostrowsky (2005)
Chlorination	Solubility in polar solvents	chlorine gas	Hirsch and Vostrowsky (2005)
Noncovalent exohedral functionalization	Solubility in polar solvents	streptavidin	Hirsch and Vostrowsky (2005)
Covalent grafting on intumescent flame retardant	Better dispersion in matrix; solubility and stability in polar solvents; enhanced network structure at very low nanotube loading	poly(diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate)	Ma et al. (2008)
Atom transfer radical polymerization	Creation of anchor groups for further modification	styrene and methyl methacrylate	Baskaran et al. (2004)
In situ surface reversible addition-fragmentation chain transfer polymerization	Solubility in polar solvents	styrene and <i>N</i> -isopropylacrylamide	Xu et al. (2007)
Electrografting	Solubility in polar solvents	polyacrylonitrile	Petrov et al. (2004)
Radiation polymerization	Solubility in polar solvents	ethanol, poly(acrylic acid), acrylic acid	Chen et al. (2006)
Liquid- and gas-phase oxidization with thermal treatment	Increased acidity or alkalinity; improved flame-retardant properties	nitric acid	Goncalves et al. (2012)

1 control mechanisms likely would be in place to reduce environmental releases in facilities that process  
 2 MWCNTs (Fleury et al., 2011; Methner et al., 2010). Cleaning of processing equipment and facilities can  
 3 lead to release of MWCNTs to air or wastewater (Fleury et al., 2011). MWCNTs released during this  
 4 stage might still contain some of the impurities listed in Section 2.2.3.1 and Appendix C.

5 Release of by-products from CNT processing also might occur. One modeling study notes the  
 6 potential for release of phenol from the production of nitric acid, a substance commonly used in CNT  
 7 purification (Eckelman et al., 2012). The release of other substances used during purification is also  
 8 possible.

1           The accidental release scenarios for MWCNTs during processing are similar to those in the  
 2 material synthesis stage (see Section 2.2.2.2). Additionally, spills of solutions containing dispersed  
 3 MWCNTs might occur during the processing stage, which could result in the release of MWCNTs to  
 4 wastewater.

5           Table 2-5 summarizes potential release scenarios from the material processing stage of  
 6 MWCNTs. No release scenarios for decaBDE are summarized here because the activities specified for  
 7 this stage are not anticipated to occur for decaBDE.

---

**Table 2-5. Potential release scenarios during material processing.**

---

Processes included in material processing life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Purification	N/A	Air release possible due to physical purification methods such as flocculation, microfiltration, centrifugation, etc. (see Appendix C)
Functionalization	N/A	Air and water release possible during functionalization reactions; release depends on method of functionalization
Dispersion	N/A	Air release possible, especially during dry mixing
Handling/packaging	N/A	Air release possible during dry processes
Equipment cleaning	N/A	Air and water release possible
Accidental releases (spills, equipment malfunction, etc.)	N/A	Water release possible from spills in liquid-phase reactions and once MWCNTs are dispersed in solution; air release possible from fugitive emissions

N/A = Not Applicable

## 2.2.4. Product Manufacturing

8           In this section, product manufacturing for decaBDE and MWCNTs is described. This life-cycle  
 9 stage is considered to include the manufacture of flame-retardant formulations, the manufacture of textiles  
 10 containing either decaBDE- or MWCNT-based flame retardants, and the manufacture of end-use products  
 11 containing flame-retardant materials, such as furniture.



## 2.2.4.1. Life-Cycle Processes

### *Decabromodiphenyl Ether*

1 In a typical decaBDE flame-retardant formulation, decaBDE and antimony trioxide (a synergist  
2 used to enhance the activity of decaBDE) are first mixed as a dispersion in water ([EU, 2002](#)). This mix is  
3 stored in tanks and then piped directly into a closed vessel ([EU, 2002](#)). The decaBDE-antimony trioxide-  
4 water dispersion is added to emulsion polymers and mixed in this closed vessel to formulate the flame  
5 retardant ([EU, 2002](#)). One analysis found trace amounts of polybrominated dibenzo-p-dioxins (PBDDs)  
6 and PBDFs as impurities in commercial mixtures of decaBDE ([Ren et al., 2011](#)). No data were found that  
7 describe other characteristics of decaBDE flame-retardant formulations or the by-products of their  
8 manufacture.

9 During application, the decaBDE flame-retardant formulation is typically back-coated, or applied  
10 as a resin to the reverse surface of textiles along with a binding agent, such as latex or a copolymer (see  
11 Section 1.2.2.2). Due to the high efficiency of decaBDE flame retardants, they can be used in  
12 formulations with low loadings compared to other brominated flame retardants ([Pure Strategies Inc.,](#)  
13 [2005](#)). Typical loadings of decaBDE in textiles range from 30 to 40% by dry weight of the dry coating  
14 with different loadings applied to different types of fabrics (30–40 g/m<sup>3</sup> in cotton to 70–80 g/m<sup>3</sup> for velour  
15 fabrics) ([EU, 2002](#)). After application, the decaBDE flame-retardant upholstery textile is cut, shaped, and  
16 glued or stapled to furniture.

### *Multiwalled Carbon Nanotubes*

17 CNTs can be dispersed in polymers by in situ polymerization or by using a twin-screw extruder (a  
18 specialized machine using two screws to mix, compound, and react polymers) [(Laxminarayana et al.  
19 (2005) as cited in Kohler et al. ([2008](#))). One study described the manufacture of a “high heat”  
20 acrylonitrile-butadiene-styrene polymer matrix filled with CNTs ([Fleury et al., 2011](#)). According to this  
21 study, masterbatch granules (1–4 mm long) consisting of thermoplastic resin and 15% CNTs by weight  
22 are mixed with the pure polymer matrix in injection molding and extrusion processes (where  
23 thermoplastics are fed into a heated vessel and forced into a mold cavity where they cool) ([Fleury et al.,](#)  
24 [2011](#)). Little information is available regarding the ingredients and characteristics of MWCNT flame-  
25 retardant formulations and possible by-products from their manufacture. Thermocyl™, an MWCNT  
26 flame retardant, includes silicone resins containing MWCNTs ([Luizi, 2009](#)). In another formulation,  
27 MWCNTs have been used in place of ammonium polyphosphate, a traditional phosphorus-based flame  
28 retardant, as a filler with polymethyl methacrylate (PMMA) and polyamide-6 ([Motzkus et al., 2012](#)).  
29 General components of MWCNT flame-retardant formulations include epoxies, polyesters, and  
30 vinyl esters ([Alberding et al., 2011](#)).

1 MWCNTs can be applied to textiles as a flame-retardant coating by (1) soaking the textile or (2)  
2 spray coating the surface of the textile ([Luizi, 2009](#)). The soaking application method for MWCNTs is  
3 similar to that used to apply decaBDE flame-retardant coatings (see Figure 1-3). In a recent study,  
4 researchers immersed cotton and polyester textiles in an MWCNT dispersion and maintained constant  
5 motion to embed functionalized MWCNTs in the textiles ([Gonçalves et al., 2012](#)). The authors reported  
6 acetic acid, sodium chloride, sodium carbonate, and sodium hydroxide as auxiliary reagents for this  
7 embedding process ([Gonçalves et al., 2012](#)). An alternative immersion method involves soaking a textile  
8 in a solution containing CNTs and then treating it with a crosslinking agent (similar to a binder), heating,  
9 rinsing, and drying the textile (with or without heat) ([Alimohammadi et al., 2011](#)). Uddin and Nyden  
10 ([2011a](#)) and Davis and Kim ([2010](#)) described a similar immersion method involving multiple treatments  
11 with polymeric solutions to create a coating consisting of layers of polyacrylic acid/MWCNT-  
12 polyethylenimine/ polyethylenimine. Flame-retardant-treated materials also can be cured using UV  
13 radiation ([Lu et al., 2011a](#)). Lee et al. ([2010](#)) mentioned the spray application of CNTs in solution to  
14 thinly coat wafers, but they did not describe the process in detail. The few laboratory-scale studies  
15 investigating MWCNT flame retardants in textiles have reported MWCNT loadings ranging from 0.5 to  
16 4% by mass ([Grzybowski, 2009](#); [Kashiwagi et al., 2005b](#); [Kashiwagi et al., 2005a](#); [Kashiwagi et al.,](#)  
17 [2004](#)), which are about an order of magnitude lower than those for decaBDE. Thermocyl™, a commercial  
18 MWCNT flame retardant, has been incorporated into polyethylene at a loading of 1% ([Luizi, 2009](#)). After  
19 application, the MWCNT flame-retardant upholstery is cut, shaped, and glued or stapled to furniture.

## 2.2.4.2. Potential Releases during Product Manufacture

### *Decabromodiphenyl Ether*

20 Release scenarios for product manufacturing are likely to be similar to those in the material  
21 synthesis and processing stages, but release amounts are probably lower ([U.S. EPA, 2005a](#); [EU, 2002](#)).  
22 Additionally, releases from this stage likely will not be decaBDE, but rather decaBDE in a polymer  
23 matrix. As discussed, decaBDE generally is synthesized as a powder and then mixed into solution when  
24 the flame retardant is formulated, minimizing releases of decaBDE to dust ([U.S. EPA, 2005a](#)).  
25 Nevertheless, manufacture of decaBDE flame-retardant coatings could release vapors if mixing and  
26 handling of raw decaBDE occurs in an open system ([U.S. EPA, 2005a](#)). One study found that  
27 environmental release was most likely to occur during the mixing of decaBDE powder and cleaning  
28 operations of the flame-retardant formulation stage ([EU, 2002](#)). Formulation of flame retardants,  
29 however, generally occurs in closed systems with engineering controls that regulate temperature and  
30 pressure to minimize potential releases ([U.S. EPA, 2005a](#); [EU, 2002](#)). Releases of decaBDE in this stage  
31 also can contain the impurities listed in Section 2.2.4.1.

1 The application of decaBDE flame-retardant coatings to upholstery textiles could result in the  
2 release of aerosolized decaBDE due to thermal processing, but release would occur only if the  
3 manufacturing plant does not have engineering controls in place to prevent such releases. Cutting, sewing,  
4 shaping, stapling, and other textile finishing processes could result in the airborne release of free  
5 decaBDE or decaBDE in a polymer matrix through abrasion. Equipment cleaning also could lead to the  
6 release of decaBDE in wastewater during the processing stages of product manufacture.

7 The accidental release scenarios for decaBDE during product manufacture are similar to those in  
8 the material synthesis stage (see Section 2.2.2.2). Additionally, in this stage spills could lead to release of  
9 decaBDE flame-retardant formulations in wastewater. Volatilization is unlikely due to the low volatility  
10 of decaBDE (see Table 3-1).

### *Multiwalled Carbon Nanotubes*

11 Environmental releases during the manufacture of MWCNT flame-retardant textiles can occur as  
12 a result of the following activities: mixing, handling/packaging, application of the flame retardant to  
13 textiles, textile processing/finishing, and accidents ([Zhou and Gong, 2008](#)). Few data are available that  
14 describe releases from commercial-scale manufacture of MWCNT flame-retardant textiles. Therefore,  
15 this section also relies on CNT release data from R&D facilities. Release of MWCNT bundles is possible  
16 when nanotubes are blended with polymers to formulate the flame retardant; however, releases are  
17 anticipated to be smaller for blending of masterbatches as opposed to blending of pure CNT powders  
18 ([Fleury et al., 2011](#)). The most critical phase for air and water releases during the formulation stage is the  
19 discharging and the cleaning of the mixing chamber ([Fleury et al., 2011](#)). Release from the formulated  
20 flame retardant is expected to be minimal, but packaging of the formulated flame retardant could result in  
21 releases. Airborne releases of CNTs ( $1.45 \mu\text{g CNT}/\text{m}^3$ ) were measured in a facility that packages  
22 Thermocyl®, an MWCNT flame-retardant coating ([Luizi, 2009](#)).

23 Application of MWCNT flame retardants to textiles also could lead to air or water releases.  
24 Currently, how a particular production method used to incorporate MWCNT flame retardant in the textile  
25 matrix might influence release potential and subsequent exposure potential is unknown. Any spray  
26 application could lead to the potential airborne releases of matrix-bound MWCNTs if the application does  
27 not occur in a closed environment. One study observed airborne release of both nanoparticles and fine  
28 particles when spraying an MWCNT solution onto wafers as a coating ([Lee et al., 2010](#)). The dominant  
29 particle size released during this study ranged from 50 to 110 nm and subsequent heating of the treated  
30 wafers also led to the release of particles smaller than 30 nm ([Lee et al., 2010](#)). Other data suggest that  
31 thermal processing (i.e., exposure to high temperatures and UV) might not lead to air release of  
32 MWCNTs from polymer matrices ([Nguyen et al., 2011](#)). In an analysis of an epoxy containing MWCNT,  
33 exposure to UV radiation and high temperatures (50 °C) degraded the polymer matrix, but the MWCNTs

1 formed a dense network on the composite surface and no evidence of particle release was observed  
2 ([Nguyen et al., 2011](#)). If the MWCNT flame-retardant coating is applied by soaking the textile, water  
3 release of matrix-bound MWCNTs could occur when the textile is rinsed. Additional cutting, sewing,  
4 shaping, stapling, and other textile finishing processes could result in the airborne release of free or  
5 matrix-bound MWCNTs through abrasion ([Kohler et al., 2008](#)). One study found that grinding a  
6 nanocomposite containing CNTs created a substantial amount of airborne particles made up of polymer  
7 fragments containing CNTs ([Fleury et al., 2011](#)). How applicable release from grinding of plastic  
8 nanocomposites is to release from textile applications, however, is unclear. Airborne releases of CNTs  
9 ( $1 \mu\text{g CNT/m}^3$ ) have been measured in a facility processing textiles treated with Thermocyl® ([Luizi,](#)  
10 [2009](#)). Most manufacturing facilities, however, would have controls in place to prevent or minimize  
11 airborne releases to the environment. Equipment cleaning at any point in this life-cycle stage could lead to  
12 release of MWCNTs to wastewater. Not enough is known about the other components of MWCNT flame-  
13 retardant formulations to hypothesize about other substances that might be released as a part of the flame-  
14 retardant product matrix, but the use of different substances in MWCNT flame-retardant formulations  
15 might lead to different release characteristics.

16 The accidental release scenarios for MWCNTs during product manufacture are similar to those in  
17 the material synthesis stage (see Section 2.2.2.2). In the product manufacturing stage, spills of MWCNT  
18 flame-retardant formulation might also occur and could result in the release of MWCNTs to wastewater.  
19 Table 2-6 outlines potential release scenarios from the product manufacturing stage of decaBDE and  
20 MWCNT flame-retardant textiles.

Table 2-6. Potential release scenarios during product manufacturing.

Processes included in product manufacturing life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Formulation of flame retardant	Air release possible when mixing dry decaBDE into product formulation	Air release possible when mixing dry MWCNTs into product formulation
Handling/packaging	Air release possible	Air release possible
Flame retardant application to textile	Air or water release possible depending on application method	Air or water release possible depending on application method; for example, if substances are sprayed onto textiles, release to air can occur
Thermal processing	Air release possible	Preliminary evidence on air release due to high heat is mixed
Rinsing/drying	Water release possible	Water release possible
Equipment cleaning	Air and water release possible	Air and water release possible
Textile processing	Air release possible due to cutting, sewing, shaping, etc.	Air release possible due to cutting, sewing, shaping, and other finishing processes
Furniture production	Air release possible due to cutting, stapling, etc.	Air release possible due to cutting, stapling, and other finishing processes
Accidental releases (e.g., spills, equipment malfunction)	Air and water release possible	Air and water release possible

## 2.3. Storage and Distribution

### 2.3.1.1. Life-Cycle Processes

1           The storage and distribution stage concerns the handling and transport of (1) decaBDE and  
 2 MWCNTs, (2) decaBDE and MWCNT flame-retardant formulations, and (3) decaBDE and MWCNT  
 3 flame-retardant upholstery textiles. The main method of transport for these materials is not known, but  
 4 likely would be by truck, train, or cargo ship.

5           **DecaBDE and MWCNTs**, if not immediately incorporated into a flame-retardant formulation,  
 6 likely would be stored at the site of synthesis/processing in sealed receptacles until they are incorporated  
 7 into flame-retardant formulations or transported to sites where manufacture of the flame retardant occurs.

8           **DecaBDE and MWCNT flame-retardant formulations** are typically stored at manufacturing  
 9 plants in drums, tanks, or more permanent storage vessels until they are packaged and sent to textile  
 10 manufacturers ([U.S. EPA, 2005a](#)).

1           **DecaBDE and MWCNT flame-retardant upholstery textiles** and end-use products likely also  
2 would be stored at the site of manufacture (or an intermediate storage site) and then transported to retail  
3 locations.

### 2.3.1.2. Potential Releases during Storage and Distribution

4           Storage and distribution of (1) decaBDE and MWCNTs, (2) decaBDE and MWCNT flame-  
5 retardant formulations, and (3) flame-retardant textiles could result in releases to the environment, but all  
6 release scenarios are unlikely:

7           **Releases of decaBDE and MWCNTs** separate from flame-retardant formulations are likely to be  
8 negligible. Release would be due primarily to accidents, as the materials would be stored in sealed  
9 receptacles after synthesis. Exposure of the receptacles to high heat/fire could lead to the airborne release  
10 of decaBDE or MWCNTs (see Section 2.2.2.2 for more details).

11           **Releases from flame-retardant formulations** could result in releases of decaBDE or MWCNTs  
12 to the environment ([U.S. EPA, 2005a](#)). The possible scenarios for release of decaBDE and MWCNT  
13 flame-retardant formulations during storage and distribution include damage to containers holding the  
14 flame-retardant formulation, leakage resulting from mishandling of containers, or faulty or improper  
15 stacking of cartons in transport vehicles. If the containers are sealed properly and not damaged during  
16 transport, releases of product prior to application might be limited to spills.

17           **Releases from flame-retardant upholstery textiles** could result from accidental exposure to  
18 high heat/fire, off-gassing of volatile components, and infestation with pests. Exposure of the flame-  
19 retardant upholstery textiles to high heat/fire during storage and distribution could lead to the degradation  
20 of the polymer matrix and subsequent airborne release of decaBDE and MWCNTs (both free and matrix  
21 bound) (see Sections 2.2.2.2 and 2.4.2 for more details). Off-gassing of the volatile components of  
22 decaBDE or MWCNT flame retardants also could occur in poorly ventilated areas that experience high  
23 temperatures (e.g., storage units, warehouses). DecaBDE and MWCNTs themselves, however, are not  
24 highly volatile (see Table 1-8, Table 1-9, and Table 3-1). Infestation of textile or furniture storage  
25 facilities with rodents or other pests also could lead to the release of decaBDE or MWCNT flame  
26 retardant materials to the environment.

27           Table 2-7 outlines potential release scenarios from the storage and distribution stage of  
28 (1) decaBDE and MWCNTs, (2) decaBDE and MWCNT flame-retardant formulations, and (3) decaBDE  
29 and MWCNT flame-retardant upholstery textiles.

Table 2-7. Potential release scenarios during storage and distribution.

	Processes included in storage and distribution life-cycle stage	Information on release	
		DecaBDE	MWCNTs
1	Storage/transport of raw materials (decaBDE and MWCNTs)	Release unlikely if properly stored	Release unlikely if properly stored
	Accidental releases of raw materials (decaBDE and MWCNTs)	Air release possible due to storage container defects	Air release possible due to storage container defects
2	Storage/transport of flame-retardant formulation	Release unlikely if properly stored	Release unlikely if properly stored
	Accidental releases of flame-retardant formulation	Water release possible due to spills from mishandling or faulty packaging	Water release possible due to spills from mishandling or faulty packaging
3	Storage/transport of treated textiles	Small air release possible if properly stored	Small air release possible if properly stored
	Accidental releases of treated textiles	Air release possible due to exposure to high heat, pest infestation, etc.	Release possible due to pest infestation; preliminary evidence suggests that release due to high heat is unlikely

## 2.4. Use

### 2.4.1. Life-Cycle Processes

1 A wide variety of textiles contain flame-retardant coatings (see Section 1.2). Upholstery textiles  
 2 are expected to be used in public places where people of all ages will sit, lie, or walk on them. Some  
 3 unintended uses of upholstery textiles include outdoor use, repurposing for use in other products, burning  
 4 as kindling, or mouthing by children. Repurposing for use in other products and burning as kindling are  
 5 covered in Section 2.5. In general, upholstery textiles are likely to have a lifespan of at least 10 years ([EU,](#)  
 6 [2002](#)).

### 2.4.2. Potential Releases during the Use Stage

7 Environmental releases are expected from upholstery textiles coated with flame retardants due to  
 8 (1) the potential use scenarios for the upholstery textiles and (2) the physicochemical properties of  
 9 decaBDE and MWCNTs. The anticipated long lifespan of upholstery textiles (>10 years) suggests that  
 10 releases in this stage could occur over several years ([EU, 2002](#)). Indeed, environmental concentrations of

1 decaBDE in buildings with products containing decaBDE can be high, especially in dust (see Sections  
2 4.1.2.5 and 4.1.2.6). One of the most important pathways for these high environmental concentrations is  
3 through airborne releases of decaBDE sorbed to dust in the environment (see Section 3.2). No similar  
4 concentration data resulting from consumer use are available for MWCNTs. The following characteristics  
5 of flame-retardant upholstery textiles, however, are expected to reduce releases of decaBDE and  
6 MWCNTs ([EU, 2002](#)):

- 7 • Flame-retardant coatings must meet durability requirements to comply with regulations (see  
8 Section 1.2.1);
- 9 • Flame retardant is often applied to the back of the fabric, minimizing wear and tear; and
- 10 • Upholstery textiles are unlikely to be washed frequently.

11 The integrity of the flame-retardant coating depends on the strength of the formulation that bonds  
12 it to the textile surface ([Som et al., 2011](#); [NRC, 2000](#)). Both decaBDE and MWCNT flame-retardant  
13 textile coatings considered in this case study are additive, suggesting that release from upholstery textiles  
14 could occur during the use stage. DecaBDE/antimony trioxide flame-retardant formulations are  
15 considered relatively durable, however, due to the copolymer resin that bonds to the textile fibers ([Pure  
16 Strategies Inc., 2005](#)). Even if migration of decaBDE through the polymer occurred, it would be expected  
17 to be very slow due to the high molecular weight of decaBDE ([Lassen et al., 1999](#)). In a substance flow  
18 analysis of plastics containing decaBDE, however, Lassen et al. (1999) found that release of decaBDE  
19 was expected to be greatest during the use stage. In general, CNTs are not likely to be released because  
20 they are very stable and do not readily degrade; they could, however, be released if the polymer matrix  
21 degrades ([Kohler et al., 2008](#)), or they could be released as a component of the polymer matrix. Even  
22 though CNTs might be embedded in a matrix, depending on the production method, a portion of a tube or  
23 a group of tubes could be left partially exposed in the final product.

24 Regular use of upholstered furniture (e.g., sitting, walking, lying) could abrade the textile surface  
25 and release small amounts of free or matrix-bound decaBDE or MWCNTs either into the air or onto the  
26 skin of users. Early unpublished evidence presented at a public meeting indicates that very small amounts  
27 of MWCNTs could be released as aerosols after subjecting an MWCNT-polymer nanocomposite to  
28 simulated wear and tear tests ([Uddin and Nyden, 2011b](#)). Washing of textiles also could lead to water  
29 release of matrix-bound decaBDE or MWCNTs. By some estimates, the principal source of decaBDE  
30 release in wastewater is due to textile washing ([EU, 2002](#)). Most flame-retardant upholstery textiles will  
31 be used indoors, minimizing exposure to UV light and weathering. Upholstery textiles that are back-  
32 coated (a common application method) with decaBDE or MWCNT flame retardant likely will not be  
33 subject to significant abrasion, washing, or UV light. Additionally, most releases of decaBDE or



1 MWCNTs initially will be to the indoor environment, but they could spread outdoors through  
2 environmental transport mechanisms (see Chapter 3) ([U.S. EPA, 2010b](#); [Lassen et al., 1999](#)).

3 The above processes could result in airborne release of decaBDE or releases in wastewater ([U.S.](#)  
4 [EPA, 2010b](#)). Although these processes also could result in release of MWCNTs to the air or to  
5 wastewater, less degradation of upholstery textiles is expected for MWCNT-treated composites than for  
6 traditional materials (see Section 1.3.3). As mentioned in Section 2.2.4.2, Nguyen et al. ([2011](#)) found that  
7 exposure of an epoxy containing MWCNTs to conditions of high heat and UV radiation can cause  
8 MWCNTs to form a dense network on the surface of composites, which might minimize environmental  
9 release. The authors also found that the epoxy containing MWCNTs degraded more slowly than unfilled  
10 epoxy or an epoxy containing another nanoscale material ([Nguyen et al., 2011](#)). A similar study found  
11 that when PMMA is filled with silane-coated MWCNTs the amount of submicrometric airborne particles  
12 emitted decreased when the polymer is exposed to fire compared to pristine PMMA ([Motzkus et al.,](#)  
13 [2012](#)). The authors noted that the release of airborne particles depends on a variety of factors, including  
14 the type of polymer matrix, the combustion process, and the type of surface treatment ([Motzkus et al.,](#)  
15 [2012](#)). A lack of data precludes a determination of whether similar MWCNT releases could be expected  
16 to occur in textiles containing MWCNTs.

17 Unintended uses also could lead to the release of decaBDE and MWCNTs from flame-retardant  
18 textiles. Use of flame-retardant upholstery textiles outdoors could lead to weathering, which could  
19 degrade the polymer matrix and release decaBDE or MWCNTs. Mouthing by small children, pets, or  
20 rodents on flame-retardant textiles could lead to the release of decaBDE or MWCNT directly into  
21 children's, pets', or rodents' mouths if the back-coating is exposed and the integrity of the fabric is  
22 compromised. Preliminary unpublished evidence presented at a public meeting, however, suggests that  
23 few MWCNTs are released from a flame-retardant nanocomposite when subjected to simulated chewing  
24 tests ([Uddin and Nyden, 2011b](#)). Accidental contact of flame-retardant textiles with fire and high heat  
25 also could occur and would lead to possible airborne releases, particularly of decaBDE (see Section  
26 2.2.2.2 for more details). No data were found, however, that describe the likelihood of these releases from  
27 this application.

28 Table 2-8 outlines potential release scenarios from the use stage of decaBDE and MWCNT  
29 flame-retardant textiles.

Table 2-8. Potential release scenarios during product use.

Processes included in use life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Intended use (e.g., sitting, standing)	Release possible due to abrasion or other physical/mechanical activities, resulting in direct release to individual in contact with the textile or to air as particle-bound substance (e.g., due to abrasion, release to dust)	Release possible due to abrasion or other physical/mechanical activities, resulting in direct release to individual in contact with the textile or to air as particle-bound substance (e.g., due to abrasion, release to dust)
Cleaning	Water release possible, but infrequent	Water release possible, but infrequent
Unintended use (outdoor use)	Air release possible due to weathering/degradation of the polymer; outdoor use could result in release to water or soil	Air release possible due to weathering/degradation of the polymer; outdoor use could result in release to water or soil
Unintended use (mouthing)	Direct release to mouth likely if polymer matrix surface is accessible and degraded	Direct release to mouth likely if polymer matrix surface is accessible and degraded
Accidental releases	Air release possible due to exposure to high heat or fire	Preliminary evidence suggests that air release due to high heat is unlikely

## 2.5. Reuse, Recycling, and End of Life

1           The reuse, recycling, and end-of-life stage encompasses a variety of different transformation and  
2 disposal processes for (1) decaBDE and MWCNTs, (2) decaBDE and MWCNT flame-retardant  
3 formulations, and (3) decaBDE and MWCNT flame-retardant upholstery textiles. What the primary reuse,  
4 recycling, and end-of-life treatments are for decaBDE and MWCNTs and decaBDE and MWCNT flame-  
5 retardant formulations are unclear. The reuse, recycling, and end-of-life treatments for flame-retardant  
6 upholstery textiles containing decaBDE and MWCNTs, however, are expected to be similar.

### 2.5.1. Reuse and Recycling

#### 2.5.1.1. Life-Cycle Processes

7           Reuse or recycling of decaBDE and MWCNTs or decaBDE and MWCNT flame-retardant  
8 formulations is unlikely. On the other hand, textile waste often is recovered and reused or recycled

1 ([Kohler et al., 2008](#)); upholstered furniture is sometimes reused, but is rarely recycled ([CalRecycle,](#)  
2 [2002](#)). Upholstery could be donated to charitable organizations and resold for residential use.  
3 Additionally, upholstery textiles could be informally repurposed into clothing, blankets, and other textile  
4 products. Due to the difficulty of recycling furniture and flame-retardant materials, flame-retardant  
5 furniture is typically land-filled ([CalRecycle, 2002](#); [Lassen et al., 1999](#)). Of the small portion of  
6 upholstered furniture that is recycled, about 60% of the material is recycled and 25–30% is composted  
7 ([CalRecycle, 2002](#)). No data were found that describe the proportion of other upholstery textiles (e.g.,  
8 mattress ticking or curtains) that are typically recycled.

9         The main types of textile recycling processes are fiber-to-fiber recycling and polymer reduction  
10 recycling. During the fiber-to-fiber process, textiles are shredded and blended with other fibers to create a  
11 new mixture ready for spinning ([Kohler et al., 2008](#)). During the polymer reduction process, textiles are  
12 cut and granulated to form pellets that are processed to break down the polymer to the molecular level to  
13 be reused as raw material ([Kohler et al., 2008](#)). No data were found that described the prevalence of each  
14 recycling process.

### 2.5.1.2. Potential Releases during the Reuse/Recycling Stage

15         Release of decaBDE and MWCNTs beyond releases described in the use stage is unlikely to  
16 occur during reuse of flame-retardant upholstery textiles. Older textiles could release greater levels of  
17 decaBDE and MWCNTs, however, due to increased degradation of the material. Informal repurposing of  
18 flame-retardant textiles likely would require cutting and shredding, resulting in possible air release of  
19 decaBDE or MWCNTs. Airborne releases of decaBDE and MWCNTs could occur during recycling of  
20 flame-retardant textiles. Recycling subjects textiles to a variety of mechanical, thermal, and chemical  
21 treatments that could result in the airborne releases of additive flame retardants from fibers ([Kohler et al.,](#)  
22 [2008](#)). One analysis found airborne releases of decaBDE at a plastic recycling plant with the highest  
23 concentrations of airborne particles measured near the shredder ([Sjödín et al., 2001](#)). Although releases  
24 from recycling of upholstery textiles containing decaBDE flame retardant might be similar to those of  
25 plastics, the processing of plastics is likely to differ from that of textiles. Recycling processes, such as  
26 shredding, milling, and thermal processing, could lead to the airborne release of CNTs from upholstery  
27 textiles if carried out in uncontrolled environments ([Chaudhry et al., 2009](#)). Airborne releases during  
28 recycling of textiles likely would be in the form of CNTs in a polymer matrix ([Chaudhry et al., 2009](#)).  
29 Downcycling, the conversion of waste materials into new materials of lesser quality and reduced  
30 functionality, could lead to cross-contamination of other materials with CNTs, for example, if MWCNT-  
31 treated textiles were shredded and mixed with other textiles for use as insulation ([Chaudhry et al., 2009](#)).  
32 Release of decaBDE or MWCNTs to water also could occur during chemical treatment and processing.

1 Although release of decaBDE and MWCNTs is possible during recycling of flame-retardant textiles, no  
2 data were found that indicate the likelihood of release from recycling processes.

3 Table 2-9 outlines potential release scenarios from the reuse/recycling stage of decaBDE and  
4 MWCNT flame-retardant textiles.

---

Table 2-9. Potential release scenarios during reuse and recycling.

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Processes included in reuse/recycling life-cycle stage	Information on release	
	DecaBDE	MWCNTs
General reuse (product kept intact)	Air release possible if textile degrades	Air release possible if textile degrades
Repurposing (product manipulated)	Air release possible due to cutting, shredding, and other abrasive processes	Air release possible due to cutting, shredding, and other abrasive processes
Recycling (product broken down)	Air and water release possible due to mechanical, thermal, and chemical treatment	Air and water release possible due to mechanical, thermal, and chemical treatment

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## 2.5.2. Incineration

### 2.5.2.1. Life-Cycle Processes

5 The incineration of decaBDE and MWCNTs or decaBDE and MWCNT flame-retardant  
6 formulations is unlikely, but any incineration likely would occur in a hazardous waste incinerator.  
7 Upholstery textiles treated with decaBDE or MWCNT flame-retardant coatings might be sent to  
8 municipal incinerators for processing. Municipal incinerators generally provide a well-controlled  
9 environment with pollution control mechanisms and sufficiently high temperatures (850 °C) to destroy  
10 most materials ([Kohler et al., 2008](#)). Processing in municipal facilities is likely to result in complete  
11 incineration of the upholstery textiles. Alternatively, upholstery textiles also might be incinerated in less  
12 well-controlled facilities or burned in open fires as a rudimentary form of waste management or as  
13 kindling. These incineration methods are likely to result in incomplete incineration of the upholstery  
14 textiles. No data were found that describe the prevalence of incineration as a form of disposal for  
15 upholstery textiles or what proportion of incinerated textiles is processed at well-controlled incineration  
16 facilities.

### 2.5.2.2. Potential Releases during the Incineration Stage

1 Airborne releases of decaBDE and MWCNTs from well-controlled incineration are expected to  
2 be negligible, but incomplete incineration (e.g., open fires) could lead to some airborne release. Little  
3 empirical data exist that describe the prevalence of decaBDE in incinerator residues, but decaBDE is  
4 expected to be destroyed at the high-temperature incineration used at most municipal incineration  
5 facilities ([Palm et al., 2002](#); [Lassen et al., 1999](#)). These temperatures also are sufficiently high to prevent  
6 the formation of PBDFs and PBDDs during incineration of decaBDE (see Section 2.2.2.2). In one study  
7 of atmospheric concentrations of PBDEs near solid waste incinerators, the authors found that incineration  
8 facilities do not represent a substantial proportion of atmospheric releases of decaBDE ([Agrell et al.,  
9 2004](#)). Incomplete incineration, however, could lead to the airborne release of decaBDE and the  
10 formation of PBDFs, PBDDs, polychlorinated dibenzo-p-dioxins, and nonhalogenated substances such as  
11 polycyclic aromatic compounds (see Section 2.2.2.2). Current pollution control technologies for  
12 municipal incinerators are expected to effectively filter these emissions and prevent their release to the  
13 environment ([EU, 2002](#)).

14 MWCNTs also are likely to be destroyed at the high temperatures used by municipal waste  
15 incinerators ([Chaudhry et al., 2009](#); [Sobek and Bucheli, 2009](#)). If some CNTs remain following municipal  
16 incineration, however, they are expected to bind to other particles and be removed by the incinerator's  
17 filter ([Kohler et al., 2008](#)). Incinerator removal efficiency for CNTs has not been studied ([Som et al.,  
18 2011](#)). Alternatively, incomplete incineration of products containing CNTs could result in the airborne  
19 release of CNTs in a polymer matrix ([Chaudhry et al., 2009](#)). Nguyen et al. ([2011](#)) found that exposure to  
20 moderately higher temperature (50 °C) and UV radiation, however, caused MWCNTs to form a dense  
21 barrier on the surface of the polymer which prevented the release of MWCNTs to the environment. No  
22 data were found that describe potential by-products of incinerating upholstery textiles coated with  
23 MWCNT flame retardant. Due to the high temperatures and pollution control mechanisms at municipal  
24 incinerators, both decaBDE and MWCNTs in flame-retardant textiles are expected to be destroyed during  
25 well-controlled incineration. Incineration by open flame in uncontrolled environments, however, might  
26 lead to airborne releases of decaBDE and harmful by-products. Preliminary evidence suggests that  
27 MWCNTs might not be released to the environment during incomplete incineration.

28 Table 2-10 outlines potential release scenarios from the incineration stage of decaBDE and  
29 MWCNT flame-retardant textiles.

Table 2-10. Potential release scenarios during incineration.

Processes included in incineration life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Complete incineration, controlled	Release unlikely	Release unlikely
Incomplete incineration, uncontrolled	Air release of decaBDE and harmful by-products likely, likely will reach environment	Preliminary evidence suggests that air release is unlikely

## 2.5.3. Land-Filling

### 2.5.3.1. General Processes

1 Land-filling of decaBDE and MWCNTs or decaBDE and MWCNT flame-retardant formulations  
 2 is unlikely, except in the case of floor sweepings from manufacturing facilities. Upholstered furniture and  
 3 textiles generally are disposed of in municipal landfills ([Kohler et al., 2008](#)). Remaining parts from  
 4 recycled furniture, such as cover cloth materials, also are sent to the landfill ([CalRecycle, 2002](#)).  
 5 Additionally, some textiles might be disposed of in uncontrolled landfills or open dumping sites that have  
 6 no pollution control mechanisms in place. No data were found that describe the proportion of upholstery  
 7 textiles disposed of in landfills or any further processing that might occur at the landfill.

### 2.5.3.2. Potential Releases during the Land-filling Stage

8 Land-filling of decaBDE and MWCNT flame-retardant textiles could lead to water and air  
 9 releases. Mechanical land-filling processes (e.g., mixing and compacting) could lead to the airborne  
 10 release of CNTs in a polymer matrix ([Chaudhry et al., 2009](#)). Air release of decaBDE in a polymer matrix  
 11 also could occur during these processes. DecaBDE also could leach from land-filled textiles and migrate  
 12 into the underlying soil or ground water ([Rahman et al., 2001](#); [Lassen et al., 1999](#)), however, no evidence  
 13 of decaBDE in land-fill leachate has been found [(Kim et al. (2006) as cited in Wright et al. (2008)].  
 14 Additionally, this release scenario is unlikely due to the low leaching potential of decaBDE (see Table  
 15 1-8). Flame retardants containing decaBDE could volatilize to the atmosphere over time ([Rahman et al.,](#)  
 16 [2001](#)), but volatilization of decaBDE is expected to be negligible due to low volatility of decaBDE ([Palm](#)  
 17 [et al., 2002](#)) (see Table 3-1).

18 Airborne release of CNTs also is unlikely after land-filling is complete ([Chaudhry et al., 2009](#)).  
 19 Degradation of the polymer matrix material in textiles could lead to release of CNTs into leachate/soil

1 because CNTs are very stable and do not readily degrade ([Kohler et al., 2008](#)). No data were found,  
 2 however, that identify MWCNTs in land-fill leachate. Few data were identified that measure releases of  
 3 decaBDE and MWCNTs from land-filling flame-retardant textiles, but the physicochemical  
 4 characteristics of these materials suggest that such releases likely would be small. Table 2-11 outlines  
 5 potential release scenarios from the land-filling stage of decaBDE and MWCNT flame-retardant textiles.

Table 2-11. Potential release scenarios during land-filling.

Processes included in land-filling life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Disposal	Air release possible due to mixing and compacting	Air release possible due to mixing and compacting
Degradation	Air and water release unlikely	No data exist, but air and water release possible but unlikely

## 2.5.4. Wastewater Treatment Plants

### 2.5.4.1. Life-Cycle Processes

6 The wastewater treatment process consists of filtering and treating wastewater to remove solids  
 7 and contaminants. Large facilities that manufacture decaBDE and MWCNTs and decaBDE and MWCNT  
 8 flame retardants might divert their wastewater to an on-site wastewater treatment plant. Alternatively,  
 9 some wastewater from these facilities might be directly processed by municipal wastewater treatment  
 10 plants. Water releases of decaBDE and MWCNTs that occur during the storage and distribution, use, and  
 11 reuse/recycling/end-of-life stages also would be treated in municipal wastewater treatment plants.

### 2.5.4.2. Potential Releases during the Wastewater Treatment Stage

12 Release of decaBDE and MWCNTs or decaBDE and MWCNT flame-retardant formulations into  
 13 wastewater could occur throughout the life cycle. Primary releases to wastewater during manufacturing  
 14 stages are due to equipment cleaning, formulation and application of the flame retardant, and accidental  
 15 spills. Washing processes (which can involve abrasion, detergents, and water), particularly in the product  
 16 manufacturing stages, are likely to result in the release of additive flame retardants from textiles to  
 17 wastewater ([Som et al., 2011](#)). Due to the physicochemical characteristics of decaBDE and MWCNT

1 flame retardants (see Table 1-8 and Table 1-9 in Section 1.3), both materials are likely to sorb onto  
 2 particles during water treatment and be removed in sludge ([Som et al., 2011](#); [Lassen et al., 1999](#)). The  
 3 potential nonetheless exists for releases from filter backwash and other wastewater treatment plant  
 4 equipment ([EU, 2002](#)). Additionally, some of this removed sludge is deposited in landfills or spread on  
 5 agricultural soil ([EU, 2002](#); [Lassen et al., 1999](#)). This activity represents one of the most significant  
 6 potential releases to soil of decaBDE flame-retardant coatings ([Ciparis and Hale, 2005](#); [Lassen et al.,  
 7 1999](#)). The potential release of MWCNTs due to the spread of sludge on agricultural soil is unknown. The  
 8 releases of decaBDE and MWCNTs from wastewater treatment facilities are expected to be small, but  
 9 release potential greatly depends on surface chemistry in the case of MWCNTs. The removal efficiency  
 10 of wastewater treatment plants is not well characterized for decaBDE and MWCNTs and the spread of  
 11 sewage sludge onto agricultural soil could represent a significant source of decaBDE and MWCNTs to  
 12 soil. See Section 3.3.3 for information regarding decaBDE and MWCNT removal efficiency of these  
 13 wastewater treatment plants.

14 Table 2-12 outlines potential release scenarios from the wastewater treatment stage of decaBDE  
 15 and MWCNT flame-retardant textiles.

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Table 2-12. Potential release scenarios during wastewater treatment.

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Processes included in wastewater treatment life-cycle stage	Information on release	
	DecaBDE	MWCNTs
Release of effluent	Release unlikely due to sorption behavior, but filter backwash could lead to release	Release unlikely due to sorption behavior, but filter backwash could lead to release
Removal of sludge	Release to soil likely if sludge spread on agricultural fields	No data exist, but release to soil possible if sludge spread on agricultural fields

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# Chapter 3. Transport, Transformation, and Fate

1           Releases throughout the product life cycles of upholstery textile coatings containing  
2 decabromodiphenyl ether (decaBDE) or multiwalled carbon nanotube (MWCNT) flame retardant will, to  
3 some extent, lead to occurrence of primary and secondary contaminants in air, soil, and aquatic media.  
4 Chapter 3 examines what might happen to these substances after their release to the environment,  
5 including transport or transformation through chemical, physical, and biological processes. Studies  
6 investigating the transport, transformation, and fate of decaBDE and MWCNTs in the environment are  
7 summarized in Appendix D, and concentrations of BDE-209, the single isomer of deca-substituted BDE,  
8 in environmental compartments are provided in Appendix E. In general, information on environmental  
9 concentrations of MWCNTs was not found.

10           DecaBDE and MWCNTs can be released into the environment during the manufacturing, storage,  
11 distribution, use, disposal, reuse, and recycling of upholstery textiles treated with flame retardants (see  
12 Chapter 2). DecaBDE and MWCNT flame-retardant formulations are used primarily as additives that are  
13 mixed with, not chemically bound to, polymers in textile products (see Section 1.3). Because they are not  
14 chemically bound, these substances can escape from the material and become a source of contamination  
15 to surrounding environmental media ([Yu et al., 2010](#); [Vonderheide et al., 2008](#); [Moniruzzaman and](#)  
16 [Winey, 2006](#); [Song et al., 2006](#); [Söderström et al., 2004](#)). Although some, if not most, releases after the  
17 production stage are likely to be in the matrix-bound form, little information exists that describes the  
18 environmental behavior of decaBDE- and MWCNT-polymer complexes. As a result, this chapter focuses  
19 on the transport, transformation, and fate of decaBDE and MWCNTs not embedded in a polymer matrix.

20           Section 3.1 provides a brief discussion of the chemical and physical characteristics and the  
21 processes that influence behavior (e.g., mobility, persistence, bioavailability) of decaBDE and MWCNTs  
22 in environmental media. The sections that follow summarize the available information regarding the  
23 behavior of each substance in indoor and outdoor air (Section 3.2), aquatic systems (Section 3.3), and  
24 terrestrial systems (Section 3.4). A brief discussion of models that might be used for evaluating the fate  
25 and transport of these substances in environmental media is provided in Section 3.5.

## 3.1. Physicochemical Factors Influencing Transport, Transformation, and Fate

### *Decabromodiphenyl Ether*

1           The environmental fate of BDE-209 will be dictated by its chemical and physical properties and  
2 its propensity for biotic and abiotic transformation. BDE-209 could transform physically, chemically, or  
3 biologically once released to the environment, leading to substances that present a very different hazard  
4 than the untransformed material originally released. BDE-209 has been shown to biologically and  
5 photolytically debrominate (lose a bromine atom) to form lower brominated congeners that are more  
6 readily bioavailable [U.S. EPA ([2010b](#)); Vonderheide et al. ([2008](#)); Song et al. ([2006](#)); Watanabe and  
7 Sakai ([2003](#)); Darnerud et al. ([2001](#)); see Text Box 3-1 and additional sources in Appendix D, Table D-1].  
8 Because the chemical properties associated with transformation products of decaBDE influence their  
9 transport, transformation, and fate in the environment, degradation processes of decaBDE are introduced  
10 in this section. A summary of key physicochemical factors that are likely to affect partitioning<sup>10</sup> and fate  
11 of BDE-209 and related polybrominated diphenyl ethers (PBDEs) in the environment is presented in  
12 Table 3-1. Values for key physicochemical properties of BDE-209 are provided in Chapter 1 (see Table  
13 1-8).

14           Biotic debromination is the breakdown of BDE-209 into lower brominated compounds by aerobic  
15 and anaerobic microorganisms. Biotic transformation processes for BDE-209 that occur in soil, sediment,  
16 or sewage sludge have been described in recent literature (see Appendix D, Table D-1). These processes  
17 result in dehalogenation through microbe catalysis reactions that stimulate the replacement of a halogen  
18 atom (e.g., bromine, chlorine, fluorine) with a hydrogen atom ([Kuivikko et al., 2010](#); [Kim et al., 2007](#)).

19           Photolysis or photodegradation is a chemical (abiotic) process by which molecules are broken  
20 down through the absorption of light. PBDEs are vulnerable to photolysis, which induces reductive  
21 debromination causing higher brominated congeners like BDE-209 to photodegrade to form lower  
22 brominated congeners. These lower brominated congeners are potentially more stable and bioavailable in  
23 the environment due to lower molecular weight and lower octanol water partition coefficient ( $K_{ow}$ )  
24 ([Söderström et al., 2004](#)). Polybrominated dibenzofurans also have been identified as photolysis products  
25 of BDE-209. Sunlight could degrade BDE-209 in air, surficial soils, water, and surficial sediments via  
26 photolysis ([Christiansson et al., 2009](#); [Söderström et al., 2004](#)). This and other abiotic transformation  
27 processes for BDE-209 have been demonstrated in recent literature (see Appendix D, Table D-1).

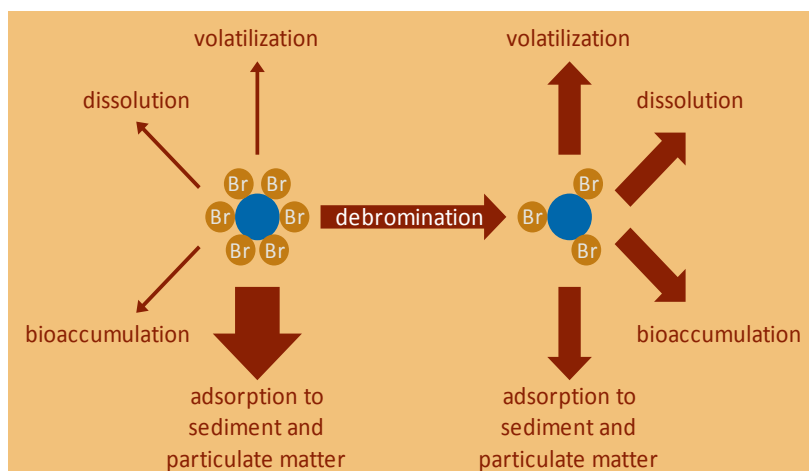
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<sup>10</sup>Partitioning refers to the potential for a chemical or other substance to move from one environmental medium to another (e.g., air, water, sediment) and the tendency to accumulate in a particular medium over another ([U.S. EPA, 2010b](#)).

### Text Box 3-1. BDE-209 Undergoes Biotic and Abiotic Debromination

Higher brominated PBDE congeners like BDE-209 (the principal constituent in decaBDE) have lower bioaccumulation potential, water solubility, and volatility, and therefore have been considered relatively safe (Watanabe and Sakai, 2003). Lower brominated congeners (including degradation products of BDE-209), however, are predicted to be more volatile, water soluble, and bioaccumulative than the higher brominated congeners, and these degradation products are therefore likely to be more bioavailable in the environment than BDE-209. Soils and sediments are major sinks for higher brominated compounds, and other pathways are relatively minor (see the illustration below; the thickness of the arrows is an indication of the strength of the pathway). The potential significance of other pathways increases for the lower brominated congeners.

Understanding the fate and potential toxicity of BDE-209 requires an understanding of the various degradation processes that dictate its persistence in the environment. Debromination of BDE-209 in the environment affects potential transport and accumulation through the food web (Huang et al., 2010) and therefore potential for human exposure through the diet. Several biotic and abiotic processes of BDE-209 degradation have been demonstrated in air, water, soil, and sediments (Vonderheide et al., 2008). Photolytic degradation by solar rays and UV light is a significant abiotic process of BDE degradation and has been studied more than other processes. Other abiotic processes include geochemical degradation by metal oxides found in certain soils and degradation by engineered nanoparticles (Vonderheide et al., 2008). Biotic degradation pathways include debromination by both aerobic and anaerobic microbes found in soil (Wang et al., 2011; Huang et al., 2010; Lee and He, 2010) and possible further degradation in plants (Huang et al., 2010). These processes proceed in a stepwise fashion, removing one bromine atom at a time, and can therefore contribute to the levels of lower brominated congeners from nona- to tetra- and even dibDEs in the environment. BDE-47 (tetraBDE) and BDE-99 (pentaBDE) are the congeners most often detected in humans and biota globally (Tokarz et al., 2008; Vonderheide et al., 2008), and debromination of BDE-209 might be an environmental source of these congeners, which are known to be toxic and face restrictions on their production (Ross et al., 2009). In accordance with the comprehensive environmental assessment (CEA) approach, some consideration of the exposure, uptake, and effects of lower brominated congeners produced during the natural debromination of BDE-209 is appropriate. Several studies have described the debromination of BDE-209 (often in the laboratory) and identified ranges of the lower brominated congeners produced; however, the specific congener profiles that are expected to occur in natural environmental systems following BDE-209 debromination have not been clearly identified.



Although higher brominated congeners primarily adsorb to solids, lower brominated congeners can readily volatilize to air, dissolve in water and interstitial spaces in soil, bioaccumulate in biota, and adsorb to solids. As a result, the fate of the parent compound BDE-209 is expected to differ substantially from its lower brominated transformation products.

Adapted from Watanabe and Sakai (2003).

- 1 Transformation also can occur with elevated temperatures (e.g., incineration, fire); thermal
- 2 breakdown products of PBDEs include polybrominated, polychlorinated, and mixed
- 3 brominated/chlorinated dibenzo-p-dioxins and dibenzofurans, and are similar to polychlorinated dibenzo-
- 4 p-dioxins/polychlorinated dibenzofurans in their persistence and toxicity (Watanabe and Sakai, 2003;
- 5 Darnerud et al., 2001; Rahman et al., 2001)

**Table 3-1. Summary of physicochemical properties that affect partitioning and fate of BDE-209.**

Physicochemical property	How does this property affect chemical partitioning and fate?
High molecular weight	<ul style="list-style-type: none"> <li>Limits bioavailability to biota</li> </ul> Sources: Kierkegaard et al. (2004); Huang et al. (2010)
Low water solubility; hydrophobic	<ul style="list-style-type: none"> <li>Expected to associate primarily with organic (carbon-rich) particles in soil, sediment, sewage sludge; percent total organic carbon likely plays a major role in transport and distribution of BDE-209 in these media</li> <li>Less mobility, strongly sorbed to solid particles such as soils, sediments, and sewage sludge</li> <li>Expected to adsorb to particles by van der Waals forces and hydrophobic attraction (Ahn et al., 2006)</li> <li>Reduced bioavailability to some aquatic biota</li> </ul> Sources: Vonderheide et al. (2008); Qui et al. (2010); U.S. EPA (2010b); Hua et al. (2003); Mikula and Svobodová (2006); Rahman et al. (2001); Zhu et al (2010); Yu et al. (2010)
Low volatility; low vapor pressure	<ul style="list-style-type: none"> <li>Vapor pressures of PBDEs are inversely related to both molecular weight (i.e., as molecular weight increases, vapor pressure decreases) and degree of bromination</li> <li>Partitioning for BDE-209 is expected to be 1% vapor phase and 99% associated with airborne particles; as the degree of bromination increases, likelihood increases for BDE congeners to partition to the particle phase in air</li> <li>Lower brominated PBDEs could be expected to be present primarily in the vapor phase and be more susceptible to long-range transport; however, BDE-209 could sorb to aerosol particles and can experience long-range transport</li> </ul> Sources: U.S. EPA (2010b); Watanabe and Sakai (2003)
High octanol/water partition coefficient ( $K_{ow}$ )	<ul style="list-style-type: none"> <li>PBDEs partition between water and sediment based on solubility and <math>K_{ow}</math></li> <li>Less mobility, strongly sorbed to soils, sediments, sludge</li> <li>Not easily distributed within surface water and ground water</li> </ul> Sources: U.S. EPA (2010b); Vonderheide et al. (2008)
Low Henry's law constant ( $K_H$ )	<ul style="list-style-type: none"> <li>PBDEs partition between water and air based on <math>K_H</math>; lower <math>K_H</math> at higher degrees of bromination; BDE-209 not expected to readily volatilize to air</li> </ul> Sources: U.S. EPA (2010b)
High octanol/air partition coefficients ( $K_{oa}$ )	<ul style="list-style-type: none"> <li>Stronger propensity to adsorb to the organic matter in soils and vegetation; indicator of chemical mobility in the atmosphere; tendency for atmospheric BDE-209 to deposit on forest canopies and other vegetative biomass</li> </ul> Sources: U.S. EPA (2010b); Wania et al. (2002); Vonderheide et al. (2008)
High lipophilicity	<ul style="list-style-type: none"> <li>Dissolves in fats, oils, lipids, and nonpolar solvents (e.g., hexane, toluene)</li> </ul> Sources: Mikula and Svobodová (2006); Rahman et al. (2001); Vonderheide et al. (2008)
	<ul style="list-style-type: none"> <li>Greater tendency to bioaccumulate and biomagnify in the food chain</li> </ul> Sources: Rahman et al. (2001); Vonderheide et al. (2008)

PBDE = polybrominated diphenyl ether; BDE-209 = single isomer of decabrominated diphenyl ether

- 1 DecaBDE formulations used in textile and other products contain the fully brominated congener,
- 2 which is less mobile in the environment than lower brominated congeners, probably due to low volatility,
- 3 water solubility, and bioaccumulation, and the high propensity to adsorb to sediments. The lower

1 brominated compounds are generally more volatile, water soluble, and bioaccumulative compared with  
2 higher brominated compounds ([Watanabe and Sakai, 2003](#)) and are believed to be structurally analogous  
3 to polychlorinated biphenyls (PCBs), so their chemical properties, persistence, and behavior in the  
4 environment are expected to follow similar patterns. PBDEs are expected to be more vulnerable to  
5 environmental degradation than PCBs, however, because their carbon-bromine bonds are weaker than the  
6 carbon-chlorine bonds of PCBs ([Shih and Wang, 2009](#); [Watanabe and Sakai, 2003](#); [Rahman et al., 2001](#)).

### ***Multiwalled Carbon Nanotubes***

7 The environmental fate of MWCNTs will be dictated by their physical and chemical properties  
8 (see Text Box 1-1). These properties influence behavior, including mobility, persistence, bioavailability,  
9 and likelihood for transformation in environmental media. A summary of key physicochemical factors  
10 that might affect partitioning of MWCNTs and their fate in the environment is provided in Table 3-2.  
11 Values for or descriptions of key physicochemical properties of MWCNTs (e.g., surface area,  
12 morphology, solubility) are provided in Table 1-9.

13 Carbon nanotubes (CNTs) are not dispersed by simple mixing because they tend to form bundles  
14 through a van der Waals attraction among tubes. As shown in Table 2-5, MWCNTs, including those in  
15 commercial products such as textiles, can be engineered to include charged functional groups to improve  
16 their dispersion or to increase their solubility in aqueous media; the treated nanoscale materials  
17 (nanomaterials) that remain dispersed tend to exhibit greater persistence in the environment ([Klaper et al.,  
18 2010](#); [Saeed, 2010](#); [Kohler et al., 2008](#); [Luoma, 2008](#)). CNTs in textiles might also be coated with a  
19 surface coating, such as a polymer ([Kohler et al., 2008](#)). These surface coatings could be degraded by  
20 chemical or biological reactions, affecting persistence of the MWCNTs over time in ways that depend on  
21 both the presence of a coating and the type of coating used.

22 Environmental conditions (e.g., redox potential, pH, temperature, UV light, ionic strength, and  
23 characteristics of other toxins present) are likely to affect the behavior and environmental fate (e.g.,  
24 mobility, persistence, bioavailability) of MWCNTs ([Tóth et al., 2011](#); [Zhang et al., 2011a](#); [Helland et al.,  
25 2007](#)) (see Text Box 1-1). The same is true for environmental processes such as interactions with natural  
26 organic matter (NOM), which will alter the surface chemistry of the MWCNTs ([Petersen et al., 2011](#)).  
27 Metals, such as lead, cadmium, and copper, hydrophobic organic chemicals and other toxic organics (e.g.,  
28 polycyclic aromatic hydrocarbons), and other pollutants (e.g., phenol, dopamine) can sorb strongly to  
29 CNTs ([Li et al., 2011](#); [Tóth et al., 2011](#); [Cho et al., 2008](#); [Petersen et al., 2008](#); [Chen et al., 2007](#); [Helland  
30 et al., 2007](#)). These associations might dictate CNT mobility and bioavailability. Factors that have been  
31 shown to influence adsorption of organic contaminants to MWCNTs include MWCNT surface oxidation  
32 (adsorption capacity decreases with increasing oxygen content), and pH (effects differ based on the  
33 contaminant) ([Li et al., 2011](#); [Tóth et al., 2011](#); [Cho et al., 2008](#)).

**Table 3-2. Summary of physicochemical properties that affect partitioning and fate of nanomaterials such as multiwalled carbon nanotubes (MWCNTs).**

Physicochemical property	How does this property affect chemical partitioning and fate?
Small size; single particle versus cluster	<ul style="list-style-type: none"> <li>• Single particles versus bundles or clusters will differ in their mobility (and ultimate fate) in environmental media. Generally, nanoparticle clusters are less mobile in the environment than individual nanoparticles.</li> </ul> Sources: Ma-Hock et al. (2007)
High surface area-to-volume ratio	<ul style="list-style-type: none"> <li>• Large surface area enhances chemical reactivity and clustering</li> <li>• Might cause other molecules to adhere and be transported with MWCNTs</li> </ul> Source: Kohler et al. (2008); O'Driscoll et al. (2010)
Distinct morphology	<ul style="list-style-type: none"> <li>• Concentrically nested multiple graphene sheets that frequently exhibit "disturbed wall texture;" irregular shape increases chemical reactivity</li> <li>• Differences in morphology based on variations in synthesis</li> <li>• Shape can affect the kinetics of deposition and transport in the environment; depending on surface structure and shape, MWCNTs might exhibit different reactivity</li> </ul> Sources: Kohler et al. (2008); Oberdorster et al. (2005)
Low water solubility; hydrophobic	<ul style="list-style-type: none"> <li>• Will result in poor dispersion</li> <li>• Prone to bundling in the water column and settling to sediments</li> <li>• Hydrophobic interactions play major role in adsorption of organic contaminants (Li et al., 2011)</li> <li>• Functionalization and presence of surface-active agents (surfactants, dissolved organic matter) can improve their dispersion/increase solubility in aqueous media</li> </ul> Sources: Helland et al. (2007); Christian et al. (2008); Klaper et al. (2010); Saeed (2010); Kohler et al. (2008); Luoma (2008); Li et al. (2011)
Potential lipophilicity	<ul style="list-style-type: none"> <li>• Might interact with lipids in abiotic and biotic media; might be taken up by microbial communities and plant roots</li> </ul> Sources: Helland et al. (2007); Oberdorster et al. (2006); Wu et al. (2006)

## 3.2. Transport, Transformation, and Fate in Air

- 1 BDE-209 or MWCNTs released from the flame-retardant upholstery textile coatings life cycle  
 2 could reach indoor and outdoor air in several ways. For example:
- 3 • BDE-209 or MWCNTs can be directly released into ambient air during all stages of the  
 4 product life cycle, as previously described in Chapter 2. BDE-209 or MWCNTs that remain  
 5 in the particle phase can disperse through air away from the source of release.
  - 6 • Particulate BDE-209 or MWCNTs can become suspended in the surrounding indoor or  
 7 outdoor air during multiple stages of the product life cycle.
  - 8 • Particulate BDE-209 or MWCNTs might remain suspended and transport through the  
 9 atmosphere or be deposited onto surfaces. Particles that have been deposited on surfaces  
 10 could become resuspended in the air and redeposited elsewhere.

### *Decabromodiphenyl Ether*

1 If released indoors, BDE-209 can distribute indoors to air, dust, vacuums, and air filter systems. If  
2 the source of BDE-209 is inside a building, levels of BDE-209 in indoor air can be much higher than in  
3 outdoor air ([Hale et al., 2006](#)). Indoor air sources could also contribute to outdoor air concentrations.  
4 Variability in the indoor air and dust levels of BDE-209 can be influenced by indoor/outdoor exchange  
5 rates, building ventilation rates, and the number and age of all PBDE-treated products (e.g., electronics,  
6 mattresses, draperies, furniture) present in the building ([Hazrati and Harrad, 2006](#)).

7 As mentioned earlier, BDE-209 has very low vapor pressure and a high octanol water partition  
8 coefficient and is therefore more likely to be transported on particles in the air than as a vapor (see Table  
9 3-1) ([Breivik et al., 2006](#)). Approximately 99 % of BDE-209 in ambient air is expected to be present in  
10 the particle phase ([U.S. EPA, 2010b](#)). Particles could remain suspended in air or deposit on surfaces with  
11 the potential for resuspension. Because nonvolatile compounds like BDE-209 tend to sorb to particles,  
12 they likely would be concentrated in house dust and could experience an extended indoor lifetime  
13 ([Kemmlein et al., 2003](#)).

14 When attached to particles, BDE-209 can have an extended residence time and persistence in the  
15 atmosphere. Longer residence time in the atmosphere allows more time for the particles to be mobilized  
16 by wind and other forces and makes long-range atmospheric transport (LRT) in the atmosphere possible  
17 ([Gouin et al., 2006](#); [Wania and Dugani, 2003](#)). Evidence exists for LRT of PBDEs to remote ecosystems,  
18 including the Arctic ([de Wit et al., 2010](#); [Su et al., 2009](#); [Agrell et al., 2004](#)); some literature suggests that  
19 PBDEs in remote Arctic regions originated in urban areas in North America ([Breivik et al., 2006](#)).

20 LRT has been considered by some to be the reason for PBDE occurrence in rural and more  
21 remote sites. Some evidence has shown LRT of BDE-209 adsorbed to airborne particulate matter at  
22 regional and global scales ([Vonderheide et al., 2008](#)), although other researchers have suggested that the  
23 potential for LRT of BDE-209 is low. Atmospheric deposition of BDE-209 and other PBDEs is thought  
24 to be a main source of these contaminants in background waters and soils ([Vonderheide et al., 2008](#)).

25 Understanding of BDE-209 LRT behavior is limited. As stated previously, BDE-209 in the air is  
26 primarily attached to particles ([U.S. EPA, 2010b](#); [Su et al., 2009](#)). Efforts by Mueller and Nowack ([2008](#))  
27 to model atmospheric transport of engineered nanoparticles can be used to infer that materials adsorbed to  
28 particles, such as BDE-209, will eventually deposit or wash out (wet deposition) in aquatic or terrestrial  
29 systems. In turn, the fate of BDE-209 in air is likely dictated by the characteristics of the particles to  
30 which it adsorbs.

31 Plants exposed to BDE-209 from air can accumulate BDE-209 and act as transfer vectors in the  
32 food chain. Airborne BDE-209-laden particles could attach to leaves and other aboveground parts of  
33 plants and translocate to different tissues of the plant. Salamova and Hites ([2010](#)) evaluated PBDE levels



1 in air samples and tree bark and determined that BDE-209 concentration in tree bark was strongly  
2 correlated with its concentration in the air and precipitation. The highest air and tree bark concentrations  
3 occurred at urban sites.

4 Breakdown and transformation of BDE-209 in the air by photolysis also can occur (see Section  
5 3.1 and Text Box 3-1), and studies that evaluated this phenomenon in air are presented in Appendix D,  
6 Table D-1. Temperature variability could be an important factor that explains seasonal patterns of  
7 BDE-209 burdens in air because changes in temperature affect gas-solid partitioning coefficients and  
8 subsequently the transfer and retention of BDE-209 in air ([Vonderheide et al., 2008](#)).

9 Section 4.1.2 and Section E.1 of Appendix E provide summaries of studies with BDE-209  
10 concentration data in building dust and indoor/ambient air.

### *Multiwalled Carbon Nanotubes*

11 Similar to BDE-209, if released indoors, MWCNTs could distribute to indoor air and dust, and  
12 these sources could be a major contributor to outdoor air concentrations. Several processes and factors  
13 could influence the behavior (e.g., mobility, persistence, bioavailability) and ultimately the fate of  
14 airborne MWCNTs in indoor and outdoor environments, including size—whether they are travelling as  
15 individual particles of varying sizes or as larger bundles—surface chemistry, interactions with other  
16 airborne particles and chemical compounds, residence time in the air, and distance traveled prior to  
17 deposition ([Kohler et al., 2008](#); [U.S. EPA, 2007](#)). Like BDE-209, the fate of airborne nanomaterials  
18 outdoors also could be influenced by meteorological factors, including wind, temperature, and  
19 precipitation ([Navarro et al., 2008](#)).

20 Information in the recent literature regarding the behavior of airborne MWCNTs is limited. No  
21 studies have examined transport mechanisms for MWCNTs in air. Yang et al. ([2009](#)) examined the  
22 atmospheric aging of CNTs under normal ambient conditions ( $20 \pm 0.5^\circ\text{C}$ , relative humidity =  $50 \pm 1\%$ )  
23 and found that CNT surface area and pore volume (volume of space [holes] per gram nanotube; provided  
24 in  $\text{cm}^3/\text{g}$ ) decreased over time (up to 7–15 months) and coincided with decreases in surface oxygen of the  
25 CNT as it aged. For MWCNTs, these conditions stabilized within 15–18 months. The total structural-  
26 defect concentration also appeared to be lowered as the CNTs aged. The authors theorized that during  
27 CNT aging under ambient conditions, oxygen leaves the surface of the CNTs. The structure then repairs  
28 itself and becomes more thermodynamically stable with fixed values of surface area, pore volume, and  
29 structural defects. Based on these results, the authors stated that CNT “physicochemical properties can be  
30 characterized with reliability only after samples have sufficiently aged” ([Yang et al., 2009](#)).

31 In the laboratory, Zhu et al. ([2011](#)) observed that MWCNTs exposed to air under ambient  
32 temperature were slowly oxidized and shortened. The degree of oxidation increased over time, and  
33 MWCNTs were almost totally transformed into amorphous carbon after 15 days.

1 Complete transformation of pure, airborne CNTs to carbon dioxide could occur during  
2 incineration at temperatures greater than 850°C and oxygen levels exceeding 21%. Under oxidative  
3 conditions, MWCNTs have been shown to burn off completely at 740 °C ([Som et al., 2011](#); [Kohler et al.,  
4 2008](#)).

5 Section 4.1.2.4 describes MWCNT air concentration data collected in occupational settings. No  
6 data were found on residential or consumer exposures to MWCNTs in air. Literature containing  
7 concentrations of MWCNTs in outdoor air also was not found.

### 3.3. Transport, Transformation, and Fate in Water and Sediment

8 BDE-209 or MWCNTs released from the flame-retardant upholstery textile coating life cycle  
9 could enter aquatic systems in several ways. For example:

- 10 • BDE-209 or MWCNTs in ambient air subsequently could be deposited or washed out to  
11 aquatic systems.
- 12 • Erosion of contaminated soil could release BDE-209 or MWCNTs to surface waters.
- 13 • Runoff flowing along the ground surface could transfer BDE-209 or MWCNTs in  
14 contaminated soil to nearby waterways.
- 15 • Wastewater effluents containing BDE-209 or MWCNTs could be a source of contamination  
16 to receiving water bodies near the discharge location.
- 17 • BDE-209 or MWCNTs could leach from land-filled sewage sludge into subsoil and ground  
18 water and migrate to surface water or sediment.

#### 3.3.1. Surface Water and Sediment (Inland and Coastal)

##### *Decabromodiphenyl Ether*

19 Water solubility and  $K_{ow}$  are important physicochemical factors for predicting behavior of BDE-  
20 209 in the aqueous phase—and these parameters predict that BDE-209 will partition to the particulate  
21 phase (e.g., sorb to suspended organic matter) in water or bind strongly to sediments ([U.S. EPA, 2010b](#);  
22 [Hale et al., 2006](#); [Watanabe and Sakai, 2003](#)). The lower brominated congeners are more water soluble  
23 than the higher brominated congeners and are expected to be more mobile in water ([Watanabe and Sakai,  
24 2003](#)).

25 Sediment is a sink and reservoir for PBDEs such as BDE-209. In general, BDE-209 is the  
26 dominant congener in sediment samples ([Tokarz et al., 2008](#)); notably higher concentrations in urban and

1 industrial areas and near outfalls of wastewater treatment plants have been measured ([U.S. EPA, 2010b](#))  
2 (see Appendix E). Whether the higher concentration of BDE-209 in sediment samples is due to greater  
3 BDE-209 use or less environmental degradation compared with other congeners is unknown. The  
4 physicochemical properties of BDE-209 and the characteristics of sediment both affect the bioavailability  
5 of BDE-209 in sediment. The bioavailability of BDE-209 in sediment is expected to be limited due to its  
6 strong hydrophobicity and large molecular size ([Liu et al., 2011c](#)). Due to its tendency to sink to  
7 sediments, BDE-209 might be bioavailable to benthic organisms, but generally not to water-column-  
8 dwelling organisms. Benthic organisms might, therefore, act as vectors for the transport of decaBDE  
9 through the food web (see Section 4.3).

10 The amount of organic matter in the sediment is an important factor controlling the partitioning of  
11 BDE-209 in sediments ([Liu et al., 2011c](#)). In a study conducted by Liu et al. ([2011c](#)), the authors  
12 concluded that desorption of BDE-209 in sediment was more difficult as contaminant-sorbent interaction  
13 time increased, likely because of entrapment of BDE-209 molecules in the micropores of organic matter.  
14 Total desorption also decreased with increased total organic carbon in the sediments.

15 Physicochemical properties of PBDEs and the characteristics of sediment might not serve as  
16 perfect predictors of levels in surface waters due to microbial or photolytic degradation processes that  
17 could reduce concentrations of the material. Elevated quantities of hydroxylated PBDEs (a possible  
18 oxidation product of PBDEs) have been measured in surface waters near sewage treatment plants  
19 ([Vonderheide et al., 2008](#)). Anaerobic microbial reductive debromination is potentially a driving  
20 transformation process in sediment (see Section 3.1 and Appendix D, Table D-1); the process, however,  
21 can be very slow.

22 Appendix E provides a summary of studies with BDE-209 concentration data in surface water  
23 and sediment. Most identified studies focus on sediment concentrations of BDE-209.

### *Multiwalled Carbon Nanotubes*

24 The hydrophobicity and van der Waals interactions of MWCNTs imply they will partition to the  
25 particulate phase when introduced to aquatic systems ([Kennedy et al., 2008](#)). Pure MWCNTs are  
26 insoluble in water and are prone to bundling in the surface water column and settling to sediments—  
27 making benthic organisms potential vectors for the transport of MWCNTs through the food web  
28 ([Christian et al., 2008](#)) (see Section 4.3). MWCNTs suspended in NOM solutions have greater potential  
29 for dispersion in natural waters ([O'Driscoll et al., 2010](#)). Results of the O'Driscoll et al. ([2010](#)) study  
30 suggested that smaller diameter MWCNTs stay suspended in NOM solutions much longer than larger  
31 diameter MWCNTs. Dissolved organic matter has been shown to debundle MWCNTs and induce  
32 conformational and electrostatic stabilization of carbon-based nanomaterials under environmentally  
33 relevant conditions ([Hyung and Kim, 2008](#); [Wang et al., 2008](#); [Hyung et al., 2007](#)).

1 Changing conditions such as ionic strength and pH of an aqueous solution can influence sorption  
2 behaviors of CNTs and subsequently the mobility, persistence, and bioavailability of these compounds in  
3 water. Zhang et al. ([2011a](#)) suggested that the overall effect of increasing ionic strength is that more  
4 MWCNTs will transfer out of the aqueous phase and sorption will increase. The authors also indicated  
5 that, in general, decreasing the pH of aqueous solutions enhances MWCNT bundling. The presence of  
6 dissolved organic matter, however, contributes to stabilization of MWCNTs in solution and suspended  
7 MWCNTs become less sensitive to changes in ionic strength or solution pH ([Zhang et al., 2011a](#)).  
8 Similarly, Hyung and Kim ([2008](#)) determined that adsorption capacity was directly proportional to the  
9 aromatic carbon content of the organic matter and the ionic strength of the solution and indirectly  
10 proportional to pH. Adsorption strength was indirectly proportional to ionic strength and not significantly  
11 changed by pH.

12 Functionalization of MWCNTs can improve their dispersion or increase their solubility in  
13 aqueous media, thereby increasing their mobility. As mentioned previously, engineered surface  
14 modifications (e.g., functional groups and coatings) are employed to improve CNT dispersion in aqueous  
15 suspension. Column stability and settling experiments have shown pure MWCNTs will settle and sink to  
16 sediment as described previously. The presence of functional groups slows this settling, especially in  
17 combination with NOM ([Kennedy et al., 2008](#); [Hyung et al., 2007](#)).

18 As discussed in Section 3.1, MWCNTs can act as environmental adsorbates of metals,  
19 hydrophobic organic compounds, and other toxic organics ([Li et al., 2011](#); [Cho et al., 2008](#); [Petersen et  
20 al., 2008](#); [Chen et al., 2007](#); [Helland et al., 2007](#)), and the properties of the adsorbants might dictate  
21 MWCNT mobility and dispersion in surface water.

22 Studies relevant to MWCNT fate and transport in aqueous media are summarized in Appendix D,  
23 Table D-2. No data were found on concentrations of MWCNTs in surface water and sediment.

### 3.3.2. Ground Water

#### *Decabromodiphenyl Ether*

24 BDE-209 present in soil could leach into subsoil and ground water. Based on its physicochemical  
25 properties, BDE-209 does not dissolve in water, but could sorb to suspended organic matter in the ground  
26 water plume and migrate to surface water ([U.S. EPA, 2010b](#)). No data were found on concentrations of  
27 BDE-209 in ground water.

#### *Multiwalled Carbon Nanotubes*

28 Similar to BDE-209, MWCNTs in soil could leach into subsoil and ground water and migrate to  
29 surface water. No data were found on concentrations of MWCNTs in ground water.

### 3.3.3. Wastewater

#### *Decabromodiphenyl Ether*

1 As introduced in Chapter 2, manufacturers, homes, and public buildings could be significant  
2 sources of BDE-209 to wastewater treatment plants and municipal sewage treatment facilities ([Hale et al.,  
3 2006](#)). Because of its hydrophobicity and tendency to partition to solids, most BDE-209 in wastewater  
4 would be expected to sorb to settling solids (i.e., will not remain in effluent) during the sewage treatment  
5 process ([Ricklund et al., 2009](#); [North, 2004](#)).

6 BDE-209 partitions strongly to particulate matter, so sewage sludge is expected to be a major sink  
7 for BDE-209, while effluent is likely dominated by the more water soluble lower brominated congeners.  
8 Sewage sludge applied to agricultural fields could be a source of BDE-209 to soils ([Huang et al., 2010](#);  
9 [Vrkoslavová et al., 2010](#); [U.S. EPA, 2009b](#); [Vonderheide et al., 2008](#); [Knoth et al., 2007](#); [Hale et al.,  
10 2006](#); [Law et al., 2006b](#); [Sellström et al., 2005](#)). Runoff along the surface of the ground then could  
11 transfer BDE-209 in the sewage sludge to nearby terrestrial systems or waterways. BDE-209-  
12 contaminated sludge could be disposed of in landfills (and possibly leach to subsoils and ground water) or  
13 incinerated (introducing emissions to the atmosphere).

14 Wastewater effluents, although not dominated by the higher brominated PBDEs, might be a  
15 source of BDE-209 and transformation product contamination to receiving water bodies of local aquatic  
16 ecosystems near the discharge location ([Peng et al., 2009](#); [Song et al., 2006](#)). Wastewater irrigation for  
17 farmlands could be a source of PBDEs in agricultural soils. The mobility of BDE-209 in the receiving soil  
18 could be enhanced if it sorbs to dissolved organic matter in the irrigation water ([Wang et al., 2010b](#)).

19 Recent studies that present concentrations of BDE-209 in wastewater effluent and sludge are  
20 presented in Section 4.1.2.2 and Section E.1 of Appendix E.

#### *Multiwalled Carbon Nanotubes*

21 Information in the recent literature regarding the behavior of MWCNTs in wastewater is limited.  
22 Because of its hydrophobicity and tendency to form bundles, however, pure MWCNTs likely would be  
23 removed by settling (i.e., be removed from the effluent) during the sewage treatment process.  
24 Functionalized MWCNTs could have improved dispersion and increased solubility in wastewater, thereby  
25 increasing their mobility and persistence in wastewater effluents.

26 As discussed in Section 3.1, MWCNTs can act as environmental adsorbates of metals,  
27 hydrophobic organic compounds, and other toxic organics ([Li et al., 2011](#); [Cho et al., 2008](#); [Petersen et  
28 al., 2008](#); [Chen et al., 2007](#); [Helland et al., 2007](#)), and these adsorbants might dictate CNT mobility and  
29 dispersion in wastewater. He et al. ([2012](#)) studied the behavior of MWCNTs stabilized by humic acid

1 during the coagulation-flocculation-sedimentation process of drinking water treatment and found that  
2 humic acid-stabilized MWCNTs were effectively sequestered by this process.

3 Literature containing concentrations of MWCNTs in wastewater effluent or sludge was not  
4 found.

### 3.4. Transport, Transformation, and Fate in Soil

5 BDE-209 or MWCNTs released from the flame-retardant upholstery textile coatings life cycle  
6 could enter terrestrial ecosystems in several ways. For example:

- 7 • BDE-209 or MWCNTs in ambient air subsequently could be deposited on soil and plants.  
8 Some particles that deposit on soil or plants might experience secondary transport via wind  
9 and become resuspended into ambient air and redeposited into nearby terrestrial ecosystems.
- 10 • Runoff flowing along the ground surface could transfer BDE-209 or MWCNTs in  
11 contaminated soil to nearby terrestrial ecosystems.
- 12 • Disposal products containing BDE-209 or MWCNTs could be deposited in solid waste  
13 landfills. Sewage sludge containing BDE-209 or MWCNTs also might be land-filled.  
14 BDE-209 or MWCNTS in land-filled waste could leach into subsoils.

#### *Decabromodiphenyl Ether*

15 Similar to sediments, soils are a major sink for PBDEs, including BDE-209. BDE-209 released  
16 from the flame-retardant upholstery textile coating life cycle can enter terrestrial ecosystems and  
17 distribute in soil and plants.

18 As with sediment, water solubility (hydrophobicity) and  $K_{ow}$  are important physicochemical  
19 factors for predicting behavior of BDE-209 in soil, and these parameters predict that BDE-209 will  
20 associate primarily with organic (carbon-rich) particles in soil and experience limited mobility ([U.S. EPA,](#)  
21 [2010b](#); [Yu et al., 2010](#); [Zhu et al., 2010](#)). In addition, percent total organic carbon likely plays a major  
22 role in BDE-209 transport and distribution in soil ([Zou et al., 2007](#)).

23 Plants exposed to BDE-209 from soil also can accumulate BDE-209 and potentially transform  
24 BDE-209 to lower brominated compounds. Debromination in this context has been investigated only in  
25 the soil-plant system, however, not in plants alone; the possibility therefore remains that debromination  
26 might occur exclusively in the soil, after which plants take up the transformation products ([Huang et al.,](#)  
27 [2010](#)). If present in soils, BDE-209 could contact plant roots and partition to root lipids due to its high  
28 lipophilicity and thereby transport into plant tissues ([Huang et al., 2010](#); [Vrkoslavová et al., 2010](#)). Huang  
29 et al. ([2010](#)) studied the uptake, translocation, and metabolism of BDE-209 in six plant species and found  
30 that root lipid content was positively correlated with BDE-209 uptake in those species. Accumulation of

1 BDE-209 occurred in the roots and shoots of all plants. The translocation factor, measured as the  
2  $\text{Concentration}_{\text{shoot}}/\text{Concentration}_{\text{root}}$  of BDE-209, however, was inversely related to BDE-209  
3 concentration in the roots, suggesting root lipids restrict translocation of BDE-209 from roots to shoots  
4 because of its partitioning to root lipids. In contrast to Huang et al. (2010), the study conducted by  
5 Vrkoslavová et al. (2010) provided evidence of translocation of BDE-209 and other PBDEs in plants from  
6 the root lipids of tobacco plants to other plant tissues. Concentrations in soil will further depend on the  
7 amount of vegetative cover, which also could scavenge BDE-209 (U.S. EPA, 2010b).

8 Evidence of BDE-209 debromination (transformation) by soil microorganisms and photolysis in  
9 surface soils was presented earlier (see Section 3.1 and Appendix D, Table D-1). Other studies relevant to  
10 the fate and transport of BDE-209 in soil and plants are provided in Appendix D, Table D-3. Evidence  
11 that BDE-209 affects soil microbial community structure and function is also available; some of these  
12 studies are also discussed in Section 5.2.2.1 and Section F.2.3 of Appendix F.

13 Recent studies that present soil concentrations of BDE-209 have been identified; some of these  
14 data are presented in Section 4.1.2.3 and Section E.1 of Appendix E.

#### *Multiwalled Carbon Nanotubes*

15 MWCNTs released from textile products can enter terrestrial ecosystems and be transported in  
16 several ways, as outlined previously. The propensity of MWCNTs to adsorb to soil surfaces can make  
17 them less mobile (Borm et al., 2006; Wiesner et al., 2006). MWCNTs modified with surface coatings to  
18 enhance their aqueous stability or change their surface charge will exhibit varied environmental behavior  
19 versus that of pure MWCNTs (Petersen et al., 2011).

20 Petersen et al. (2011) examined sorption profiles of pure MWCNTs and MWCNTs functionalized  
21 with a polyethylenimine surface coating and determined that sorption isotherms for pure MWCNTs were  
22 nearly linear, whereas isotherms for modified MWCNTs were nonlinear, indicating that surface coating  
23 can influence MWCNT interactions with soils. The authors also suggested that MWCNT characteristics  
24 (such as presence of surface coating) are better predictors of sorption behavior than soil type (and organic  
25 carbon content).

26 Properties of the soil environment (e.g., soil type, soil organic matter, pH, ionic strength, presence  
27 of other pollutants) also could affect particle transport, and general information on how those properties  
28 affect nanoparticles (not specific to MWCNTs) is available in the literature (Navarro et al., 2008; U.S.  
29 EPA, 2007).

30 Plants could be exposed to MWCNTs in air, water, and soil. As with BDE-209, airborne  
31 MWCNTs could attach to leaves and other aerial parts of plants and be translocated to different tissues of  
32 the plant, in which case plants also might act as transfer vectors for MWCNTs in the food chain. If  
33 MWCNTs are present in soils, plant roots could interact with those associated with soil material and in

1 soil pore water ([Navarro et al., 2008](#)). Additionally, bioaccumulation might be possible for carbon-based  
2 nanomaterials ([Navarro et al., 2008](#)).

3 Studies relevant to the fate and transport of CNTs in soil are provided in Appendix D, Table D-4.  
4 Studies that examined MWCNT uptake, translocation, and transformation in plants were not found.  
5 Literature that presents soil concentrations of MWCNTs has not been identified.

## 3.5. Multimedia Models to Predict Environmental Fate and Transport

### *Decabromodiphenyl Ether*

6 Multimedia models to predict environmental fate and transport of BDE-209 and PBDE congener  
7 profiles in environmental media have been used in recent studies. Breivik et al. ([2006](#)) used a multimedia  
8 fate and transport model to provide further understanding of how temporal variability and forest coverage  
9 help control LRT distance for BDE-209 and determined that the fate of atmospheric BDE-209 is likely to  
10 be controlled by deposition. Results of their study suggested that the variability of precipitation and the  
11 occurrence of periods without precipitation occurring with strong winds can impact LRT of BDE-209.  
12 They determined that the “forest filter effect” might also be important to the LRT of BDE-209; scenarios  
13 with a forest yielded lower estimates of air travel distance than scenarios without a forest. Gouin et al.  
14 ([2005](#)) used a multimedia mass-balance model to assess the importance of seasonal variability (including  
15 snow pack, temperature, forest canopy) on concentrations of PBDEs in air, although results were not  
16 specific to BDE-209. The authors concluded that PBDE concentrations experience a “spring-pulse” due to  
17 particle-bound deposition of PBDEs in the snow pack during winter, followed by transfer of PBDEs to  
18 the soil surface following snow melt and volatilization back into the atmosphere as springtime  
19 temperatures increase. Emerging spring foliage then takes up PBDEs, decreasing atmospheric  
20 concentrations during the summer months and inhibiting LRT.

21 Bogdal et al. ([2010](#)) used PBDE measurement data for the Lake Thun catchment area,  
22 Switzerland, in air, lake water, lake sediment, and tributary water, and combined results from a  
23 multimedia fate model that used site-specific environmental parameters from the lake catchment to  
24 predict PBDE congener patterns in water and sediment. They incorporated measured loadings of PBDEs  
25 in air, tributaries, and wastewater into their model. The authors reported that their model successfully  
26 predicted general PBDE congener patterns in water and sediment, but that the model tended to  
27 underestimate concentrations in water and overestimate concentrations in sediment relative to measured



1 concentrations. The parameter driving this discrepancy appeared to be partitioning of PBDEs between the  
2 aqueous dissolved phase and suspended particulate matter phase in the water column.

### *Multiwalled Carbon Nanotubes*

3 Although empirical data on MWCNT concentrations in the environment are lacking, some  
4 researchers have used modeling to simulate movement of CNTs through environmental compartments  
5 and to derive predicted environmental concentrations (PECs). Mueller and Nowack ([2008](#)) used substance  
6 flow analysis to model CNTs in air, soil, and water (not sediment) in Switzerland based on simplifying  
7 assumptions. PECs were calculated for “realistic” and “high exposure” scenarios and are provided in  
8 Table 3-3.

9 Gottschalk et al. ([2009](#)) described a probabilistic material flow analysis framework to derive  
10 probability distributions of PECs for engineered CNTs in soil, sludge-treated soil, air, surface water,  
11 sediment, and sewage treatment plant effluent and sludge for the United States, Europe, and Switzerland  
12 (see Table 3-3). As noted in Gottschalk et al. ([2010](#)), although both studies were designed to estimate  
13 PECs in environmental media, the two study designs were quite different and the methodologies used  
14 varied considerably, making a direct comparison of PECs difficult. The differences included the model  
15 type (deterministic versus probabilistic); model scale [Gottschalk et al. ([2009](#)) considered additional  
16 environmental compartments (sediment and ground water), more flows associated with these additional  
17 compartments, as well as production, manufacturing, and recycling processes]; model input data [newly  
18 available model input data were used in Gottschalk et al. ([2009](#))]; and amended categorization of the  
19 products and allocation of the CNT mass to the product categories.

20 Another study employed the USEtox model to carry out a life-cycle-based analysis of the aquatic  
21 toxicity impacts associated with CNT synthesis ([Eckelman et al., 2012](#)). This study used information on  
22 the physicochemical properties of CNTs to model fate and transport of CNTs in freshwater systems under  
23 the authors described as “realistic” and “worst-case” or “conservative” scenarios. Based on information  
24 from Gottschalk et al. ([2009](#)), the realistic scenario assumed the fraction of CNTs removed from the water  
25 column due to clustering and settling to be 90%. For the 10% remaining in the water column, this  
26 scenario assumed a CNT exposure factor (defined by USEtox as the dissolved fraction of CNTs in the  
27 water column) of 98%, with most of the remaining 2% partitioning to suspended solids. This realistic  
28 scenario, which utilized Monte Carlo analysis, calculated a mean residence time in fresh water to be on  
29 the order of days. The conservative scenario assumed an exposure factor in the water column of 100%  
30 and estimated the freshwater residence time for CNTs as 143 days. This study did not distinguish between  
31 single-walled and multiwalled CNTs.

Table 3-3. Predicted environmental concentrations of CNTs using fate and transport modeling.

Medium	Mueller and Nowack (2008)	Gottschalk et al. (2009) <sup>a</sup>
Air ( $\mu\text{g}/\text{m}^3$ )	$1.5 \times 10^{-3}$ (realistic); $2.3 \times 10^{-3}$ (high exposure)	$1 \times 10^{-6}$ (United States) $3 \times 10^{-6}$ (Europe) $8 \times 10^{-6}$ (Switzerland)
Soil ( $\mu\text{g}/\text{kg}$ or $\Delta\mu\text{g}/\text{kg}\text{-yr}$ )	$1 \times 10^{-2}$ (realistic); $2 \times 10^{-2}$ (high exposure)	$5.6 \times 10^{-4}$ (United States) $1.5 \times 10^{-3}$ (Europe) $1.9 \times 10^{-3}$ (Switzerland)
Sludge-treated soil ( $\Delta\mu\text{g}/\text{kg}\text{-yr}$ )	ND	$3.1 \times 10^{-2}$ (United States) $7.4 \times 10^{-2}$ (Europe) ND (Switzerland) <sup>b</sup>
Surface water ( $\mu\text{g}/\text{L}$ )	$5 \times 10^{-4}$ (realistic); $8 \times 10^{-4}$ (high exposure)	$1 \times 10^{-6}$ (United States) $4 \times 10^{-6}$ (Europe) $3 \times 10^{-6}$ (Switzerland)
Sediment ( $\Delta\mu\text{g}/\text{kg}\text{-yr}$ )	ND	$4.6 \times 10^{-2}$ (United States) $2.4 \times 10^{-1}$ (Europe) $2.3 \times 10^{-1}$ (Switzerland)
Sewage treatment plant (STP) effluent ( $\mu\text{g}/\text{L}$ )	ND	$8.6 \times 10^{-3}$ (United States) $1.5 \times 10^{-2}$ (Europe) $1.2 \times 10^{-2}$ (Switzerland)
STP sludge ( $\text{mg}/\text{kg}$ )	ND	$6.8 \times 10^{-2}$ (United States) $6.2 \times 10^{-2}$ (Europe) $6.9 \times 10^{-2}$ (Switzerland)

<sup>a</sup>For Gottschalk et al. (2009), air, surface water, STP effluent, and STP sludge concentrations are modes (most frequent values) from 2008. For soil, sludge-treated soil, and sediment, values are modes that represent annual increases in concentrations ( $\Delta\mu\text{g}/\text{kg}\text{-yr}$ ).

<sup>b</sup>In Switzerland, sewage sludge is not applied to soil.

ND = no data

1 Cullen et al. (2010) simulated subsurface mobility of MWCNTs compared with nanofullerenes  
2 ( $\text{nC}_{60}$ ) under a range of hydrologic and geological conditions (homogeneous and heterogeneous) using a  
3 two-dimensional finite element model. In general, nanoparticles in systems with the same average  
4 hydraulic properties were predicted to be less mobile if the systems were heterogeneous as opposed to  
5 homogeneous. For the conditions evaluated, MWCNTs were predicted to be much more mobile compared  
6 with  $\text{nC}_{60}$  because of two factors—nanoparticle shape and size. The smaller, spherical  $\text{nC}_{60}$  were more  
7 efficiently collected on soil surfaces compared with the larger, cylindrical MWCNTs.

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# Chapter 4. Exposure-Dose

1            Releases of decabromodiphenyl ether (decaBDE) and multiwalled carbon nanotubes (MWCNTs)  
2 to the indoor and outdoor environments can occur at multiple stages of the product life cycle for flame-  
3 retardant upholstery textile coating (Chapter 2), and subsequent transport, transformation, and fate  
4 processes dictate how decaBDE and MWCNT distribute through various environmental media once  
5 released (Chapter 3). Exposure describes the pathways through which contact occurs between  
6 contaminants in the environment and living organisms and abiotic receptors. Toxicokinetics (i.e.,  
7 absorption, distribution, metabolism, excretion [ADME]) describe the processes that relate exposure (or  
8 dosage) to the internal dose, which refers to the quantity of a chemical or material that is taken up and  
9 absorbed by living organisms ([U.S. EPA, 2010c](#)).<sup>11</sup>

10            Section 4.1 provides an introduction to analytical techniques for identifying, characterizing, and  
11 measuring decaBDE and MWCNTs in various matrices. The different metrics recommended for  
12 characterizing exposure and dose of decaBDE and MWCNTs are also discussed, and available  
13 concentration data in various indoor and outdoor media are presented. In the absence of data quantifying  
14 decaBDE or MWCNT exposures at the point of contact, measured concentrations of decaBDE and  
15 MWCNT in surrounding media can be used to estimate exposures using a scenario evaluation approach.  
16 Sections 4.2 and 4.3 expand on the release scenarios presented in Chapter 2 to discuss the potential  
17 human and ecological exposure pathways that link those releases to receptors. No data were identified  
18 regarding relevant exposure pathways leading to impacts on abiotic resources (e.g., the manmade  
19 environment); as a result, this comprehensive environmental assessment case study does not include a  
20 discussion of exposure scenarios that would influence abiotic receptors. Although broad potential impacts  
21 on society and the global environment are discussed in Section 5.3, exposure is either not considered

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<sup>11</sup>The term “dose” is described generally by the U.S. Environmental Protection Agency (EPA) Integrated Risk Information System (IRIS) as “[t]he amount of a substance available for interactions with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism.” Several specific forms of dose are also described by IRIS, but the definitions of these terms are not used consistently across the risk assessment community. The following definitions of specific forms of dose are provided by IRIS: “The POTENTIAL DOSE is the amount ingested, inhaled, or applied to the skin. The APPLIED DOSE is the amount presented to an absorption barrier and available for absorption (although not necessarily having yet crossed the outer boundary of the organism). The ABSORBED DOSE is the amount crossing a specific absorption barrier (e.g. the exchange boundaries of the skin, lung, and digestive tract) through uptake processes. INTERNAL DOSE is a more general term denoting the amount absorbed without respect to specific absorption barriers or exchange boundaries. The amount of the chemical available for interaction by any particular organ or cell is termed the DELIVERED or BIOLOGICALLY EFFECTIVE DOSE for that organ or cell.”

1 germane to the discussion of the impact (such as for economic impacts of manufacturing MWCNTs) or  
2 the exposure characteristics related to the impact are already included in the general discussion that  
3 follows (higher potential exposures levels related to such as for socioeconomic impacts).

4 Probable exposure scenarios throughout the flame-retardant upholstery textile coating life cycle  
5 are identified for workers, consumers, the general public, and highly exposed populations in Section 4.2  
6 and for aquatic and terrestrial biota in Section 4.3. These scenarios describe the conditions under which  
7 exposures might occur; this information can be used in combination with measured or modeled  
8 concentrations in environmental media from Section 4.1 and exposure factors to estimate exposures.  
9 Kinetic information then can be used to determine or estimate the internal dose that results from external  
10 exposures. When available, point-of-contact measurements, administered dosages, tissue or body burdens,  
11 and scenario-specific exposure guidelines and recommendations are provided, and the toxicokinetics of  
12 decaBDE and MWCNTs are described. Finally, Section 4.4 discusses aggregate exposures to decaBDE or  
13 MWCNTs from multiple sources and Section 4.5 discusses cumulative exposures to multiple related  
14 stressors. Measured concentrations of decaBDE in environmental media are provided in Appendix E (no  
15 data on environmental concentrations of MWCNTs were found), and studies describing toxicokinetics of  
16 polybrominated diphenyl ethers (PBDEs) and carbon nanotubes (CNTs) in mammals are summarized in  
17 Appendix F.

18 As described in Section 2.2.4, both decaBDE and MWCNTs are expected to be incorporated into  
19 a polymer or other type of matrix in the flame-retardant formulation applied to upholstery textiles, and  
20 both the free and matrix-bound forms of these substances might be released during the product life cycle.  
21 Very little data relevant to BDE-209 and MWCNT exposures, however, have been generated for the  
22 matrix-bound forms of these substances. This lack of data necessitates a reliance on the existing data for  
23 free MWCNTs and BDE-209 in the discussion throughout this chapter. The extent to which exposure  
24 characteristics and dose implications differ between the free and matrix-bound forms of BDE-209 and  
25 MWCNTs, however, is unknown at this time.

## 4.1. Detection, Measurement, and Characterization

26 Exposure scenario evaluation requires information on measured, modeled, or reasonably  
27 estimated concentrations of a stressor in exposure media. As introduced in Chapter 1, PBDEs and  
28 MWCNTs represent two groups of compounds, each encompassing substances that span a range of  
29 physicochemical characteristics and properties. As a result, developing reliable analytical techniques for  
30 detecting, measuring, and characterizing the full range and makeup of PBDEs and MWCNTs in  
31 environmental media can present challenges. Text Box 4-1 provides an abbreviated discussion of a few

1 common analytical techniques and the general challenges associated with them. Appendix B summarizes  
2 common analytical techniques for each substance, and presents the strengths and limitations of each  
3 technique.

### *Decabromodiphenyl Ether*

4 The diversity of known PBDE congeners makes the characterization of exposure to a single  
5 congener such as decaBDE difficult, as described in Text Box 4-1. Identifying the specific source of  
6 decaBDE in environmental samples is even more difficult. DecaBDE is present in dust in many different  
7 environments, but the source of the dust could be from manufacturing, wear, or breakdown of many  
8 consumer products, including electronics, foams, and polymer textile coatings on furniture such as  
9 couches and mattresses. Some research has been conducted using forensic microscopy to characterize the

#### **Text Box 4-1. Detecting, Measuring, and Characterizing PBDEs and MWCNTs**

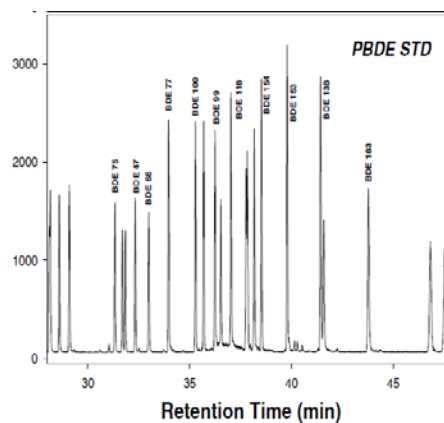
Mass spectrometry is used most frequently to detect **polybrominated diphenyl ethers (PBDEs)**, and gas chromatography (GC) is employed to measure and characterize PBDE mixtures. High-resolution mass spectrometry is the most selective method, but is also expensive and labor intensive. Low-resolution mass spectrometry is insensitive to congeners with more than six bromines (like BDE-209), but optimization of aspects like reagent gas, source temperature, and source pressure can increase sensitivity.

Accurate characterization in environmental samples has proven more problematic for BDE-209 than for lesser brominated congeners. How a GC system is set up can contribute to variation in measurements. For example, use of high temperatures and longer column lengths can lead to degradation of higher brominated congeners and quicker evaporation of higher molecular weight congeners.

Distinguishing between certain PCBs and PBDEs is difficult with most systems, which can lead to imprecise measurements. Additionally, not all PBDE congeners are commercially available for use as standards (approximately 160 of the 209 congeners are currently available). Determining whether unidentified peaks in chromatograms (see gas chromatograph output to right) are due to these nonstandardized PBDE congeners or to other compounds can be challenging ([Stapleton, 2006](#)).

Because of the tendency of **multiwalled carbon nanotubes (MWCNTs)** to clump together, multiple, orthogonal techniques are recommended to characterize MWCNTs adequately in exposure media ([Petersen and Henry, 2012](#)). A variety of well-developed electron microscopy and mass spectrometry techniques exist for characterizing MWCNTs, which are summarized in Appendix B. Several detection and quantification techniques are available for MWCNTs in aqueous media, but fewer are available for evaluating MWCNTs in other media. Due to the challenges associated with detecting, measuring, and characterizing very small concentrations of highly reactive and polydispersed particles, successful protocols for extracting MWCNTs from relevant matrices or media (e.g., textiles, polymers, body fluids) could differ from those used to extract traditional compounds for exposure studies based on preliminary, unpublished evidence presented at a public meeting ([Uddin and Nyden, 2011a](#); [Uddin and Nyden, 2011b](#)). Additionally, many detection methods rely on knowledge of properties of the material as produced, which can change dramatically during subsequent stages of the product life cycle. Currently, the main application for detection methods is to verify concentrations of as-manufactured MWCNTs during laboratory-based experiments.

Radioactive labeling is a precise quantification method that works in any medium, but CNTs must be radioactively labeled prior to dispersal in environmental media for this method to work. In aqueous suspensions, the most straightforward method for quantification is gravimetric assessments of suspended materials. The nominal concentration at the start of the study must be known, however, because deviation from that nominal value is what is measured.



Example Gas Chromatograph Output for a PBDE Mixture with Multiple Unidentified Peaks ([Stapleton, 2006](#))

1 source and transfer mechanisms of BDE-209 in indoor environments, but the results are qualitative  
2 ([Lagalante et al., 2011](#); [Webster et al., 2009](#)). PBDEs are persistent pollutants, so quantifying whether  
3 exposure and body burdens of the lower brominated PBDEs are the result of weathering and breakdown  
4 of BDE-209 or from other PBDEs such as pentaBDE and octaBDE (widely used until recently)  
5 ([Stapleton, 2006](#)), is difficult.

### ***Multiwalled Carbon Nanotubes***

6 Configurations of MWCNTs can vary depending on the type of material or substrate used in their  
7 manufacture (see Section 2.2). Text Box 4-2 provides examples of the specific physicochemical  
8 properties of MWCNTs that influence exposure, uptake, and dose. Single analytical techniques used alone  
9 are generally not sufficient for characterizing all of the properties of MWCNTs that can influence  
10 exposure; to characterize the presence and form of MWCNTs in media adequately, multiple analytical  
11 methods must be used in tandem (see Text Box 4–1 and Appendix B).

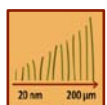
12 The potential for human exposure from upholstery textiles coated with flame retardants is  
13 currently difficult to assess because data are not yet available on production of MWCNTs for flame-  
14 retardant upholstery textiles (see Section 2.2.4). Furthermore, very little information is available on  
15 whether or how MWCNTs might migrate out of a product matrix, as well as what methods could be used  
16 to quantify exposure concentrations of matrix-bound MWCNTs and partially exposed MWCNTs (i.e.,  
17 ends of MWCNTs “sticking out” from the matrix). Understanding the behavior of the material requires  
18 comparing potentially similar applications, such as machining of CNT composites and the resultant  
19 exposure. Machining of CNT composites could generate particles or fibers similar to those generated  
20 from the wear and breakdown particles or fibers similar to those generated from the wear and breakdown  
21 of MWCNT composites, so these studies are useful from an exposure assessment perspective. Estimating  
22 exposures during other product life-cycle stages also might be possible by evaluating similar applications  
23 or alterations of materials containing MWCNTs. Such assumptions, however, could yield conclusions that  
24 are very different from the actual behavior and exposure potential of the MWCNTs in flame-retardant  
25 upholstery textile applications.

## Text Box 4-2. Specific Physicochemical Properties of MWCNTs Shown to Influence Exposure, Kinetics, and Dose

As introduced in Text Box 1-1, the physicochemical characteristics of multiwalled carbon nanotubes (MWCNTs) can be altered (both intentionally and unintentionally) by using different methods, materials, and processing techniques under different ambient conditions, and these characteristics can change further over the course of the life cycle. Several studies have explored how changes in individual MWCNT characteristics can affect exposure, kinetics, and dose. The following physicochemical characteristics have been identified as contributing to changes in the behavior of CNTs in vitro and in vivo [as summarized by Johnston et al. (2010)]. Because most studies have focused on the inhalation and dermal routes of exposure, data are extremely limited for the oral route.



**Dispersion State.** Individual CNTs often form larger bundles that range from tightly aggregated (i.e., thick and ropy) to loosely agglomerated (i.e., tangled, like steel wool). Following inhalation, long, well dispersed CNTs are more likely to deposit deeper in the respiratory tract, where they might be taken up by cells via phagocytosis (i.e., engulfed by the cell membrane). Well-dispersed CNTs are more likely to translocate to other sites following deposition in the lung, leading to a shift in CNT presence from the active airways to the interstitium and alveolar walls, and ultimately to the circulatory system. Up to a certain size limit, bundles of CNTs tend to be more biopersistent in the lung than well-dispersed CNTs, remaining in the conducting airways or entering macrophages at the point of contact. Studies with skin cells (keratinocytes) also have demonstrated that dermal uptake of free MWCNTs can depend largely on the dispersion state of the MWCNTs, with limited uptake in the absence of large bundles.



**Morphology.** Short (usually defined as <math><15 \mu\text{m}</math>) CNTs are more readily taken up into cells, but they also are more readily cleared (for example, via macrophages following inhalation). Longer CNTs, on the other hand, are more persistent at the deposition site and might get “stuck” in the cell membrane, resulting in “frustrated” phagocytosis or endocytosis. The length of CNTs might be more important than functionalization, as neutral, positively, or negatively charged CNTs are consistently internalized when CNT length remains <math><2 \mu\text{m}</math>. CNTs engineered with rounded or open ends also will exhibit different uptake mechanisms into cells. CNTs with rounded tips enter cells at a perpendicular angle, whereas CNTs with open ends enter cells at a parallel angle to the cell surface (Shi et al., 2011). The ratio of MWCNT length to diameter (i.e., aspect ratio), which can be a relevant exposure metric for fibers like asbestos, also can help predict the deposition sites of CNTs in the respiratory tract, internalization success of CNTs into cells, the speed at which uptake will occur, and the potential for subsequent translocation. CNTs with higher aspect ratios, for example, are more likely to deposit deeper in the lung, undergo frustrated internalization, take longer to achieve the ideal entry angle into cells, and are more likely to translocate to pleura than CNTs with lower aspect ratios.



**Surface Functionalization.** CNTs often are treated or complexed with surfactants or other compounds designed to functionalize them for a specific purpose (e.g., remain dispersed in water, interact with specific proteins). Some surface functionalizations also can influence biopersistence of CNTs; for example, some CNTs functionalized to be water soluble will be eliminated rapidly from the body, and CNTs functionalized to interact with specific proteins might be more readily taken up by cells, including macrophages, which contribute to CNT clearance.



**Contaminants.** Several contaminants can be introduced during the manufacture of CNTs, including metals like iron and nickel and various forms of carbon. Such impurities can “hitch a ride” with the CNTs to a biological surface or interior of a cell, and contaminants that are not trapped within the central cavity of the CNT the could be bioavailable. Although purification processes often are used (with mixed success) to remove metal contaminants, these processes tend to alter other characteristics of the the CNTs, including length and morphology, which makes isolating the effect of metal adsorbates on receptors difficult.



## 4.1.1. Dose and Exposure Metrics

### *Decabromodiphenyl Ether*

1 Environmental concentrations of decaBDE are commonly quantified in terms of mass (e.g.,  
2 picograms, nanograms) per volume (e.g., m<sup>3</sup>, L) for air and water measurements or mass per weight (e.g.,  
3 grams dry weight, grams wet weight) of soil, sediment, or tissue samples ([Frederiksen et al., 2009](#)).  
4 Human exposure to decaBDE and subsequent dose has been quantified by detection of BDE-209 in the  
5 serum, breast milk, adipose tissue, and hair of humans ([Darnerud et al., 2001](#)).

### *Multiwalled Carbon Nanotubes*

6 Dosages of free MWCNTs usually are expressed or quantified by mass concentration (like for  
7 decaBDE) or by particle/fiber count of individual MWCNTs or MWCNT bundles in a particular quantity  
8 of a medium over an established period of time ([Aschberger et al., 2010](#); [Pauluhn, 2010a](#)). Because  
9 exposures to MWCNTs might involve only a small amount of mass but a large number of particles/fibers,  
10 the appropriateness of traditional mass-based exposure and dose metrics for estimating and measuring  
11 toxicologically relevant doses of engineered nanoscale materials (nanomaterials) is under debate  
12 ([Aschberger et al., 2011](#)).

13 Use of time-adjusted, mass-based metrics historically has been the accepted paradigm for  
14 quantifying exposure and dose for most chemical substances. For example, mass concentration has been  
15 used for more than 50 years as the metric for characterizing aerosol exposures. Recent research has  
16 challenged the ability of mass concentration to capture appropriate nanomaterial dose-response  
17 relationships, however, by illustrating that airborne nanoscale particles—including both engineered  
18 nanomaterials and nanoscale particulate matter—can be more toxic than larger airborne particles of the  
19 same composition on a mass-for-mass basis ([Maynard and Aitken, 2007](#)). Despite acknowledgment in the  
20 scientific community that mass-based dose metrics might not be appropriate for nanomaterials, an  
21 alternative unifying metric for characterizing dose has not yet been established, and no single metric  
22 appears to be suitable for all nanomaterials or exposure situations  
23 ([Pauluhn, 2010b](#); [Maynard and Aitken, 2007](#)).

24 Some research in animal models has shown that toxic effects of some MWCNTs do follow a  
25 more traditional dose-related curve based on the administered mass concentration of MWCNTs [for  
26 example, Ma-Hock ([2009](#)), as described in Section 5.1.3, and Asharani et al. ([2008](#)), as described in  
27 Section 5.2.1.2], indicating that mass can be considered an appropriate dose metric for some MWCNTs  
28 under certain exposure conditions. To what degree variations in other MWCNT characteristics (e.g.,  
29 length, width, bundling state) influence the appropriate application of mass-based metrics for MWCNTs  
30 is not well understood. CNTs might induce toxic effects beyond those expected based on mass

1 concentration, however, which has been demonstrated in comparative tests of nanoparticulate carbon and  
2 quartz, commonly used indicator compounds ([Donaldson et al., 2006](#)).

3 Alternative characteristics that have been considered as potentially relevant dose metrics for some  
4 nanomaterials include particle size, surface area, surface chemistry, particle count per particle size, and  
5 particle ([Aschberger et al., 2011](#); [Maynard and Aitken, 2007](#)). Although surface area has been shown to  
6 be a better dose metric than mass in several rodent studies ([Aschberger et al., 2011](#); [Sager and](#)  
7 [Castranova, 2009](#); [Tran et al., 2000](#); [Oberdorster, 1996](#)), surface area has not been routinely measured or  
8 recorded when examining occupational exposures ([Aschberger et al., 2011](#)). Calculating surface area after  
9 study completion is complicated by the differences in measurement techniques, the dynamic behavior of  
10 MWCNTs (i.e., propensity to form bundles), and lack of thorough reporting.

11 Because the physical form of MWCNTs resembles fibers, other characteristics such as length,  
12 diameter, aspect ratio, bundling state, and fiber count have been considered as characteristics potentially  
13 relevant to quantifying potential exposures and doses of CNTs. Using fiber count as a dose metric can be  
14 challenging, however, because MWCNT fibers generally are not uniform in size, and different sizes  
15 might elicit different effects (see Text Box 5–1). The diameters of MWCNTs in general can range from  
16 10 to 200 nm ([Hou et al., 2008](#)), and the lengths can vary widely, often by tens of microns ([Donaldson et](#)  
17 [al., 2006](#)).

18 Bundling also can be a relevant characteristic for considering dose-response relationships.  
19 Researchers have noted that MWCNTs tend to form bundles, which then can combine into small  
20 “clumps,” some of which are nonrespirable ([Pauluhn, 2010a](#)). For inhalation exposures, these larger  
21 clumps are therefore less toxic than free MWCNTs and MWCNT bundles in the respirable range, despite  
22 the larger mass concentration. Characterization of inhalation exposure and subsequent dose based on  
23 bundle size or aerodynamic diameter could therefore be more appropriate than characterization based on  
24 mass or particle count. Bundling of CNTs also could result in a toxic impact that is not observed with the  
25 same mass of dispersed CNTs. For example, bundled CNTs could trigger an immune-system foreign-  
26 body response because larger structures are potentially better recognized by macrophages ([Johnston et al.,](#)  
27 [2010](#)) (see Text Box 5-1). In vitro plant assays have shown that clustered MWCNTs fail to disperse  
28 throughout the culture, limiting exposure to a few cells ([Tan and Fugetsu, 2007](#)). Increasing the mass of  
29 clustered MWCNTs did not increase dispersion, rather this caused the clusters to grow larger and  
30 precipitate out of solution but did not cause a higher percentage of plant cells to be affected [Tan and  
31 Fugetsu ([2007](#)), described further in Section 5.2.2.2].

32 Aspect ratio, which refers to the ratio of a compound’s length to diameter, has been shown by  
33 some to be an important characteristic for driving exposure and dose of CNTs ([Kim et al., 2011](#); [Poland et](#)  
34 [al., 2008](#)). The fiber-like structure of CNTs can be considered similar to asbestos, causing many

1 researchers to predict that the toxicity of CNTs will be driven by differences in aspect ratio, with CNTs  
2 having higher aspect ratios more frequently depositing deeper in the lungs and translocating to the pleura,  
3 where mesothelioma, other cancers, and fibrosis (all effects of asbestos exposures) can occur  
4 ([Kim et al., 2011](#)). The utility of morphological parameters like length, width, and aspect ratio for dose  
5 quantification is limited, however, by inconsistencies in the literature regarding what constitutes “long”  
6 versus “short” or “high aspect ratio” versus “low aspect ratio.” These distinctions are usually relative,  
7 based on the materials compared in an individual study; specific incremental changes in length, width, or  
8 aspect ratio have not yet been correlated to quantitative changes in dose.

9 It is possible that no single dose metric can accurately predict the toxicity of MWCNTs;  
10 consideration of multiple characteristics together therefore has been proposed as a potential alternative.  
11 For example, aspect ratio and bundling state might need to be considered together. Long, thin CNTs (i.e.,  
12 those with higher aspect ratios) can penetrate deeply into airways, while bundled CNTs are more likely to  
13 deposit in the upper airway. Particles in the upper airway can be removed through mucociliary processes,  
14 whereas deposits in deeper regions are more likely to persist or translocate from the lung to other tissues  
15 where they might shift the location of toxic effects ([Johnston et al., 2010](#)).

16 Measuring potential exposures outside of well-controlled experimental settings—for example, in  
17 occupational settings—introduces a different set of challenges that can only be addressed currently by  
18 using multiple instruments and analytical techniques. As described in Text Box 4-1 and Appendix B,  
19 however, many of the techniques needed for detection, measurement, and characterization of MWCNTs  
20 are limited by inadequate levels of detection or restrictive measurement ranges for morphological  
21 parameters. For example, a common method for counting fibers in workplace air, the National Institute  
22 for Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM) 7400, ([NIOSH,](#)  
23 [1994](#)) does not detect fibers or bundles with diameters less than 0.25  $\mu\text{m}$  and does not differentiate  
24 between MWCNTs and other fibers ([Gustavsson et al., 2011](#)). Another method that can be used to  
25 estimate MWCNT mass concentrations in workplace air is NMAM 5040, but this method measures  
26 elemental carbon as a proxy for MWCNTs and does not automatically account for background  
27 contributions of other forms of particulate carbon ([Birch, 2003](#)).

28 The metrics primarily used to determine potential exposure levels of MWCNTs in occupational  
29 air are total particle count by size fraction, total dust or particle mass, respirable<sup>12</sup> dust or particle mass,

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<sup>12</sup>The respirable particulate fraction is generally defined as the “fraction of inhaled airborne particles that can penetrate beyond the terminal bronchioles into the gas-exchange region of the lungs” ([WHO, 1999](#)). The National Institute for Occupational Safety and Health considers particles with aerodynamic diameters  $>10 \mu\text{m}$  to be larger than respirable ([Bartley and Feldman, 1998](#)).

1 inhalable<sup>13</sup> dust or particle mass, total elemental carbon mass, and total or respirable fiber count  
2 ([Gustavsson et al., 2011](#)). The instruments required to capture these measurements include a suite of real-  
3 time, direct monitoring particle samplers and particle counters and a variety of area and personal air  
4 filters. The particles and fibers collected by these samplers and filters, however, are not limited to  
5 MWCNTs; instead, all particles or fibers within a certain size range are collected and counted, which  
6 might lead to overestimation of exposure concentrations. This lack of specificity introduces a degree of  
7 uncertainty that can be reduced only with adequate characterization of the samples collected on the filters  
8 ([Gustavsson et al., 2011](#)). In general, characterization involves a form of electron microscopy to verify  
9 morphological features and energy-dispersive spectroscopy to verify the chemical identity of the samples.  
10 In summary, most estimates of workplace exposure are derived by relating real-time data on particle or  
11 fiber counts with filter samples analyzed to determine particle or fiber mass, particle or fiber morphology,  
12 and chemical composition; all analytical techniques involved in this multi-step estimation of exposure  
13 concentrations have analytical limitations that produce estimates with varying amounts of uncertainty  
14 ([Dahm et al., 2011](#)).

## 4.1.2. Concentrations in Environmental Media and Indoor Environments

15 As described in the previous section, exposures can be estimated by combining knowledge of  
16 concentrations in exposure media with assumptions about contact of humans, biota, or abiotic surfaces  
17 with those media. The following sections describe the information available on concentrations of  
18 BDE-209, MWCNTs, and related substances in environmental media (i.e., air, water, soil).

### 4.1.2.1. Outdoor Air

#### *Decabromodiphenyl Ether*

19 Research has shown that BDE-209 comprises between 6 and 31% of total PBDE concentrations  
20 in outdoor air ([Frederiksen et al., 2009](#)). Outdoor air generally has lower concentrations of total PBDEs,  
21 which can be one or two orders of magnitude lower than in indoor air (see Appendix E). This lower  
22 concentration is partly due to the dilution factor of outdoor environments, but also occurs because indoor  
23 environments contain more sources of PBDEs such as electronics, furniture, plastics, and coatings in  
24 enclosed spaces ([Daso et al., 2010](#)).

---

<sup>13</sup>The inhalable particulate fraction is generally defined as the “fraction of a dust cloud that can be breathed into the nose or mouth” ([WHO, 1999](#)), which could include both particles with sizes within the respirable range and particles that are larger than respirable.

1 Mean levels of BDE-209 measured in outdoor air from locations throughout the United States  
2 range from 1.4 to 60.1 pg/m<sup>3</sup> ([U.S. EPA, 2010b](#)). Sampling locations included rural, agricultural, and  
3 urban locations. The highest level detected was 65 pg/m<sup>3</sup> in urban Chicago, and the lowest level was  
4 0.2 pg/m<sup>3</sup> at an agricultural site in Indiana ([Hoh et al., 2005](#)). International studies have reported mean  
5 BDE-209 levels ranging from 1.6 to 53.3 pg/m<sup>3</sup> ([Chang et al., 2009](#)). The lowest environmental  
6 concentration reported in the literature was 0.091 pg/m<sup>3</sup> in the Canadian High Arctic ([Su et al., 2007](#)), and  
7 the highest level reported was 105 pg/m<sup>3</sup> in Southern Ontario, Canada, nearly all of which was sorbed to  
8 aerosol particles ([Gouin et al., 2006](#)). Information from additional studies of concentrations in air is  
9 available in Appendix E, Table E-2.

### *Multiwalled Carbon Nanotubes*

10 A recent review of toxicity and exposure to CNTs indicates that ambient exposure to CNTs is  
11 possible, but very little outdoor environmental sampling data are available ([Aschberger et al., 2010](#)).  
12 Dahm et al. ([2011](#)) measured background elemental carbon (inhalable fraction) outside CNT primary and  
13 secondary manufacturing facilities. Concentrations ranged from not detected (limit of detection 0.2 to  
14 0.5 µg elemental carbon/filter) to 0.76 µg/m<sup>3</sup> at MWCNT manufacturing facilities. This information is of  
15 limited utility, however, because elemental carbon particles can be produced by many sources, and no  
16 electron microscopic analysis was conducted to determine if the particles collected included CNTs.

17 Researchers have found MWCNTs in methane or propane flames from kitchen stoves, and  
18 automotive exhaust is thought to be a source of MWCNTs ([Aschberger et al., 2010](#)). CNTs were found in  
19 the lung tissues of World Trade Center patients following the collapse of the buildings on  
20 September 11, 2001, which indicates that dust or smoke in urban environments can contain CNTs  
21 ([Aschberger et al., 2010](#)).

22 As summarized in Table 3-3, two life-cycle-based models estimated flow of CNTs and other  
23 nanomaterials from the products containing them to environmental compartments ([Gottschalk et al., 2009](#);  
24 [Mueller and Nowack, 2008](#)). The predicted environmental concentrations (PECs) of CNTs in the air were  
25 estimated by Mueller and Nowack ([2008](#)) as  $1.5 \times 10^{-3}$  and  $2.3 \times 10^{-3}$  µg/m<sup>3</sup> for the realistic exposure and  
26 high exposure scenarios, respectively; concentrations in airborne dust were not examined. Gottschalk et  
27 al. ([2009](#)) estimated a mode PEC of  $1 \times 10^{-6}$  µg/m<sup>3</sup> CNTs in U.S. air for 2008. Differences between the  
28 models and the resulting estimates are discussed in Section 3.5.

#### 4.1.2.2. Aquatic Systems – Sediment and Surface Water

##### *Decabromodiphenyl Ether*

1 In aquatic systems (including both water and sediment), BDE-209 is the predominant PBDE  
2 congener detected (49% to nearly 97% of the total PBDEs), with most detected in sediment. BDE-209 has  
3 been observed in both sediments and surface waters in multiple locations in the United States, from  
4 California to Delaware and Wisconsin to Mississippi ([Ashley et al., 2006](#); [Raff and Hites, 2004](#)). Surface  
5 water in the San Francisco Bay estuary of California was found to contain BDE-209 at concentrations  
6 below the limit of detection (reported as 20–200 pg/L for individual congeners) to 191.0 pg/L water, with  
7 all but one of the detectable concentrations ranging between 12.2 and 87.8 pg/L ([Oros et al., 2005](#)).  
8 Levels of BDE-209 observed in sediment ranged from below the level of detection (reported as 0.1 to  
9 1.5 ng/g dry weight) up to 3,150,000 ng/g in sediment downstream of a wastewater treatment plant for a  
10 plastics manufacturer in North Carolina ([La Guardia et al., 2007](#)). In another study, the highest total  
11 PBDE concentration in suspended sediment from the Mississippi River and five tributaries was  
12 1548 ng/g, with BDE-209 accounting for an average of 96.8% of the total observed PBDE concentration  
13 at the 31 sampling sites ([Raff and Hites, 2004](#)). Appendix E, Table E-3 provides additional information  
14 on these studies.

15 As detailed above, detected levels of BDE-209 in surface water are many times lower than those  
16 in sediment, which is consistent with assumptions based on the physical properties and environmental fate  
17 of BDE-209 discussed in Chapter 3. The highest level of BDE-209 detected in surface water was  
18 191 pg/L, equivalent to 191 parts per quadrillion, whereas the highest amount in sediment was  
19 3,150,000 ng/g, equivalent to 3150 parts per million. These two measurements differ by a factor of  
20 approximately 165 million.

21 Mean levels of BDE-209 in sewage sludge in the United States have varied widely, ranging from  
22 84.8 to 58,800 ng/g dry weight ([La Guardia et al., 2007](#); [Hale et al., 2001](#)). In these studies, BDE-209 was  
23 the most frequent PBDE congener detected. International studies have shown levels ranging from 68.5 to  
24 880 ng/g dry weight ([Clarke et al., 2008](#); [Wang et al., 2007](#)). A mean effluent BDE-209 concentration of  
25 1730 pg/L was reported from a sewage treatment plant in California ([North, 2004](#)). Internationally,  
26 effluent concentrations have ranged from 310 to 1170 ng/L ([Eljarrat et al., 2007](#); [de Boer et al., 2003](#)).  
27 See Appendix E, Table E-4 for additional information on these studies.

##### *Multiwalled Carbon Nanotubes*

28 No data were found on environmental concentrations of MWCNTs in aquatic environments, but  
29 as summarized in Table 3-3, two substance flow analyses have estimated PECs of CNTs in surface water  
30 ([Gottschalk et al., 2009](#); [Mueller and Nowack, 2008](#)). Mueller and Nowack ([2008](#)) estimated surface

1 water CNT PECs of  $5 \times 10^{-4}$  and  $8 \times 10^{-4}$   $\mu\text{g/L}$  for the realistic and high exposure scenarios, respectively.  
2 Gottschalk et al. (2009) estimated not only a mode PEC of  $1 \times 10^{-6}$   $\mu\text{g/L}$  for CNTs in surface water, but  
3 also an annual increase of  $4.6 \times 10^{-2}$   $\mu\text{g/kg-yr}$  to U.S. sediment.

#### 4.1.2.3. Terrestrial Systems – Soil

##### *Decabromodiphenyl Ether*

4 Mean levels of BDE-209 observed in U.S. surface soils in two studies ranged from 0.6 to  
5 15.3 ng/g dry weight [(Offenberg et al., 2006) as cited in U.S. EPA (2010b); (Yun et al., 2008)]. The range  
6 of concentrations in international studies was 0.028–2220 ng/g dry weight (Sellström et al., 2005). Both  
7 the lowest and highest levels of BDE-209 detected were from a study in Sweden. The only other  
8 international studies examined BDE-209 levels in Chinese soil; these measurements ranged from 2.38 to  
9 6319.6 ng/g dry weight (Luo et al., 2009; Zou et al., 2007). Appendix E, Table E-5 presents additional  
10 information on these studies.

##### *Multiwalled Carbon Nanotubes*

11 No data were found on environmental concentrations of MWCNTs in surface soil samples, but as  
12 summarized in Table 3-3, two substance flow analyses have estimated PECs of CNTs in soil (Gottschalk  
13 et al., 2009; Mueller and Nowack, 2008). Mueller and Nowack (2008) estimated soil CNT PECs of  
14  $1 \times 10^{-2}$  and  $2 \times 10^{-2}$   $\mu\text{g/kg}$  for the realistic and high exposure scenarios, respectively. Gottschalk et al.  
15 (2009) estimated an annual increase of  $5.6 \times 10^{-4}$   $\mu\text{g/kg-yr}$  to U.S. soil.

#### 4.1.2.4. Occupational Settings – Air

##### *Decabromodiphenyl Ether*

16 No studies were found that measured levels of BDE-209 in air in facilities where textiles  
17 containing BDE-209 are manufactured. Outdoor air at an automobile shredding facility, however, was  
18 found to have BDE-209 levels ranging from 45.5 to 1940  $\text{pg/m}^3$  (Charles et al., 2005). Given that  
19 BDE-209 is used in automobile upholstery, the textiles in the automobiles could have contributed to the  
20 observed levels. BDE-209 levels have been measured in indoor occupational settings, including  
21 e-recycling facilities, circuit-board assembly halls, and computer facilities. Reported levels in the air  
22 ranged from a median of 220  $\text{pg/m}^3$  in a circuit-board assembly hall to a high of 833,000  $\text{pg/m}^3$  in an e-  
23 recycling facility (Frederiksen et al., 2009; Charles et al., 2005). See Appendix E, Table E-2 for a  
24 summary of additional studies reporting indoor and outdoor air monitoring results.

## *Multiwalled Carbon Nanotubes*

1 No studies were found that measured MWCNT concentrations in air in facilities where textiles  
2 containing MWCNTs are manufactured. Multiple studies have collected particles and fibers in workplace  
3 air to attempt to estimate MWCNT concentrations at the emission source, in area air, and in the personal  
4 breathing zone of workers in small laboratories or research and development facilities ([Johnson et al.,  
5 2010](#); [Lee et al., 2010](#); [Methner et al., 2010](#); [Bello et al., 2008](#); [Han et al., 2008](#)), as well as in larger pilot  
6 plants and manufacturing and handling facilities ([Dahm et al., 2011](#); [Lee et al., 2010](#); [Takaya et al., 2010](#)).  
7 Some of these studies are discussed below, and Appendix E, Table E-6 presents additional information on  
8 particle, fiber, and MWCNT concentrations for the studies that reported quantitative concentration values  
9 associated with MWCNTs.

### Concentrations in MWCNT Research Laboratories

10 Han et al. ([2008](#)) measured concentrations of total particles in the area air and personal breathing  
11 zones of workers in an MWCNT research facility. Two particle sizers were used to count particles with  
12 sizes ranging from 14 to 630 nm and 0.5 to 20  $\mu\text{m}$ , respectively, and a portable aethalometer measured the  
13 mass of carbon black in the total particulate matter in the air. All fibers with aspect ratios greater than 3:1  
14 were collected on filters and analyzed using electron microscopy, and MWCNTs were distinguished from  
15 asbestos fibers using energy-dispersive spectroscopy. During the blending process, which creates a  
16 uniform size-distributed CNT powder, particulate matter concentrations in the air near the open blender  
17 ranged from 434.5  $\mu\text{g}/\text{m}^3$  without exposure controls to no detection (limit of detection not reported) with  
18 exposure controls. The maximum MWCNT number concentration ranged between 172.9 (area air sample)  
19 and 193.6 (personal air sample) fibers per  $\text{cm}^3$  air during blending without exposure controls, and  
20 between 0.018 (personal air sample) and 0.05 (area air sample) fiber per  $\text{cm}^3$  air during blending with  
21 exposure controls. During weighing and spraying, particulate matter concentrations ranged from 36.6  
22 (area air sample) to 193.0 (personal air sample)  $\mu\text{g}/\text{m}^3$  without exposure controls and from below the level  
23 of detection (area air sample; limit of detection not reported) to 30.9  $\mu\text{g}/\text{m}^3$  (personal air sample) with  
24 exposure controls. The maximum MWCNT number concentrations during weighing and spraying were  
25 below detection (limit of detection not reported) in the absence of controls, and up to 1.997 fibers per  $\text{cm}^3$   
26 air after controls ([Han et al., 2008](#)). The reason for the increase in MWCNTs following implementation of  
27 exposure controls (in this case, the control was “a simple fan”) was not discussed. The maximum  
28 MWCNT length observed was 1.5  $\mu\text{m}$ , which is smaller than the World Health Organization’s minimum  
29 length of 5  $\mu\text{m}$  for classification as a fiber ([Aschberger et al., 2010](#)).

30 Using a suite of real-time particle sizers, particle counters, and filters with electron microscopy  
31 and energy-dispersive spectroscopy analyses, Methner et al. ([2010](#)) measured and characterized



1 particulate matter in carbon-based nanomaterial research and development facilities. The highest particle  
2 number concentration for particles ranging in size from 10–1000 nm was measured when engineering  
3 controls were turned off during the opening of an MWCNT growth chamber of a pulsed laser deposition  
4 reactor. The maximum particle number concentration was not higher than 42,400 particles per cm<sup>3</sup> in the  
5 absence of engineering controls, but when the same activity was performed in a sealed system with  
6 vacuum exhaust, the particle number was reduced to 300 particles per cm<sup>3</sup> ([Methner et al., 2010](#)).

7         Johnson et al. ([2010](#)) used real-time particle sizers to count total particles per liter air for six size  
8 cuts (300, 500, 1000, 3000, 5000, and 10,000 nm) and per cubic centimeter air for the cumulative 10- to  
9 1000-nm size fraction of particles released to the air in a laboratory while two tasks were being performed  
10 with raw and functionalized MWCNTs. The first task involved weighing MWCNTs and transferring them  
11 to a beaker of stirring water, and the second task involved sonicating a previously mixed solution  
12 containing reconstituted water and 100 mg/L MWCNTs with 100 mg/L natural organic matter. Filter  
13 samples also were collected at the emission source (i.e., as close as possible to the instruments used for  
14 each task) and in area air, and samples were analyzed using electron microscopy and energy-dispersive  
15 spectroscopy. In general, particle number concentrations in the air were inversely proportional to particle  
16 size, with either zero or very few particles detected for the 5000- and 10,000-nm size cuts for both types  
17 of MWCNTs used in both tasks. The maximum background-adjusted particle number concentrations for  
18 the raw MWCNTs occurred within the 300-nm size fraction; these concentrations were  
19 123,403 particles/L air (above the upper limit of quantification) during weighing and transferring and  
20 42,796 particles/L air during sonication ([Johnson et al., 2010](#)). The particle number concentrations  
21 measured for the functionalized MWCNTs (MWCNT-OH) exhibited different trends from those for the  
22 raw MWCNTs. First, no additional 300-nm particles were detected above the background level during  
23 weighing and transferring. Second, particle counts were higher during sonication of functionalized  
24 MWCNTs than during weighing and transferring, which is opposite of the trend observed for the raw  
25 MWCNTs. Whereas the maximum background-adjusted particle number concentration was 3065  
26 particles/L air (500-nm size fraction) during weighing and transferring, the maximum concentration was  
27 144,623 particles/L air (above the limit of quantification; 300-nm size fraction) during sonication of  
28 functionalized MWCNTs. The particle number concentrations measured for the cumulative 1 to 1000-nm  
29 size range were 1576 and 2776 particle/cm<sup>3</sup> air for the raw MWCNTs and 676 and 726 particles/cm<sup>3</sup> for  
30 the functionalized MWCNTs during weighing/transferring and sonicating, respectively. Johnson et al.  
31 ([2010](#)) proposed that the cumulative measurements do not follow the same trends as the size cut  
32 measurements because of the inclusion of particles smaller than 300-nm in the cumulative particle  
33 counter.

1 Bello et al. (2008) used a real-time particle sizer and a particle counter to count total particles  
2 with sizes ranging from 5.6 to 560 nm and 10 to 1000 nm, respectively in the area air of a university  
3 research laboratory. Personal air samples also were collected on filters and analyzed using scanning  
4 electron microscopy and energy-dispersive spectroscopy. Bello et al. (2008) found that removal of  
5 MWCNTs from the reactor furnace and detachment of MWCNTs from the nanotube growth substrate  
6 during chemical vapor deposition (CVD) did not increase total airborne particle concentrations compared  
7 to background. Additionally, no MWCNTs were observed in the personal air sample of a furnace operator  
8 (Bello et al., 2008).

9 In a later study, Bello et al. (2009) measured particulate matter, respirable particulate matter, and  
10 respirable fibers in a laboratory during dry and wet machining of composite materials with and without  
11 CNTs. Particle sizers were used to detect and count all particles with sizes ranging from 5 nm to 20  $\mu\text{m}$ ,  
12 and particles and fibers in the respirable range were collected on filters near the source (i.e., 10 cm away  
13 from the machined composite) and in the breathing zone of the operator; filter samples were analyzed  
14 using electron microscopy. Although the dry-cutting process did result in statistically significant increases  
15 in airborne particles and fibers, no statistically significant differences were noted in the particle number,  
16 particle sizes, or total dust generated by dry cutting the composites with and without CNTs. Furthermore,  
17 analyses of filter samples revealed no single or bundled CNTs in the particles and fibers collected, and no  
18 CNTs were observed “sticking out” of the CNT composites (Bello et al., 2009).

### Concentrations in MWCNT Manufacturing and Packing Facilities

19 Dahm et al. (2011) used a series of filters to measure the inhalable size fractions of elemental  
20 carbon and determine CNT and carbon nanofiber “structure” counts (defined as “single CNTs to large  
21 agglomerates” viewed using electron microscopy) in the area air and personal breathing zones of six  
22 pilot-scale CNT or carbon nanofiber primary and secondary manufacturing facilities. Sampling was  
23 conducted while workers performed various tasks, including harvesting, sonicating, weighing, extruding,  
24 manually transferring, and mixing MWCNTs; spray coating a product with an MWCNT solution; milling  
25 MWCNT composites; and collecting and disposing of waste from MWCNT work areas. The elemental  
26 carbon concentrations in the personal breathing zone samples generally were higher than the area air  
27 samples. Inhalable elemental carbon concentrations in personal breathing zones ranged from 1.13  $\mu\text{g}/\text{m}^3$   
28 (sonicating, sieving, and spray coating) to 2.74  $\mu\text{g}/\text{m}^3$  (harvesting) at the primary MWCNT manufacturing  
29 facilities and from 0.8  $\mu\text{g}/\text{m}^3$  (office work outside lab space) to 7.86  $\mu\text{g}/\text{m}^3$  (extrusion, weighing, and  
30 batch mixing) at the secondary MWCNT manufacturing facilities. The CNT structure counts in the  
31 personal breathing zones ranged from 0.010 structure/ $\text{cm}^3$  (sonicating, sieving, and spray coating) to  
32 0.399 structure/ $\text{cm}^3$  (harvesting) at the primary facilities, and from none observed (weighing, sonicating,

1 milling) to 0.242 structure/cm<sup>3</sup> (extrusion, weighing, and batch mixing) at the primary and secondary  
2 MWCNT manufacturing facilities ([Dahm et al., 2011](#)).

3 Inhalable elemental carbon concentrations in area air samples from Dahm et al ([2011](#)) ranged  
4 from not detected (sonicating, sieving, and spray coating; limits of detection ranged from 0.2 to 0.5 µg  
5 elemental carbon/filter) to 4.62 µg/m<sup>3</sup> (harvesting) and from not detected (weighing, sonicating, milling,  
6 and mixing) to 1.01 µg/m<sup>3</sup> (extrusion, weighing, and batch mixing) at the primary and secondary  
7 MWCNT manufacturing facilities, respectively. The CNT structure counts ranged from none observed  
8 (production and harvesting) to 0.134 structure/cm<sup>3</sup> (harvesting at a different facility) and from none  
9 observed (weighing, milling) to 0.008 structure/cm<sup>3</sup> (extrusion, weighing, and batch mixing) in the area  
10 air samples at the primary and secondary MWCNT manufacturing facilities, respectively ([Dahm et al.,  
11 2011](#)).

12 Lee et al. ([2010](#)) collected filter samples to measure respirable dust concentrations in the area air  
13 and personal breathing zones of workers at three MWCNT manufacturing facilities and four research and  
14 development laboratories throughout a normal workday. Fibers with aspect ratios greater than 3:1 were  
15 collected on the filters and analyzed using electron microscopy, and MWCNTs were chemically identified  
16 using energy-dispersive spectroscopy. A suite of particle sizers, differential mobility analyzers, and  
17 particle counters also was used to count particles with sizes ranging from 14 to 500 nm, and a dust  
18 monitor was used to capture number concentrations of particle ranges from 0.25 to 32 µm in diameter. A  
19 portable aethalometer measured the mass of carbon black in the total particulate matter in the air. Lee et  
20 al. ([2010](#)) generally found that the highest increases in particle number concentrations compared to  
21 background were observed following the opening of the chemical vapor disposition (CVD) chamber after  
22 MWCNT synthesis. Increases in carbon black concentrations at this time were minimal, however,  
23 suggesting that most of the particles released were more likely to be metal catalysts than MWCNTs.  
24 Furthermore, the authors reported only one measurement of a detectable amount of MWCNTs on one  
25 filter from a single facility (0.00312 tube/cm<sup>3</sup>); the study authors could not determine whether the lack of  
26 MWCNT detection reflected a lack of MWCNTs in workplace air or flaws in the sampling process or  
27 analytical methods.

28 Total dust and respirable dust concentrations were measured in a study of two MWCNT packing  
29 facilities, one of which was manually operated and the other automated [([Takaya et al., 2010](#)) English  
30 translation available only for abstract]. Total dust concentrations in the area air of both MWCNT packing  
31 facilities were approximately 240 µg/m<sup>3</sup>. Both total and respirable dust concentrations, however, were  
32 substantially higher in the manual packing facility (total: 2390 µg/m<sup>3</sup>; respirable: 390 µg/m<sup>3</sup>) than in the  
33 automated packing facility (total: 290 µg/m<sup>3</sup>; respirable: 80 µg/m<sup>3</sup>).

#### 4.1.2.5. Residential Settings – Air and Dust

##### *Decabromodiphenyl Ether*

1 Two U.S.-based studies evaluated residential indoor air levels of BDE-209. Levels of BDE-209 in  
2 the air ranged from below the limit of detection (limit of detection not reported) to 94 pg/m<sup>3</sup> for the living  
3 room and 173.6 pg/m<sup>3</sup> for personal air (i.e., breathing zone) ([Allen et al., 2007](#)). A study in Sweden  
4 detected BDE-209 at 257 pg/m<sup>3</sup> in the living room air in one of five household samples, while all other  
5 samples in the study were below the limit of detection (173 pg/m<sup>3</sup>) ([Petersen and Henry, 2012](#)). Appendix  
6 E, Table E-2 provides a summary of additional indoor air studies.

7 Levels of BDE-209 in household dust are orders of magnitude higher than in other matrices by  
8 weight, and BDE-209 is the main PBDE contaminant in household dust ([Daso et al., 2010](#)). BDE-209 has  
9 been found in household dust in U.S. studies at median levels ranging from 665 to 2000 ng/g dry weight  
10 ([Frederiksen et al., 2009](#)). In international studies, median levels of BDE-209 in house dust ranged from  
11 60 ng/g dry weight (Germany) to 7100 ng/g dry weight (United Kingdom) ([Frederiksen et al., 2009](#)). See  
12 Appendix E, Table E-1 for additional studies that report observed levels of BDE-209 in household dust.

##### *Multiwalled Carbon Nanotubes*

13 No data were found on concentrations of MWCNTs in household air or dust.

#### 4.1.2.6. Nonresidential Settings – Air and Dust

##### *Decabromodiphenyl Ether*

14 BDE-209 is one of the main PBDE contaminants in office dust ([Watkins et al., 2011](#); [Batterman](#)  
15 [et al., 2010](#); [Harrad et al., 2008](#)). One study of U.S. office buildings found a mean concentration of  
16 6930 ng/g BDE-209 in office dust, but half of the sample sites had concentrations of 1 ng/g or  
17 concentrations below the limit of detection (limit of detection not reported) ([Batterman et al., 2010](#)).  
18 Another study of dust in U.S. offices reported an average BDE-209 concentration of 4204 ng/g  
19 (geometric mean) with a range of concentrations between 912 and 106,204 ng/g among sample sites  
20 ([Watkins et al., 2011](#)). In a study conducted in the United Kingdom, Harrad et al. ([2008](#)) reported a  
21 median concentration of 6200 ng/g BDE-209 in office dust. See Appendix E, Table E-1 for study  
22 summaries that report observed levels of BDE-209 in office dust.

23 One study conducted in U.S. office buildings examined BDE-209 concentrations in airborne  
24 particulate matter and vapor; concentrations were all below the limit of detection, which was not reported  
25 ([Batterman et al., 2010](#)). Appendix E, Table E-2 provides a summary of this study.

##### *Multiwalled Carbon Nanotubes*

26 No data were found on concentrations of MWCNTs in nonresidential air or dust.

#### 4.1.2.7. Transportation, Including Automobiles and Airplanes— Air and Dust

##### *Decabromodiphenyl Ether*

1 As discussed in Section 4.2.2.3 below, flame-retardant upholstery can be used in seats and other  
2 textiles in transportation vehicles such as automobiles and airplanes. No studies were identified that  
3 reported levels of BDE-209 in automobile or aircraft air, but several studies have investigated levels of  
4 BDE-209 in automobile or aircraft dust ([Lagalante et al., 2009](#); [Christiansson et al., 2008](#); [Harrad et al.,  
5 2008](#)). Less time is generally spent in automobiles than indoors, but levels of BDE-209 in automobile  
6 dust are about 20 times higher than in household dust ([Lagalante et al., 2009](#)). In one study, the median  
7 level of BDE-209 in passenger cars was estimated as 8.12 µg/g dust (82% of the total PBDE  
8 concentration in dust); personal automobiles generally had lower levels of decaBDE in dust than dealer  
9 vehicles ([Lagalante et al., 2009](#)). Other studies have reported median BDE-209 levels in dust from cars as  
10 high as 100 µg/g, with a highest individual sample of 2600 µg/g ([Harrad et al., 2008](#)) (see Appendix E,  
11 Table E-1 for more information). Levels of PBDE congeners in the vehicles were not statistically  
12 significantly different by vehicle manufacturer, model year, country of manufacture, seat type, or the  
13 presence of heated seats ([Lagalante et al., 2009](#)).

14 A study evaluating dust in aircraft during 20 international flights observed BDE-209  
15 concentrations ranging from below the limit of detection (value not reported) to 189,882 ng/g, with a  
16 median level of 17,262 ng/g ([Christiansson et al., 2008](#)). No other studies were found that evaluated levels  
17 of BDE-209 in air or dust of aircraft.

##### *Multiwalled Carbon Nanotubes*

18 No data were found on concentrations of MWCNTs in air or dust in vehicles or aircraft.

## 4.2. Human Exposure and Kinetics Leading to Dose

19 Limited data were found that measured or quantified human exposure to BDE-209 or MWCNTs.  
20 Data on concentrations of BDE-209 or MWCNTs measured in media such as air, soil, or dust in various  
21 settings (described in Section 4.1.2), however, can be used in conjunction with activity pattern and other  
22 exposure factor data [such as those described in *The Exposure Factors Handbook* ([U.S. EPA, 2011](#)) to  
23 inform estimates of potential exposure through the various exposure pathways and scenario characteristics  
24 described in this section.

25 The types of human exposure scenarios described here can be divided into four broad groups:  
26 occupational, consumer, general public, and highly exposed populations. For the purposes of this case  
27 study, occupational exposures include occupational exposures during synthesis, processing, or handling

1 of decaBDE and MWCNTs; manufacturing of flame retardants, application of the flame retardants to  
2 textiles, or textile finishing and upholstering; storage of the decaBDE, MWCNTs, flame-retardant  
3 formulations, treated textiles, or upholstered products; disposal of decaBDE, MWCNTs, flame-retardant  
4 formulations, treated textiles, or upholstered products; and repurposing or recycling of treated upholstery  
5 textiles and end-user products (e.g., furniture). Consumer exposure scenarios include the intended or  
6 unavoidable use of treated upholstery textiles in residential and nonresidential spaces, including on  
7 household or institutional/office furniture, in vehicles, and in aircraft; unintended uses of treated  
8 upholstery textiles or end-use products such as reuse or repurposing of furniture for something other than  
9 its original intended use; or recycling of upholstery textiles for new uses. General public exposure  
10 includes primary exposure to members of the community near manufacturing, disposal, or recycling  
11 facilities and secondary exposure to the general public through environmental routes such as air, soil, or  
12 water. Highly exposed populations refers to exposure scenarios that are expected to occur via similar  
13 pathways as outlined for consumers and the general public, but where exposure levels are expected to be  
14 higher due to key differences in population characteristics such as those described in *The Child-Specific*  
15 *Exposure Factors Handbook* ([U.S. EPA, 2008a](#)).

## 4.2.1. Occupational Exposure Pathway Scenarios

16 Limited data were found to determine the extent of occupational exposures to BDE-209 and  
17 MWCNTs during the material synthesis, processing, and handling phases or to the flame-retardant  
18 product during formulation, application, storage, and disposal phases. See Section 4.1.2.4 for BDE-209  
19 and MWCNT concentrations measured in occupational settings, which could be applied with the exposure  
20 pathways and scenario characteristics described below to estimate potential exposures through scenario  
21 evaluation.

### 4.2.1.1. Synthesis, Processing, and Handling

#### *Decabromodiphenyl Ether*

22 As discussed in Section 2.2.2, BDE-209 synthesis involves conversion of phenol to diphenyl  
23 ether, followed by bromination in the presence of a catalyst, typically aluminum bromide or iron ([WHO,](#)  
24 [1994](#)). The synthesis and drying processes are carried out in enclosed vessels, so under normal  
25 circumstances exposure is unlikely to occur during this process. After synthesis, decaBDE powders are  
26 removed from the chamber and bagged. As discussed in Section 2.2.2.2, the low vapor pressure of  
27 decaBDE results in negligible exposures to decaBDE as a vapor during synthesis or bagging, but  
28 exposures to decaBDE adsorbed to dust could occur ([EU, 2002](#)). DecaBDE adsorbed to dust is expected

1 to settle quickly to surfaces in the occupational environment; no data were found to determine the extent  
2 of exposures to decaBDE and decaBDE adsorbed to dust during the synthesis, processing, and handling  
3 phases. The pathways through which workers might be exposed to decaBDE and decaBDE adsorbed to  
4 dust during general synthesis, processing, and handling scenarios are described below:

- 5 • **Inhalation.** Bagging and other handling of decaBDE powders might be the activities most  
6 likely to lead to exposures. Aerosol particles in the inhalable size range could be inhaled by  
7 workers if respirators are not worn.
- 8 • **Oral.** Secondary oral exposures might occur if inhaled decaBDE or decaBDE that deposits  
9 on the skin, food, or food-contact surfaces are subsequently ingested.
- 10 • **Dermal.** DecaBDE might settle on the skin if proper personal protective equipment is not  
11 worn.

### *Multiwalled Carbon Nanotubes*

12 As discussed in Section 2.2.2, synthesis of MWCNTs is achieved by one of three processes:  
13 CVD, arc discharge, and laser ablation. Although many facilities use engineering controls (e.g., fume  
14 hoods, closed production systems, high-efficiency particulate air-filtered vacuums) and require workers to  
15 wear personal protective equipment (e.g., gloves, respirators, paper face masks, safety glasses, lab coats,  
16 Tyvek clean suits) to minimize exposure to MWCNTs ([Dahm et al., 2011](#)), not all facilities comply with  
17 the *General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories*, which  
18 outlines the recommendations by NIOSH ([2012](#)). Many facilities do not employ the same level of  
19 protective measures, and in many cases, the filtration technologies and personal protective equipment are  
20 not appropriate for or sufficiently protective against exposures to nanomaterials ([Dahm et al., 2011](#)).  
21 Therefore, exposure during handling and other operations might still occur, for example, when a reaction  
22 chamber is opened to recover MWCNTs; while extracting, weighing, or manually transporting materials;  
23 or during maintenance and cleaning of equipment ([Dahm et al., 2011](#); [Fleury et al., 2011](#); [Aschberger et  
24 al., 2010](#)). Workers performing each operation are expected to be exposed to peak concentrations of  
25 MWCNTs for only a short time while carrying out MWCNT handling tasks, but multiple production  
26 cycles might occur within a day, resulting in several opportunities for short-duration, acute exposures  
27 throughout the workday ([Dahm et al., 2011](#); [Lee et al., 2010](#)). Most occupational exposure studies to date  
28 have examined these short-duration, task-specific exposures instead of full-shift exposures, and task-  
29 specific exposures have been evaluated only for a limited set of handling operations (see Section 4.1.2.4).  
30 In general, MWCNTs observed in air and settled on surfaces in occupational environments during  
31 synthesis, processing, and handling are in bundled form, but exposure to single MWCNTs is possible  
32 ([NIOSH, 2010](#)). The pathways through which workers might be exposed to MWCNTs and MWCNT  
33 bundles during synthesis, processing, and handling scenarios are described below:

- 1 • **Inhalation.** Handling dry powder might be the activity most likely to lead to inhalation  
2 exposures during production. Dahm et al. (2011) and Johnson et al. (2010) observed that  
3 workers handling dry powder often turned off vents, hoods, fans and other engineering  
4 controls to avoid disturbing and dispersing MWCNTs. Handling processes such as weighing,  
5 blending, transfer to containers, or maintenance also could result in inhalation exposure  
6 ([Dahm et al., 2011](#); [Fleury et al., 2011](#); [Aschberger et al., 2010](#)).
- 7 • **Oral.** Secondary oral exposures might occur if inhaled MWCNTs or MWCNTs that deposit  
8 on the skin, food, or food-contact surfaces are subsequently ingested.
- 9 • **Dermal.** Particles generated during manufacturing and processing of CNTs can land on the  
10 skin of workers if proper personal protective equipment is not worn ([Lam et al., 2006](#)). A  
11 study evaluating occupational exposure to CNTs during synthesis, processing, and handling  
12 estimated (using adsorbed metals as proxy) that on average, 0.2 to 6 mg of single-walled  
13 carbon nanotubes are deposited on the gloves covering each hand of workers during routine  
14 operations. Although the cotton gloves worn by workers could have adsorbed more CNTs  
15 than bare skin or latex, the study illustrates that dermal exposure to CNTs could occur in  
16 laboratory settings ([Maynard et al., 2004](#)).

#### 4.2.1.2. Formulation of Flame Retardant, Application to Textiles, Upholstering

##### *Decabromodiphenyl Ether*

17 As discussed in Section 2.2.4, decaBDE powder is mixed with other ingredients to create a paint-  
18 like flame-retardant product, after which the flame retardant is back-coated onto a textile intended for use  
19 as upholstery. No data were found on the extent of occupational exposures to decaBDE during  
20 formulation of the flame retardant, application of the flame retardant to textiles, or textile finishing and  
21 upholstery. As with exposures during the previous life-cycle stages, exposures to decaBDE vapors  
22 during the product manufacturing stages are expected to be low due to the low vapor pressure of this  
23 congener; however, exposures to decaBDE adsorbed to dust or attached to the product matrix could  
24 occur.

25 The first step in the product manufacturing chain is compounding (i.e., mixing) decaBDE powder  
26 with antimony trioxide in water, which typically occurs under local exhaust ventilation ([EU, 2002](#)). The  
27 mixture is then added, through a closed system, to the emulsion polymers in a sealed mixing vessel. Use  
28 of ventilation controls and a closed system in generating the flame-retardant coating is expected to greatly  
29 reduce the chance of occupational exposures during these stages under normal circumstances. Exposures  
30 might still occur to decaBDE adsorbed to dust, however, when the decaBDE powder is emptied into the  
31 mixer. Exposures also could occur during transfer of materials; equipment cleaning, maintenance, and  
32 repair; and as the result of accidental spills or releases ([EU, 2002](#)).

33 The potential for occupational exposure also exists when the flame-retardant polymer mixture is  
34 applied to the textile as a resin back-coating. DecaBDE flame retardant is typically not added manually,  
35 and exposures are expected to be greatest during handling and cleaning of coating equipment ([EU, 2002](#)),



1 but accidental spills and releases also might occur. Occupational exposures to decaBDE adsorbed to dust,  
2 in the polymer matrix, or attached to textile fibers or scraps might occur as a result of cutting, sewing, and  
3 otherwise abrading the decaBDE-treated upholstery textile product during textile finishing and  
4 application to a consumer end-use product.

5 The pathways through which workers might be exposed to decaBDE during general formulation  
6 of the flame retardant, application of the flame retardant to the textile, and textile finishing and  
7 upholstering scenarios are expected to be comparable to those described in Section 4.2.1.1 on exposures  
8 during synthesis, processing, and handling. Additional considerations pertaining to exposures to decaBDE  
9 in combination with polymer ingredients, textile fibers or scraps, or other product constituents during  
10 these scenarios are described below:

- 11 • **Inhalation.** Abrading textiles during tailoring and upholstering could lead to inhalation of  
12 decaBDE, other product ingredients, and textile dusts.
- 13 • **Oral.** Secondary oral exposures might occur if inhaled decaBDE and associated product  
14 constituents or decaBDE particles that deposit on the skin, food, or food-contact surfaces are  
15 subsequently ingested.
- 16 • **Dermal.** DecaBDE and associated product constituents generated during product  
17 manufacturing can land on the skin of workers if proper personal protective equipment is not  
18 worn. The liquid flame-retardant coating also can be spilled directly onto the skin.

### *Multiwalled Carbon Nanotubes*

19 No data were found on occupational exposures to MWCNTs during formulation of the flame  
20 retardant, application of the flame retardant to textiles, or textile finishing and upholstering. Furthermore,  
21 information on the processes for preparing MWCNT flame retardants and for applying them to textiles  
22 are lacking. To confer the desired flame-retardant properties of MWCNTs to the textile product, however,  
23 MWCNTs must be well dispersed in a polymer medium. To promote dispersion, MWCNTs are  
24 sometimes ground or pulverized, which could lead to the release of single MWCNTs or bundles.  
25 MWCNTs also might be mixed or sonicated, which could generate airborne water droplets, or mists,  
26 containing nanomaterials that then can be inhaled or deposited on surfaces ([Fleury et al., 2011](#);  
27 [Aschberger et al., 2010](#); [Johnson et al., 2010](#)).

28 As described in Section 2.2.4.1, one industry representative reported that textiles can be  
29 immersed or spray coated with MWCNT flame retardants. The immersion method could result in worker  
30 exposures similar to those for decaBDE, and exposures are expected to be highest during equipment  
31 handling and cleaning. Should MWCNT flame retardants be sprayed onto textiles, however, MWCNTs in  
32 the wet polymer matrix might be released as mists, which can occur even with nonvolatile liquids ([U.S.](#)  
33 [EPA, 2005a](#)).

1 Exposures to MWCNTs also might occur when the treated upholstery textile is machined, drilled  
2 ([Aschberger et al., 2010](#)), or otherwise abraded during the textile finishing or upholstering processes. Wet  
3 and dry machining of advanced nanomaterial composite systems were evaluated for generation of  
4 respirable CNTs. Wet-cutting methods were not found to produce exposures significantly different from  
5 background, while dry-cutting methods created statistically significant quantities of nanoscale and fine  
6 particles and fibers composed of the composite material (i.e., no single or bundled CNTs were observed  
7 in the samples) ([Bello et al., 2009](#)).

8 Equipment cleaning can be a key contributor to work exposure during product manufacture,  
9 application, and upholstering. One study identified equipment cleaning as one of the most important  
10 occupational exposure scenarios because it often requires workers to be in direct contact with molten  
11 polymers and residues containing CNTs ([Fleury et al., 2011](#)).

12 The pathways through which workers might be exposed to single MWCNTs or MWCNT bundles  
13 during general formulation of the flame retardant, application of the flame retardant to the textile, and  
14 textile finishing and upholstering scenarios are expected to be comparable to those described in Section  
15 4.2.1.1 on exposures during synthesis, processing, and handling. Additional considerations pertaining to  
16 exposures to MWCNTs in combination with polymer ingredients, textile fibers or scraps, or other product  
17 constituents during these scenarios are described below:

- 18 • **Inhalation.** Spray coating textiles with MWCNT flame retardants could result in inhalation  
19 exposures to mists containing MWCNT embedded in a liquid polymer mixture. Dry-cutting  
20 MWCNT-treated textiles during tailoring and upholstering could lead to inhalation of fine  
21 and ultrafine particles comprising MWCNT-polymer composites and textile dusts.
- 22 • **Oral.** Secondary oral exposures might occur if inhaled MWCNTs in mists and particulate  
23 form or the MWCNT mists or particles that deposit on the skin, food, or food-contact  
24 surfaces are subsequently ingested
- 25 • **Dermal.** MWCNTs in mists and particulate form generated during product manufacturing  
26 can land on the skin of workers if proper personal protective equipment is not worn  
27 ([Aschberger et al., 2010](#); [Johnson et al., 2010](#); [Lam et al., 2006](#)). The liquid flame-retardant  
28 coating also can be spilled directly onto the skin.

#### 4.2.1.3. Storage of DecaBDE, MWCNTs, Flame-Retardant Formulations, Treated Textiles, and Upholstered Products

29 As described in Section 2.3, decaBDE, MWCNTs, and the flame-retardant formulations to which  
30 they are added are expected to be stored in sealed receptacles that would limit potential for worker  
31 exposures to these materials during storage. Defective packaging and accidental spills or releases,  
32 however, could lead to rare exposures during storage operations.

1           Although no information was identified regarding procedures for storing treated upholstery  
2 textiles, these products are likely packaged to protect them from exposure to elements like water and light  
3 that could damage their aesthetics. Such packaging also is expected to limit exposures of workers to the  
4 flame-retardant coatings. Once the textiles have been applied as upholstery to end-use products, these  
5 products also are expected to be enclosed in protective packaging. Some surfaces of bulkier products  
6 (e.g., furniture), however, might remain uncovered, which could lead to worker exposures during storage  
7 operations, or exposures might occur during application and removal of packaging materials to and from  
8 the product. Dust also can accumulate in storage facilities that frequently store textiles and textile  
9 products, and decaBDE or MWCNTs that escape from the product matrix could sorb to dust particles.  
10 Ventilation technologies and other contamination-prevention strategies like those used by manufacturing  
11 facilities are not expected to be in place in storage facilities. Dust that has settled on surfaces in storage  
12 facilities can be disturbed by worker operations, resuspended, and transported to other locations.

13           Although neither decaBDE nor MWCNTs are expected to be highly volatile, off gassing of more  
14 volatile components of the treated textiles might occur during storage of treated textiles or upholstered  
15 products. Furthermore, due to the additive nature of decaBDE and MWCNT flame retardants, covalent  
16 bonding between the flame retardant and the textile does not occur, suggesting that flame-retardant  
17 coatings that are loosely attached to the textile surface might slough off during storage or handling.  
18 However, because decaBDE and MWCNT flame retardants are generally added to the back of the textile,  
19 the likelihood of this detachment seems low.

#### *Decabromodiphenyl Ether*

20           No data were found on occupational exposures to decaBDE during storage throughout the  
21 product life cycle of flame-retardant upholstery textile coating. A study examining residential exposures  
22 to a range of PBDEs, however, did identify the age of furniture as one of the drivers of exposure, with  
23 higher BDE-209 body burdens in children aged 2–5 years correlating with newer furniture (e.g., couches,  
24 mattresses) ([Rose et al., 2010](#)). Whether furniture is currently treated more often with decaBDE flame  
25 retardants than previously or whether the age of the furniture influences the rate of decaBDE release (with  
26 greater amounts released from newer furniture), however, is unclear, which limits the applicability of this  
27 finding to the refinement of realistic exposure scenarios.

28           The pathways through which workers might be exposed to decaBDE alone or decaBDE adsorbed  
29 to dust during storage of decaBDE and decaBDE flame-retardant formulations are expected to be  
30 comparable to those described in Sections 4.2.1.1 and 4.2.1.2 on exposures during synthesis, processing,  
31 and handling and during formulation of the flame retardant, application to textiles, and upholstering.  
32 Additional considerations pertaining to exposures to decaBDE alone or in combination with polymer

1 ingredients, textile fibers or scraps, or other product constituents during general treated textile of  
2 upholstered product storage scenarios are described below:

- 3 • **Inhalation.** Workers could inhale volatile components of the flame-retardant coating or  
4 decaBDE adsorbed to dust in storage facilities, particularly facilities that are not well  
5 ventilated. Furthermore, decaBDE adsorbed to dust could be resuspended in the air by worker  
6 activities, and subsequently inhaled. PBDE exposures have not been measured at textile  
7 storage facilities, but they have been measured at electronic waste storage facilities. The  
8 median estimated inhalation exposure to BDE-99 (the highest measured PBDE in air) in male  
9 workers was 0.0011 ng/kg body weight (bw)/day ([Muenhor et al., 2010](#)). Although BDE-209  
10 exposures are likely to differ due to lower volatility and greater propensity to adsorb to  
11 particles, debromination of BDE-209 could result in worker exposures to lower brominated  
12 congeners.
- 13 • **Oral.** Higher levels of dust in textile storage facilities could lead to increased transport of  
14 decaBDE adsorbed to dust. This could result in oral exposures to decaBDE in dusts  
15 transported to break rooms, homes (via clothes), and other locations where decaBDE  
16 adsorbed to dust can be unintentionally ingested while eating or due to hand-to-mouth  
17 activity. In electronic waste storage facilities, the median exposure to BDE-209 via dust  
18 ingestion was 2.89 ng/kg-bw/day for average ingestion scenarios and 7.2 ng/kg-bw/day for  
19 high-end ingestion scenarios ([Muenhor et al., 2010](#)).
- 20 • **Dermal.** DecaBDE adsorbed to dust could be resuspended by worker activities and deposit  
21 on the skin of workers if proper personal protective equipment is not worn.

#### *Multiwalled Carbon Nanotubes*

22 No data were found on occupational exposures to MWCNTs during storage throughout the  
23 product life cycle of flame-retardant upholstery textile coating. The pathways through which workers  
24 might be exposed to MWCNTs alone or MWCNTs in combination with polymer ingredients, textile  
25 fibers or scraps, dusts, or other product constituents during storage of MWCNTs and MWCNT flame-  
26 retardant formulations are expected to be comparable to those described in Sections 4.2.1.1 and 4.2.1.2  
27 exposures during synthesis, processing, and handling and during formulation of the flame retardant,  
28 application to textiles, and upholstering. The pathways through which workers might be exposed to  
29 MWCNT bundles or MWCNTs adsorbed to dust during storage of treated textiles and upholstered  
30 products are not expected to differ from those described above for decaBDE (with the exception of  
31 debromination, which is not applicable to MWCNTs).

#### **4.2.1.4. Disposal and Recycling of decaBDE, MWCNTs, Flame-Retardant Formulations, Treated Textiles, and Upholstered Products**

32 As described in Section 2.5, large-scale disposal, recycling, and reuse of decaBDE, MWCNTs,  
33 and the flame-retardant formulations to which they are added are unlikely, but containers used to store

1 these products might enter the waste stream, and workers at disposal and recycling facilities could be  
2 exposed to product residues remaining in these containers.

3 Disposal and recycling of treated textiles and upholstered products, however, is prevalent. Mixing  
4 and compacting of waste for land-filling; cleaning, shredding, blending, melting, and spinning scrap  
5 textiles for recycling; and incomplete incineration of treated upholstery textiles all could result in  
6 exposure of workers ([Chaudhry et al., 2009](#)) to decaBDE and MWCNTs, primarily in combination with  
7 other product constituents and dusts.

### *Decabromodiphenyl Ether*

8 No data were found on the extent of occupational exposures to decaBDE during disposal,  
9 recycling, and reuse throughout the decaBDE flame-retardant upholstery textile coating product life cycle.  
10 As discussed in Section 4.1.2.4, BDE-209 was detected in the air outside of an automobile shredding  
11 facility ([Charles et al., 2005](#)), which suggests that exposure to BDE-209 during end-of-life operations can  
12 occur.

13 The pathways through which workers might be exposed to decaBDE during general disposal and  
14 recycling of decaBDE powder and flame-retardant formulations are expected to be comparable to those  
15 described in Section 4.2.1.1 (exposures during synthesis, processing, and handling), and worker exposure  
16 pathways for decaBDE in combination with polymer ingredients, textile fibers or scraps, or other product  
17 constituents during disposal and recycling treated textiles and upholstered product are expected to be  
18 similar to those described in Sections 4.2.1.2 (exposures during formulation of the flame retardant,  
19 application to textiles, and upholstering) and 4.2.1.3 (exposure during storage and distribution) for these  
20 products. Additional considerations pertaining to exposures to decaBDE alone or in combination with  
21 polymer ingredients, textile fibers or scraps, or other product constituents during treated textile or  
22 upholstered product disposal and recycling scenarios are described below:

- 23 • **Inhalation.** Workers operating machines that abrade or destroy textile materials, those  
24 handling these products, and other workers in the vicinity of operations that agitate or abrade  
25 textile materials can inhale decaBDE adsorbed to dust and other product constituents, as  
26 observed by Sjodin et al. ([2001](#)) at an e-waste recycling plant where electronics are stored,  
27 dismantled, and shredded. Workers at incineration facilities also might inhale small particles  
28 comprising decaBDE and other substances in the incinerator as well as polybrominated  
29 dibenzofurans (PBDFs) and polybrominated dibenzo-p-dioxins (PBDDs) (see Section  
30 2.5.2.2) if treated textiles and upholstered products are not incinerated at sufficiently high  
31 temperatures.
- 32 • **Oral.** No additional considerations.
- 33 • **Dermal.** Workers at disposal and recycling facilities might come into physical contact with  
34 the decaBDE flame-retardant coating on an upholstery textile during the process of moving or  
35 handling products. DecaBDE could migrate directly to skin of workers if proper personal  
36 protective equipment is not worn.

### *Multiwalled Carbon Nanotubes*

1 No data were found on occupational exposures to MWCNTs during disposal and recycling  
2 throughout the product life cycle of flame-retardant upholstery textile coating. The pathways through  
3 which workers might be exposed to MWCNTs during general disposal and recycling of MWCNTs and  
4 flame-retardant formulations are expected to be comparable to those described in Section 4.2.1.1  
5 (exposures during synthesis, processing, and handling); worker exposure pathways for MWCNTs in  
6 combination with polymer ingredients, textile fibers or scraps, or other product constituents during  
7 disposal and recycling of treated textiles and upholstered products are expected to be similar to those  
8 described in Sections 4.2.1.2 (exposures during formulation of the flame retardant, application to textiles,  
9 and upholstering) and 4.2.1.3 (exposure during storage and distribution) for these products and for  
10 decaBDE (with the exception of inhalation exposures to PBDFs and PBDDs, which are not expected to be  
11 combustion by-products of MWCNTs).

### **4.2.2. Consumer Exposure Pathway Scenarios**

12 No studies were found that evaluated the potential for consumer exposure to MWCNTs from any  
13 consumer product. As a result, probable consumer exposure pathways and scenario characteristics for  
14 exposure to free MWCNTs, bundled MWCNTs, and MWCNTs in combination with the polymer matrix,  
15 textile fibers or scraps, or other product constituents cannot be differentiated at this time. As discussed in  
16 Chapter 2, different MWCNT flame-retardant production processes are expected to result in differences in  
17 release rates and release forms, which in turn will affect the magnitude of exposure during consumer use  
18 and the form of the material to which consumers are exposed ([Motzkus et al., 2012](#)) Consumer exposure  
19 scenarios that can be envisioned for decaBDE can be similarly envisioned for MWCNTs. Based on the  
20 physicochemical properties of MWCNTs, that MWCNTs and associated substances released from  
21 consumer products will be present in the particulate phase, similar to BDE-209, is reasonable. Although  
22 some differences in the nature and extent of exposures to BDE-209 and MWCNTs are presumed to exist,  
23 a lack of data on this topic necessitates the assumption of similar pathways and scenario characteristics  
24 for exposure in the discussion below. See Sections 4.1.2.5, 4.1.2.6, and 4.1.2.7 for data on concentrations  
25 of BDE-209 measured in residential, nonresidential, and general public settings, which could be applied  
26 with the exposure pathways and scenario characteristics described below to estimate potential exposures  
27 to BDE-209 through a scenario evaluation approach.

#### 4.2.2.1. Intended Use – Upholstered Products in Residential Spaces

1 As discussed in Section 4.1.2.5, PBDE concentrations in house dust tend to be higher than in  
2 other matrices, and BDE-209 is the dominant congener in house dust. Although flame-retardant  
3 upholstery textiles typically are used in nonresidential settings (see Section 4.2.2.2), some residential  
4 upholstered products, particularly mattresses, are known to contain decaBDE, and other upholstered  
5 furniture products, like couches, sometimes might be treated with decaBDE ([Rose et al., 2010](#)). One study  
6 has shown that body burdens of BDE-209 in children are positively associated with presence of new  
7 furniture, but are not associated with presence or use of electronics that often contain decaBDE ([Rose et  
8 al., 2010](#)). This finding suggests that decaBDE use in residential upholstery does contribute to overall  
9 decaBDE exposures related to the use of decaBDE in flame-retardant upholstery textiles. Higher body  
10 burdens of BDE-209 also were associated with smaller living spaces, and higher concentrations of  
11 decaBDE have been measured in the main living area of the house than in the bedroom ([Allen et al.,  
12 2008](#)), indicating that variations in decaBDE exposures can be expected due to variations in housing  
13 characteristics and human behavior patterns (i.e., time spent by individuals in different rooms or outside  
14 the house). Furthermore, decaBDE released from products is suspected to debrominate to some degree to  
15 lower brominated congeners in residential settings ([Allen et al., 2008](#)), and will therefore lead to  
16 exposures to PBDEs other than decaBDE.

17 As introduced in Section 2.4, upholstered products are expected to be used for many years, and  
18 contact with the textile might be frequent and prolonged, which could introduce substantial wear and tear  
19 to the textile product. In addition, upholstery in residential spaces might frequently be exposed to cleaning  
20 products, sweat, food, and other substances that could affect the properties of the textile and the flame-  
21 retardant coating.

22 The pathways through which consumers might be exposed in residential settings to decaBDE and  
23 MWCNTs during general consumer use scenarios for end products upholstered with decaBDE or  
24 MWCNT flame-retardant coatings are described below:

##### *Decabromodiphenyl Ether/Multiwalled Carbon Nanotubes*

- 25 • **Inhalation.** Chronic inhalation of particles of decaBDE and MWCNTs in combination with  
26 other product constituents and dust could occur following release from upholstered products  
27 over time (due to wear and tear from anticipated use, aging of materials, abrasion, UV light,  
28 water, cleaning chemicals, among other factors; see Section 2.4.2). Particulate decaBDE and  
29 MWCNTs could settle onto surfaces, where they might be disturbed and re-entrained, after  
30 which they could be inhaled by residents. Inhalation is not expected to be a primary route of  
31 exposure for decaBDE ([Johnson-Restrepo and Kannan, 2009](#); [Allen et al., 2008](#)), however,  
32 because the contribution of inhaled dust particles is expected to be minimal due to a lack of  
33 correlation between concentrations of decaBDE in dust and in air ([Allen et al., 2008](#)); see  
34 below. Whether inhalation is a primary route of consumer exposure for MWCNTs,  
35 particularly when embedded in a polymer matrix, is unknown.

- 1 • **Oral.** DecaBDE and MWCNTs in combination with other product constituents and dust  
2 could be ingested after settling on food and food-contact surfaces or following hand-to-mouth  
3 activity. Ingestion of household dusts is hypothesized to be a major exposure pathway for  
4 PBDEs ([Allen et al., 2008](#)). Johnson-Restrepo ([2009](#)) reported that most PBDE intake in  
5 toddlers, children, teenagers, and adults was attributed to the oral route of exposure via  
6 ingestion of household dust (56–77% attributed to combined oral and dermal exposure).  
7 Whether ingestion is a primary route of consumer exposure for MWCNTs, particularly when  
8 embedded in a polymer matrix, is unknown. Preliminary, unpublished studies presented at a  
9 public meeting indicate, however, that MWCNTs could be released from flame-retardant  
10 barrier fabrics and polyurethane foams in very small amounts during normal wear and tear  
11 ([Uddin and Nyden, 2011b](#)); these MWCNTs could contact skin directly during use.
- 12 • **Dermal.** Dermal exposure to decaBDE and MWCNTs in combination with other product  
13 constituents and dust might occur while touching the textile surface (particularly if the  
14 portion of the textile that has been treated with the flame-retardant coating is exposed) or  
15 touching surfaces upon which particles have settled ([Frederiksen et al., 2009](#)). Lorber ([2008](#))  
16 estimated that dermal exposure to PBDE compounds in household dust could be a significant  
17 contributor (estimated at 16%) to the body burden of PBDEs in adults. The estimated  
18 contribution of BDE-209 to body burden from dermal contact exposure was 25.2 ng per day  
19 of a total 85.9 ng total PBDEs per day from that exposure route ([Lorber, 2008](#)). Johnson-  
20 Restrepo ([2009](#)) similarly reported that the dermal route was a primary route of exposure for  
21 PBDEs (second to the oral route of exposure for contribution of human intake). Whether  
22 dermal uptake is a primary route of consumer exposure for MWCNTs, particularly when  
23 embedded in a polymer matrix, is unknown. Preliminary, unpublished studies indicate,  
24 however, that MWCNTs could be released from flame-retardant barrier fabrics and  
25 polyurethane foams in very small amounts during normal wear and tear; these MWCNTs  
26 could contact skin directly during use ([Uddin and Nyden, 2011b](#)).

#### 4.2.2.2. Intended Use – Upholstered Products in Nonresidential Spaces

27 Due to regulations requiring that upholstery textiles used in nonresidential settings pass flame-  
28 retardancy tests (see Table 1-3), many upholstery textiles in public, commercial, and institutional settings  
29 are treated with decaBDE. The characteristics of the different settings in which these products are used  
30 can vary considerably. For example, flame-retardant upholstery textiles might be used in seating for  
31 airports and other transportation hubs and in waiting rooms, office buildings, penal institutions, and other  
32 nonresidential spaces that can range from very small to very large and where consumers might spend  
33 varying amounts of time. Some scenarios for nonresidential exposures are not likely to differ from those  
34 expected from residential exposures, but a few key differences do exist. For example:

- 35 • Exposures to flame-retardant upholstery coatings in public spaces might be unavoidable.  
36 While consumers have some control over which products they bring into their home,  
37 consumers have no control over the products they encounter in public spaces.
- 38 • Some nonresidential exposures might occur over long periods of time and for extended  
39 intervals (e.g., sitting in the same office chair every day over the course of several work  
40 years), while some might occur infrequently and for short periods of time (e.g., sitting in  
41 seating at the airport waiting for a flight).



- Products in public spaces might experience higher activity levels, more frequent cleaning, and less care to the textile surface, all of which could damage or weaken the textile matrix and influence releases and exposures.

With the exception of these potential differences in exposure settings and activity patterns, the pathways and scenarios through which consumers might be exposed in nonresidential settings to decaBDE and MWCNTs during general consumer use scenarios for end products upholstered with decaBDE or MWCNT flame-retardant coatings are not expected to differ from those described previously in Section 4.2.2.1 on exposures from intended use of upholstered products in residential spaces.

#### 4.2.2.3. Intended Use – Aircraft and Automobile Upholstery

Flame-retardant upholstery can be used for seating, draperies, carpets, and other textiles in passenger cars and public and private transportation. Aircraft and automobile passengers, and those working in these environments (e.g., cab drivers, flight attendants), could be exposed to higher levels of BDE-209 due to the higher concentrations of PBDEs in dust in those environments as compared to home environments ([Lagalante et al., 2011](#); [Christiansson et al., 2008](#)). Dust generated by abrasion of treated upholstery fabric is the most likely pathway for BDE-209 exposure in automobiles ([Lagalante et al., 2011](#)). No association was found, however, between time spent in automobiles and plasma PBDE levels in children aged 2–5 years in California ([Rose et al., 2010](#)); these children spent an average 7.2 hours per week (range 0–20 hours) in the car.

Photodegradation of BDE-209 is low in cars because automobile glass blocks UVB radiation, which is the region of the spectrum most strongly absorbed by BDE-209. BDE-209 adsorbed to sodium sulfate does photodegrade in automobiles, however, and has a half-life of approximately 19 days. The congeners BDE-47 and BDE-99 are environmentally and toxicologically relevant products of BDE-209 debromination (see Text Box 3-1), but their presence in automobile dust is mainly from volatilization and weathering of products containing pentaBDE, rather than photodegradation of BDE-209 and other higher brominated congeners ([Lagalante et al., 2011](#)).

The pathways through which consumers might be exposed in vehicles (including airplanes) to decaBDE and MWCNTs during general consumer use scenarios for end products upholstered with decaBDE or MWCNT flame-retardant coatings are described below:

- **Inhalation.** Inhalation of decaBDE or MWCNTs adsorbed to dust from worn or abraded automobile upholstery is expected to occur. Inhalation exposure to photodegradates of decaBDE could occur in automobiles if automobile textiles contain decaBDE adsorbed to sodium sulfate. The recirculation of air in aircraft cabins also might affect exposure to particulate decaBDE or MWCNTs, if filters do not adequately remove these particles.

- 1 • **Oral.** Secondary oral exposures might occur if inhaled particulate decaBDE or MWCNTs or  
2 particulate decaBDE or MWCNTs that deposit on the skin are subsequently ingested.
- 3 • **Dermal.** Dermal exposures to decaBDE, MWCNTs, or decaBDE photodegradates (due to  
4 worn or abraded automobile upholstery) are expected to occur, particularly when skin touches  
5 the treated part of the textile directly. Dermal exposure also can occur when particles in the  
6 air settle on the skin. Different exposure characteristics or scenarios (e.g., children sitting in  
7 safety seats) might influence whether dermal exposure occurs, or influence the extent to  
8 which exposure occurs through this pathway.

#### 4.2.2.4. Unintended Use, Repurposing, or Reuse of Treated Textiles and Upholstered Products

9 As introduced in Section 2.4, unintended uses of upholstery textiles treated with decaBDE or  
10 MWCNT flame-retardant coatings could include repurposing of treated upholstery textiles for clothing,  
11 building insulation, other in-home or outdoor furnishings, bedding, or other purposes. The repurposing  
12 stages could introduce occupational exposures similar to those discussed in Sections 4.2.1.2 (exposures  
13 during formulation of the flame retardant, application to textiles, and upholstering) and 4.2.1.3 (exposure  
14 during storage and distribution), as products that are treated with flame-retardant coatings are broken  
15 down and reprocessed into new products.

16 Although no information was identified that directly addresses potential consumer exposures  
17 following unintended use or reuse of flame-retardant upholstery textiles, exposure pathways and scenarios  
18 from other life-cycle stages are relevant here. Most reuse scenarios might differ little from those for  
19 anticipated consumer uses, but a few key differences might occur, particularly when products are  
20 repurposed for new uses or used in unintended ways. For example:

- 21 • Similar processes to those involved with product manufacture (e.g., cutting, sewing) and  
22 storage of textiles also might be employed for repurposing treated textiles. In this scenario,  
23 however, these processes are not expected to occur in an occupational setting, but in the home  
24 or another private space, where no personal protective equipment is worn and limited control  
25 technologies are used. These processes, as employed for repurposing textiles, however, are  
26 not expected to occur as commonly or at the same scale as in a manufacturing facility.
- 27 • Older, more degraded textiles with weakened matrices might be handled directly and  
28 subjected to abrasion, thereby releasing the product constituents in the vicinity of the  
29 consumer conducting the repurposing.
- 30 • Although dermal contact with products used for their intended purpose (e.g., furniture  
31 seating) might be limited by a clothing barrier between the consumer and the treated textile,  
32 should flame-retardant upholstery textiles be repurposed into clothing, direct dermal contact  
33 might occur repeatedly over long periods of time.

34 With the exception of these potential differences in exposure characteristics, the pathways and  
35 scenarios through which consumers might be exposed to decaBDE and MWCNTs during repurposing,

1 reuse, or unintended use of treated textiles and upholstered products are not expected to differ from  
2 exposure pathways associated with the cutting, tailoring other abrasive processes involved with product  
3 manufacturing (Section 4.2.1.2); storage of textile products (Section 4.2.1.3); and consumer use in  
4 residential and nonresidential spaces (Sections 4.2.2.1 and 4.2.2.2).

### 4.2.3. General Public Exposure Pathway Scenarios through Environmental Media

5 No information was found on exposure to decaBDE or MWCNTs in the general public from  
6 environmental media (e.g., air, water, soil). See Section 4.1.2 for concentrations of BDE-209 and model  
7 estimates of MWCNTs in environmental media that could be used with the exposure pathway and  
8 scenario characteristics below to estimate potential exposures.

#### 4.2.3.1. Outdoor Air

9 Releases of decaBDE and MWCNTs to outdoor air throughout the product life cycle of the  
10 flame-retardant textile coatings are possible (see Chapter 2). Once released to air, decaBDE can sorb to  
11 particulate matter and experience long-range transport to areas distant from its source (see Section 3.2).  
12 Although this phenomenon has not been observed for MWCNTs, no evidence yet exists to preclude the  
13 possibility. As summarized in Section 4.1.2.1, decaBDE has been measured in outdoor air at  
14 concentrations much lower than those measured indoors. Nonetheless, general public exposures to  
15 decaBDE adsorbed to particulate matter in ambient air are expected to occur, with the primary route being  
16 inhalation.

17 No data are available on MWCNT concentrations in ambient air, but general public exposure  
18 pathways could be similar to those observed for particulate-phase decaBDE (see Section 4.1.2.1).

19 Other product constituents of flame-retardant textiles (e.g., pieces of the polymer matrix or the  
20 textile fabric) also can be released, and in the case of decaBDE, combustion by-products (e.g., PBDDs,  
21 PBDFs) and lower brominated transformation products are expected to be present in air as a result of the  
22 flame-retardant textile coating life cycle. As discussed in Section 3.2, the physicochemical properties of  
23 MWCNTs released to air might change over time as a result of aging, which could result in exposure of  
24 the general public to MWCNTs that are different from those when they were first synthesized or released.

#### 4.2.3.2. Water

1 Releases of decaBDE, MWCNTs, and other product constituents to wastewater and ambient  
2 water bodies throughout the product life cycle of flame-retardant textile coatings are possible (see Chapter  
3 2). Once released to water, both MWCNTs and decaBDE are expected to sorb to particulate matter in the  
4 water column or to sediments, which might limit their mobility (see Section 3.3). This behavior implies  
5 that decaBDE and MWCNTs also primarily will be removed to sludge during wastewater treatment.

6 As summarized in Section 4.1.2.2, decaBDE has been measured in surface waters at low  
7 concentrations [below levels of detection to 191.0 pg/L ([Oros et al., 2005](#))]. As a result, general public  
8 exposures to decaBDE and its transformation products in water are expected to occur, with the primary  
9 routes being dermal (through bathing and swimming) and oral (drinking and incidental ingestion during  
10 bathing and swimming).

11 No data are available on MWCNT concentrations in surface waters (see Section 4.1.2.2), but  
12 general public exposure pathways could be similar to those observed for particulate-phase decaBDE.  
13 MWCNT surface functionalization, however, might affect stability of free MWCNTs in water and  
14 efficacy of water treatment methods in removal of MWCNTs (see Section 3.3.3), which could result in  
15 more or less exposure to MWCNTs in surface and drinking water, depending on the type of  
16 functionalization.

#### 4.2.3.3. Soil

17 Releases to ambient air and water throughout the product life cycle of flame-retardant textile  
18 coatings will result in deposition of particles of decaBDE, MWCNTs, and other product constituents (see  
19 Chapter 2) to soil. Once deposited, both MWCNTs and decaBDE are expected to sorb strongly to soil,  
20 which might limit their mobility (see Section 3.4).

21 As summarized in Section 4.1.2.3, decaBDE has been measured in surface soils and is expected  
22 to be present in sludge applied to agricultural soils. As a result, general public exposures to decaBDE and  
23 its transformation products in soils are expected to occur, with the primary routes being dermal and oral  
24 (although in incidental amounts). Furthermore, decaBDE has been shown to translocate from soil to plant  
25 tissues, suggesting that decaBDE can enter the food web, and dietary oral exposures also might occur.

26 No data are available on MWCNT concentrations in surface soils (see Section 4.1.2.3), but  
27 general public exposure pathways could be similar to those observed for particulate-phase decaBDE.

## 4.2.4. Highly Exposed Populations

1           This section discusses characteristics of individuals and populations that might result in increased  
2 exposure (relative to the general population) to decaBDE and MWCNTs released during the life cycle of  
3 flame-retardant upholstery textile coating.

### *Decabromodiphenyl Ether*

4           The primary exposure pathway for decaBDE is likely to be ingestion of household dust, and dust  
5 levels in the home can vary by socioeconomic status or the type and condition of housing (see Section  
6 5.3.1). Disproportionate levels of exposure can occur in specific populations, including low-income and  
7 low-educational-attainment populations. Although race and ethnicity have not been shown to be  
8 associated with specific physiological conditions that increase susceptibility to exposure, demographic  
9 factors such as socioeconomic and educational status could cause some populations to bear a  
10 disproportionate level of the exposure burden.

11           Children are likely to experience higher exposures than the general population. Data suggest that  
12 breast-fed infants are potentially exposed to BDE-209 through their mother's milk [i.e., worldwide,  
13 median detected levels of BDE-209 in breast milk range from 0.1 to 2.9 ng/g liquid weight  
14 ([Frederiksen et al., 2009](#))]. Young children also take in more household dust than adults, with estimates  
15 for children at 100–200 mg/day compared to 50 mg/day for adults ([U.S. EPA, 2008a](#)). Increased hand-to-  
16 mouth activity contributes to increased exposures in children. Occupation also could increase exposure  
17 relative to the general population, primarily for workers involved in manufacture of decaBDE or flame  
18 retardants containing decaBDE, or textile products treated with decaBDE.

### *Multiwalled Carbon Nanotubes*

19           Similar to decaBDE, occupation could increase exposure to MWCNT relative to the general  
20 population. In occupational settings, the primary exposure pathway for MWCNTs is likely to be  
21 inhalation. Consumer exposure pathways might be similar to those envisioned for decaBDE, but  
22 MWCNTs are less likely to be released from the polymer matrix (see Section 2.4.2). Given the lack of  
23 data on consumer exposure to MWCNTs, whether the primary route of exposure for highly exposed  
24 populations would be different from that of decaBDE is difficult to determine. In general, children are  
25 more susceptible to increased inhalation exposures because of increased ventilation rates per unit of body  
26 weight and increased oral exposures due to hand-to-mouth and chewing (e.g., mouthing furniture or  
27 fabric) behaviors. The relevance of the inhalation and oral pathways for MWCNT consumer exposures,  
28 however, is unknown. In addition, lack of data on whether MWCNTs, if released from flame-retardant  
29 textiles, would partition to dust precludes a determination of whether children might experience elevated  
30 oral exposures to MWCNTs similar to those observed for decaBDE.

1 For pollutants for which inhalation exposure due to proximity to primary pollution sources is of  
2 concern, socioeconomic status has been associated with increased exposures, which also might be true for  
3 MWCNTs. As with decaBDE, race and ethnicity do not present specific physiological conditions to  
4 increase susceptibility to exposure, but demographic factors such as socioeconomic and educational status  
5 might cause some populations to experience disproportionate exposures. The possibility of increased  
6 exposure to MWCNTs due to characteristics associated with low socioeconomic status has not yet been  
7 explored in the literature.

## 4.2.5. Exposure Reference Values and Recommendations

8 A variety of exposure standards, guidelines, or recommendations are developed by different  
9 organizations with purview over specific portions of the population or situations during which exposure  
10 might occur (e.g., occupational exposures, general population drinking water exposures). Available  
11 information on these types of values for decaBDE and MWCNT are presented below. Section 5.1.1  
12 discusses how some of these values inform quantitative toxicity assessments.

### *Decabromodiphenyl Ether*

13 As of January 2011, no national-level environmental or occupational health standards had been  
14 established for decaBDE ([DOD, 2011](#)). The U.S. Environmental Protection Agency (EPA) has derived a  
15 reference dose (RfD) for decaBDE, based on developmental neurobehavioral effects, of 0.007 mg/kg/day  
16 ([U.S. EPA, 2008b](#)) (see Section 5.1). An RfD is an estimate (taking into account uncertainty) of the daily  
17 exposure to the human population, including sensitive populations, that is “likely to be without an  
18 appreciable risk of deleterious effects during a lifetime” ([U.S. EPA, 2008b](#)). EPA also has derived a  
19 cancer slope factor for decaBDE based on neoplastic nodules or carcinomas (combined) in the liver of  
20 treated male rats, of  $7 \times 10^{-3}$  per mg/kg/day. A cancer slope factor is a plausible upper bound on the  
21 estimate of risk per mg/kg/day of oral exposure ([U.S. EPA, 2008b](#)). The Agency for Toxic Substances  
22 and Disease Registry has developed a minimal risk level (MRL) for decaBDE for intermediate duration  
23 (15–365 days) oral exposure of 10 mg/kg/day ([ATSDR, 2004](#)) based on Hardy et al. ([2002](#)). MRL values  
24 are estimates of the daily exposure to a hazardous chemical that is likely to be without appreciable risks of  
25 noncancer health effects over a specific duration of exposure.<sup>14</sup> MRL values are intended as screening  
26 levels, rather than clean-up or action levels for any agency. Differences in exposure duration (chronic  
27 lifetime versus intermediate) and the key study used to derive the estimate contributed to the several-  
28 orders-of-magnitude difference between the MRL and RfD for decaBDE.

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<sup>14</sup>ATSDR – Minimal Risk Levels: <http://www.atsdr.cdc.gov/mrls/index.asp>.

### *Multiwalled Carbon Nanotubes*

1 MWCNTs can have features of both nanoparticles and fibers, and regulations exist to control  
2 particles and fibers in the workplace. MWCNTs can appear as clumps or ropes, which can be counted as  
3 single fibers if they fit the definition of a fiber. If the rope is not within the World Health Organization's  
4 definition of a fiber (greater than 5  $\mu\text{m}$  in length, with an aspect ratio greater than 3:1), however, it would  
5 not be counted as a fiber under the current measurement system. Some MWCNTs could therefore be  
6 missed using current fiber classification methods ([Donaldson et al., 2006](#)).

7 Recently, NIOSH conducted a risk analysis for CNTs to establish a guideline exposure level for  
8 occupational workers ([NIOSH, 2010](#)). They estimated a working lifetime inhalation exposure of  
9 0.2–2  $\mu\text{g}/\text{m}^3$  (8-hour time-weighted average) associated with a 10% excess risk of early-stage adverse  
10 lung effects (95% lower confidence limit estimates) based on two subchronic animal inhalation studies  
11 ([Pauluhn, 2010b](#); [Ma-Hock et al., 2009](#)) (see Section 5.1 for human health effects). The NIOSH-  
12 recommended exposure limit is 7  $\mu\text{g}/\text{m}^3$  for elemental carbon (see Table 4-1) as an 8-hour time-weighted  
13 average respirable mass airborne concentration ([NIOSH, 2010](#)). NIOSH also recommends that workplace  
14 airborne exposure to CNTs be measured by NIOSH NMAM 5040, which has an upper limit of  
15 quantitation of 7  $\mu\text{g}/\text{m}^3$  ([NIOSH, 2010](#)). Specifically, the animal-data-based risk estimates indicate that  
16 workers could have >10% excess risk of developing early-stage pulmonary fibrosis if exposed over a full  
17 working lifetime at the upper limit of quantitation for NIOSH NMAM 5040 ([NIOSH, 2010](#)). Other  
18 recommended occupational exposure limits (OELs) and general human health exposure limits for  
19 inhalation of MWCNTs and related materials are shown in Table 4-1.

20 As discussed by Schulte et al. ([2010](#)), deriving OELs for MWCNTs and other nanomaterials is  
21 complicated by the challenges associated with measuring workplace exposures (see Text Box 4-1),  
22 coupled with the variation in configurations of physicochemical properties that can influence exposure  
23 and toxicity (see Text Boxes 4-2 and 5-2). The heterogeneity in MWCNT configurations could  
24 necessitate developing OELs specific to individual formulations of MWCNTs ([Schulte et al., 2010](#)).  
25 Alternatively, OELs could be developed for groups of nanomaterials based on composition or toxic  
26 mechanism, although such classifications could exclude physicochemical characteristics that influence  
27 biological activity ([Schulte et al., 2010](#)).

**Table 4-1. Established inhalation occupational exposure levels (OELs) applicable to MWCNTs.**

OEL		Value	Reference
The Occupational Safety & Health Administration – permissible exposure limit (PEL) for respirable fraction of synthetic graphite		5000 µg/m <sup>3</sup>	Lam et al. (2006)
A review of CNT toxicity – human inhalation no-effect levels for workers derived from acute and subchronic inhalation studies with MWCNTs	INEL <sub>acute</sub>	150 µg/m <sup>3</sup>	Aschberger et al. (2010)
	INEL <sub>chronic</sub>	1 µg/m <sup>3</sup> and 2 µg/m <sup>3</sup>	
Bayer Pharmaceuticals – estimated OEL for TWA (6 hours/day, 5 days/week, 13 weeks) exposure to Baytubes® based on a no-observed adverse-effect level of 0.1 mg/m <sup>3</sup> divided by an inter-species dose-time adjustment factor of 2		50 µg/m <sup>3</sup>	Pauluhn et al. (2010a)
NIOSH – recommended exposure limit for elemental carbon as an 8-hour TWA respirable mass airborne concentration		7 µg/m <sup>3</sup>	NIOSH (2010)
Nanocyl – estimated OEL for an 8-hour TWA exposure to MWCNTs based on applying an overall assessment factor of 40 to the lowest-observed-adverse-effect level of 0.1 mg/m <sup>3</sup> in Ma-Hock et al. (2009)		2.5 µg/m <sup>3</sup>	Nanocyl (2009)
Japanese New Energy and Industrial Technology Development Organization – Interim OEL for MWCNTs based on unpublished data by unpublished study		3.0 µg/kg/day	Kobayashi et al. (unpublished) as cited in NIOSH (2010)
British Standards Institute – benchmark exposure limit based on one-tenth of the Institute’s asbestos exposure limit		0.1 fiber/cm <sup>3</sup> air	BSI (2007) as cited in NIOSH (2010)

TWA = time-weighted average

## 4.2.6. Toxicokinetics, Dose, and Body Burden

1 Toxicokinetics can be used to relate exposure and contact, such as those described in the  
 2 scenarios above, with uptake and dose. Specifically, toxicokinetics describes how a material is absorbed,  
 3 distributed, metabolized, and excreted in an organism. An understanding of the relationship between each  
 4 of these concepts, which are often referred to as ADME, leads to an understanding of the concentration,  
 5 or dose, of material that can reach—and potentially accumulate in—different tissues of the body.

### 4.2.6.1. Absorption, Distribution, Metabolism, Excretion

6 This section contains information regarding the toxicokinetic behavior of decaBDE and  
 7 MWCNTs when administered to mammals. Information regarding birds and fish is not presented in this



1 section because, when extrapolating toxicokinetic data to humans, studies conducted with rodents (rat or  
2 mouse) or nonrodent mammals (dog or monkey) are generally used. Additionally, differences among  
3 species have been noted in numerous studies of decaBDE, and the toxicokinetic behavior in response to  
4 decaBDE differs among birds, fish, and mammals. For example, fish generally debrominate decaBDE to  
5 pentaBDE congeners, while mammals debrominate decaBDE, to a lesser degree, to heptaBDE congeners.  
6 See Section 4.3 for toxicokinetic information relevant to ecological exposures. Studies examining the  
7 toxicokinetics of MWCNTs in mammals are summarized in Appendix F.

### *Decabromodiphenyl Ether*

8 Early toxicokinetic studies ([el Dareer et al., 1987](#); [NTP, 1986](#); [Norris et al., 1975](#); [Norris et al.,](#)  
9 [1973](#)) were conducted on decaBDE shortly after it was developed as a flame retardant. These studies  
10 demonstrated that decaBDE is poorly absorbed [0.3–1.5%; ([NTP, 1986](#))] from the gastrointestinal tract in  
11 rats following oral exposure and eliminated in the feces as the parent congener without prior metabolism.  
12 Essentially no elimination occurred through the urine, and more than 99% of the dose was recovered in  
13 feces by 48 hours, indicating a lack of accumulation in tissues ([Norris et al., 1975](#)). The half-life of  
14 decaBDE is relatively short; the serum half-life was reported as 15 days in a human study where workers  
15 were exposed to BDE-209 ([U.S. EPA, 2010b](#)).

16 More recent studies, although in general agreement, have reported higher absorption rates that  
17 might be due to the solvent used to administer decaBDE. In general, BDE-209 is not expected to  
18 accumulate in terrestrial organisms. Many studies, however, have reported levels of BDE-209 in humans  
19 (breast milk, serum, and umbilical cord blood), food items (dairy, eggs, infant formula), and biota (fish,  
20 shellfish), indicating that some absorption and accumulation occur over time ([Frederiksen et al., 2009](#)).  
21 Given the high trophic levels of the organisms where accumulation has been observed (humans, predatory  
22 fish, and piscivorous birds), biomagnification appears to occur in these receptors ([Environment Canada,](#)  
23 [2010](#); [U.S. EPA, 2010b](#)). Bioaccumulation and biomagnification are discussed further in Section 4.3.1.

24 Because of the low absorption of BDE-209, blood and tissue levels following acute (short-term)  
25 oral exposures are typically low and represent a small fraction of the total dose. More than 66% of the  
26 parent compound was excreted in the feces of rats following oral exposures to BDE-209 ([Riu et al., 2008](#);  
27 [Mörck et al., 2003](#)). The same experiments showed that the highest concentrations of BDE-209 were  
28 found in plasma and blood-rich tissues such as liver, kidney, adrenal glands, ovaries, heart, and the  
29 intestinal wall following a single oral exposure ([Mörck et al., 2003](#)) or 4-day gavage exposure ([Riu et al.,](#)  
30 [2008](#); [Mörck et al., 2003](#)). In these acute studies, BDE-209 was not readily distributed to adipose tissue.

31 In contrast, evidence shows that BDE-209 can accumulate in adipose tissue following chronic  
32 oral exposure. Studies by Norris et al. [1974; 1975, as cited in Hardy et al. ([2009](#))] exposed Sprague-  
33 Dawley rats to a commercial product called FR-300-BA in the diet at 0.01, 0.1, and 1.0 mg/kg/day for

1 3, 6, or 12 months. FR-300-BA comprised 77.4% BDE-209, 21.8% nonaBDE, and 0.8% octaBDE. After  
2 6 months of treatment, bromine concentrations (measured by neutron activation analysis) in adipose tissue  
3 were higher in treated rats (~3 µg/g) than in controls (~1 µg/g), but after 12 months the bromine levels in  
4 adipose tissue were similar to controls. Bromine did not accumulate in other tissues such as liver, kidney,  
5 and serum. Norris et al. [1974; 1975, as cited in ([Hardy et al., 2009](#))] also followed the elimination of  
6 bromine from male Sprague-Dawley rats that were dosed with FR-300-BA in the diet for 90 days at  
7 1.0 mg/kg/day and subsequently fed a control diet. After 10 days on a control diet, concentrations of  
8 bromine in the liver were similar to controls, but concentrations in adipose tissue were higher (~2.5 to  
9 4 µg/g) than controls (~0-2 µg/g). Another study showed a time- and dose-dependent increase of bromine  
10 levels in adipose tissue indicating accumulation following dietary exposure to decabromodiphenyl oxide  
11 (a synonym for decaBDE) at 0.01, 0.1, or 1 mg/kg/day, for up to 2 years ([Kociba et al., 1994](#)). Kociba et  
12 al. ([1994](#)) also reported that bromine content was not increased compared to controls in the kidney,  
13 muscle, or serum of rats in the same study.

14 Absorbed decaBDE is metabolized in the liver and a minor fraction of the parent compound is  
15 metabolized to lower PBDE congeners, such as tetraBDE and pentaBDE (see Text Box 3-1). Mörck et al.  
16 ([2003](#)) reported that decaBDE was the predominant substance detected in the liver metabolites, with trace  
17 levels of nonaBDE. Similarly, a minor fraction of decaBDE (less than 3%) was debrominated to lower  
18 BDE congeners in a feeding study that exposed male Sprague-Dawley rats to DE-83R (98.5% decaBDE)  
19 ([Huwe and Smith, 2007](#)).

20 Metabolism of decaBDE to lower brominated congeners by oxidative debromination is indicated  
21 by some evidence in studies of rats and fish, but the mechanisms and location of metabolic processes are  
22 not well characterized due to limited availability of toxicokinetic data ([Hakk and Letcher, 2003](#)).  
23 Metabolism of decaBDE also differs among species. In lactating cows, Kierkegaard et al. ([2007](#))  
24 suggested that decaBDE debrominates to hepta-, octa-, and nonaBDEs. Octa- and nonaBDEs were found  
25 in liver and kidney of rats fed 100 mg/kg/day BDE-209 for 3 months ([Wang et al., 2010a](#)). In contrast, in  
26 vitro studies of human hepatocytes have shown evidence of low or no metabolism, possibly because of  
27 low entry of BDE-209 into cells under the experimental conditions used ([Stapleton et al., 2009](#)).

28 Based on available studies ([Huwe and Smith, 2007](#); [Kierkegaard et al., 2007](#); [Hakk and Letcher,](#)  
29 [2003](#); [Mörck et al., 2003](#); [Sandholm et al., 2003](#)), the following pathways for debromination of decaBDE  
30 can be deduced for mammals:

- 31 1. Deiodinase enzymes can debrominate decaBDE to nona-, octa-, and heptaBDEs.
- 32 2. Debrominated neutral metabolites can undergo hydroxylation to potentially form phenols or  
33 catechols, possibly via an arene oxide, which could involve the action of cytochrome P450  
34 enzymes.

- 1 a. The formed hydroxylated BDEs can compete with thyroxine for binding to a thyroxine transport  
2 protein present in blood serum.
- 3 b. The catechols then are methylated, potentially by the action of catechol-O-methyltransferase, to  
4 form guaicols.
- 5 c. The guaiacol metabolites further oxidize to highly reactive quinones, which bind to cellular  
6 macromolecules.
- 7 d. The reactive intermediates are subject to rapid conjugation via Phase II metabolic processes,  
8 leading to water-soluble metabolites that are excreted via bile and feces, as observed in  
9 conventional and cannulated rats.

10 Two toxicokinetic studies of fetal rats were identified. In a study by Riu et al. ([2008](#)), <sup>14</sup>C-BDE-  
11 209 (99.8% pure, dissolved in peanut oil) was administered orally to pregnant rats on Gestation Days  
12 (GD) 16–19 (2 mg/kg/day). The toxicokinetic results were similar to those noted previously in this  
13 section. Approximately 72% of the dose was found in the feces and the digestive tract contents, while  
14 0.1% was excreted in the urine. The remainder of the dose was distributed in various tissues, with 6.5% in  
15 the liver and 5.3% in the digestive tract contents. All other tissues contained less than 1% of the  
16 administered dose. The fetuses (sum for the whole litter) contained 0.43% of the dose. In a recent study  
17 by Cai et al. ([2011](#)), BDE-209 and its metabolites were detected in the placenta and milk, and eventually  
18 in the fetuses or neonates when BDE-209 (prepared in peanut oil) was administered to pregnant Sprague-  
19 Dawley rats from GD 7 to Postpartum Day 4. In the same study, detectable amounts of nonaBDEs (BDE-  
20 206, 207, 208) and octaBDEs (BDE-196, 197/204, 198/203) were observed in the dosed rats. The  
21 predominant debrominated metabolites of BDE-209 detected in fetuses were nonaBDEs (BDE-208, 207,  
22 206). The level of BDE-206 in the fetal or pup bodies was significantly lower on GD 21 and Postpartum  
23 Day 4 than on GD 7. The octaBDEs BDE-196, BDE-198, and BDE-203 were observed in fetuses and  
24 pups, but were minor debromination metabolites of BDE-209.

25 No animal studies have been identified that evaluate the absorption, distribution, and excretion of  
26 decaBDE upon inhalation and dermal exposures.

### ***Multiwalled Carbon Nanotubes***

27 As discussed in Section 4.2.2, humans might be exposed to free MWCNTs, bundled MWCNTs,  
28 and MWCNTs in combination with a polymer matrix, textile fibers or scraps, or other product  
29 constituents. The bioavailability (and therefore dose) of MWCNTs is expected to differ for MWCNTs in  
30 different forms or bundling states (see Text Box 4-2). In general, CNTs, including MWCNTs, appear to  
31 be biopersistent. After intratracheal administration, MWCNTs have been observed to deposit and persist  
32 within the lung for up to several months ([Elgrabli et al., 2008b](#); [Deng et al., 2007](#)). Macrophage-mediated  
33 clearance of MWCNTs after exposure via inhalation ([Elgrabli et al., 2008a](#)), and translocation of some  
34 types of CNTs into the pleura and subpleura ([Porter et al., 2010](#); [Ryman-Rasmussen et al., 2009a](#)) have

1 been demonstrated. After oral exposure, most MWCNTs (administered at 10 µg/mouse by gavage) were  
2 evident within the feces and also remained within the stomach and small and large intestines, with no  
3 detectable transport into the blood or obvious metabolism through 28 days ([Deng et al., 2007](#)). Because  
4 only one study was identified that evaluated distribution after oral exposure, whether distribution is  
5 possible to other organs in the body following inhalation, dermal, and oral exposures to MWCNTs is not  
6 well understood.

7 Distribution of CNTs to various organs has been reported following intravenous exposure ([Deng](#)  
8 [et al., 2007](#); [Cherukuri et al., 2006](#)), with predominant localization within the liver, lungs, and spleen.  
9 This pathway, however, is not likely relevant for the exposures of concern in this evaluation (i.e.,  
10 MWCNTs used in flame-retardant coatings on upholstery textiles are unlikely to be intravenously  
11 applied).

#### 4.2.6.2. Internal Dose and Body Burden

##### *Decabromodiphenyl Ether*

12 Levels of decaBDE in human tissues have been reported in several occupational studies and in  
13 studies of the general public. A study in workers at an electronics dismantling plant in Sweden evaluated  
14 levels of five PBDEs in serum samples from plant workers. The mean concentration of BDE-209 in that  
15 study was as high as 5 ng/g lipid ([Darnerud et al., 2001](#)). Total PBDE serum levels in hospital cleaners,  
16 computer clerks, and electronics dismantlers were 3, 4, and 26 ng/g lipid, respectively ([Darnerud et al.,](#)  
17 [2001](#)). As discussed in the previous section, decaBDE can accumulate in adipose tissue over time with  
18 chronic exposure ([Hardy et al., 2009](#)). DecaBDE also might biomagnify in the food web from lower  
19 trophic levels to higher trophic levels. DecaBDE also can debrominate to lower PBDE congeners in the  
20 body, which are more bioaccumulative than decaBDE itself ([Yogui and Sericano, 2009](#)).

21 As shown in Table 4-2, the median level of BDE-209 in the serum reported in one U.S. study was  
22 less than 0.96 ng/g liquid weight. International studies reported median serum levels ranging from 0.77 to  
23 18.5 ng/g liquid weight. The highest median levels reported were in men aged 40–50 years in Norway and  
24 Sweden, and the lowest median levels were from maternal serum in a study in the Faroe Islands  
25 ([Frederiksen et al., 2009](#)).

26 BDE-209 has been detected in breast milk in American women at a measured mean concentration  
27 of 0.92 ng/g liquid weight (see Table 4-2). A study that evaluated the breast milk of women in the Pacific  
28 Northwest region of Canada and the United States observed a median level of 0.43 ng/g liquid weight.  
29 Worldwide, median detected levels of BDE-209 in breast milk ranged from 0.1 to 2.9 ng/g liquid weight  
30 ([Frederiksen et al., 2009](#)).

Table 4-2. Median tissue concentration ranges (in ng/g liquid weight) for three polybrominated diphenyl ether congeners in humans.

Country	BDE-47	BDE-99	BDE-209
<b>Breast Milk</b>			
United States	7.69–27.8 <sup>a</sup>	1.46–5.7	0.92 <sup>b</sup>
International	0.03–27.8	0.02–5.36	0.1–2.9
<b>Adipose Tissue</b>			
United States	29.3	10.3	NR
International	0.52–2.3	0.236–1.4	NR
<b>Blood (Serum)</b>			
United States	0.63–46	0.32–13	<0.96
International	0.25–4.55	0.09–1.94	1.1–18.5
<b>Cord Blood</b>			
United States	13.6–25	4.3–7.1	Below detection <sup>c</sup>
International	0.98–3.8	0.07–4.3	2.2
<b>Placenta</b>			
United States	NR	NR	NR
International	0.25–0.77	0.12–0.41	1.0

<sup>a</sup>High level observed in a joint United States/Canada study.

<sup>b</sup>Mean concentration reported.

<sup>c</sup>Detection limits not reported.

NR = Not reported.

Source: Frederiksen et al. (2009).

1 Decline in the use of decaBDE flame retardants containing BDE-209 are expected to result in a  
2 decline in breast milk concentrations over time.

3 Breastfeeding infants, and even infants who are fed infant formula, are likely to be exposed to  
4 BDE-209 through consumption of breast milk and formula. Levels of BDE-209, and levels of total  
5 PBDEs, are higher in American samples of breast milk than levels found in infant formula. The levels in  
6 both breast milk and formula, however, are far lower than the amount detected in household dust  
7 ([Frederiksen et al., 2009](#)).

### ***Multiwalled Carbon Nanotubes***

8 Based on toxicokinetic studies with rats, inhaled MWCNTs can remain in the lung following  
9 exposure for an extended period, up to six months ([Aschberger et al., 2010](#)). However, these studies

1 reported qualitative data, and no studies were found that reported levels of MWCNTs in the lung. One  
2 study did report MWCNTs in the subpleura of mice following a single inhalation exposure to 30 mg/m<sup>3</sup>;  
3 no MWCNTs were detected in the subpleura following instillations of a lower concentration (1 mg/m<sup>3</sup>)  
4 ([Ryman-Rasmussen et al., 2009a](#)). Another study reported MWCNTs with known length just under 4 μm  
5 in the pleura of mice following a single aspiration of 10–80 μg ([Porter et al., 2010](#)). This finding is  
6 notable because the pathogenic mechanism of asbestos fibers in the mesothelioma disease process occurs  
7 in the pleural cavity ([Aschberger et al., 2010](#)).

8 No detectable amounts of MWCNTs were observed in the blood following oral exposure in mice,  
9 but the MWCNTs did remain in the stomach and small and large intestines ([Deng et al., 2007](#)); the  
10 observed MWCNTs remained unchanged ([Aschberger et al., 2010](#)). As discussed in Section 4.2.6.1,  
11 MWCNTs were distributed to multiple organs following intravenous injection ([Deng et al., 2007](#);  
12 [Cherukuri et al., 2006](#)), but this exposure pathway is unlikely to be relevant for this case study.

## 4.3. Ecological Exposure and Kinetics Leading to Dose

### 4.3.1. Factors Impacting Ecological Exposure

13 In biota, potential exposure routes for decaBDE and MWCNTs include ingestion, inhalation, or  
14 direct contact. The potential for exposure via each route along with subsequent uptake and dose depends  
15 on several factors, including properties of the environmental media and physiological and behavioral  
16 characteristics of aquatic and terrestrial organisms. These factors can in turn, influence the bioavailability  
17 of decaBDE and MWCNTs. As discussed in Chapter 3, the physicochemical properties of BDE-209 and  
18 MWCNTs dictate their partitioning in the environment. This partitioning drives the exposure potentials  
19 for water-dwelling, sediment-dwelling, and terrestrial organisms. For example, BDE-209 preferentially  
20 binds to soils and sediment when released to the environment ([Hale et al., 2006](#)) and likely will be present  
21 only in limited quantities in surface water or ground water (see Section 4.1.2.2) ([U.S. EPA, 2010b](#)).  
22 Sediment-dwelling organisms are therefore key ecological receptors of BDE-209. CNTs without  
23 functionalizing surfactants are hydrophobic and will interact with other CNTs and organic matter in  
24 aquatic systems, resulting in stable suspensions and bundling followed by sedimentation ([Koelmans et al.,  
25 2009](#); [Hyung et al., 2007](#)), allowing for exposure of both water-column and benthic organisms to  
26 MWCNTs in aquatic systems ([Velzeboer et al., 2011](#)).

27 Properties of the environmental media also can influence exposure potential for MWCNTs by  
28 affecting bioavailability and MWCNT form. For example, the presence of dissolved organic matter in an

1 aquatic system can cause MWCNTs to debundle. Bacterial studies have shown that debundling of  
2 MWCNTs can result in greater cytotoxicity ([Kang et al., 2009](#)). Changes in properties such as ionic  
3 strength or the pH of a solution might influence sorption behaviors of CNTs ([Petersen et al., 2011](#)), which  
4 could differentially alter exposure levels of benthic and water-column organisms.

### 4.3.2. Absorption, Distribution, Metabolism and Excretion in Ecological Receptors

5 As discussed in Section 4.2.6, an understanding of ADME processes can be used to relate  
6 exposure concentrations to the concentration, or dose, of material that reaches the tissues of an organism.  
7 Elucidation of organism-specific ADME processes can help explain observations of high body burdens  
8 that were not predicted based on environmental fate and partitioning alone. ADME processes influence  
9 whether and for how long a material is retained in a tissue (i.e., whether the material will bioaccumulate)  
10 and how such retention rates might differ among trophic levels (i.e., whether concentrations of the  
11 material will biomagnify in a food web). Bioaccumulation and biomagnification have been shown to  
12 influence ecological exposures for decaBDE, as described further in Sections 4.3.3 and 4.3.4, and might  
13 similarly influence uptake of and exposure to MWCNTs. Bioaccumulation is the process by which an  
14 organism takes a chemical into the body through all exposure routes and dilutes the chemical through  
15 excretion, metabolism, and growth, but accumulates a net “body burden” of the chemical ([Environment  
16 Canada, 2010](#); [U.S. EPA, 2010b](#)). Biomagnification is the process by which a chemical increases in  
17 concentration in tissues as it moves up trophic levels in an ecosystem ([U.S. EPA, 2010b](#)).  
18 Bioaccumulation factors (BAFs), the ratio of the chemical contaminant in the tissue of the biota (from  
19 dietary exposure and uptake directly from media) to chemical contaminant in the medium, and  
20 biomagnification factors (BMFs), the ratio of the chemical concentration in an organism’s tissue to the  
21 concentration of the same chemical in the tissues of its diet, are used as measures of persistence and  
22 potential for impacts as a chemical moves through an ecosystem ([U.S. EPA, 2010b](#)). A substance is  
23 considered bioaccumulative when it has a high BAF, generally greater than 5000 (U.S. EPA, Final Rule  
24 40 Code of Federal Regulations 372). Bioaccumulation studies that show body burdens in organisms in  
25 remote locations far from a direct, nondietary exposure source (e.g., water, air), such as those in  
26 Greenland peregrine falcons or Florida coastal sharks, are indicative of trophic biomagnification through  
27 the food web ([Environment Canada, 2010](#)). Biomagnification can be modeled using fugacity-based  
28 dynamic fate models that consider environmental conditions, ecosystem properties, and food-web  
29 dynamics ([Lim and Lastoskie, 2011](#)).

1 Ecological receptors are likely to be exposed to decaBDE or MWCNTs through treated products  
2 or scraps and debris from products generated during end-of-life stages of the product life cycle  
3 (see Chapter 2). The materials released during these processes can contain components other than the  
4 contaminant of concern (e.g., textile material, glue, composite ingredients). As discussed at the beginning  
5 of this chapter and throughout Section 4.2, studies are lacking on the matrix-bound state of these  
6 compounds and how exposure characteristics and dose implications differ for the free and matrix-bound  
7 forms. As for the discussion of human exposures in Section 4.2, exposure considerations for ecological  
8 receptors are informed by data on BDE-209 and MWCNTs not embedded in a polymer matrix or  
9 associated with other product ingredients (e.g., textile fibers, coating ingredients). Field studies have  
10 found raw PBDEs in environmental media, which indicates that the compounds can leach from the  
11 product matrix (see Appendix E). No data are currently available regarding leachability or environmental  
12 release of free MWCNTs from their source products in the environment.

### 4.3.3. Exposure Pathways in Aquatic Systems

13 PBDEs primarily transition to the sediment in aquatic ecosystems ([Mikula and Svobodová,](#)  
14 [2006](#)); as a result, benthic organisms might take up decaBDE via absorption or ingestion of sediment.  
15 Secondary exposure via movement through the food web results in greater body burdens of PBDEs in  
16 predatory fish than in herbivorous or omnivorous fish ([Mikula and Svobodová, 2006](#)). In fish, uptake of  
17 PBDE from the water column via gills is limited by the large molecular size of PBDEs, but dietary uptake  
18 efficiencies have been shown to range from 40 to 92% ([Mikula and Svobodová, 2006](#)). Due to the  
19 tendency for PBDEs to partition into sediment and the inefficiency of uptake via gills, the more likely  
20 route of exposure for fish is secondary exposure due to bioaccumulation and biomagnification in the food  
21 web. Information on ecological uptake pathways for MWCNTs in aquatic environments is limited, but  
22 existing studies indicate that some water-dwelling organisms can take up MWCNTs stabilized in organic  
23 matter via absorption in the gut ([Kennedy et al., 2008](#)). Functionalization also could affect uptake by  
24 aquatic organisms by altering the binding between the MWCNTs and body tissues ([Li and Huang, 2011](#)).

#### Toxicokinetics and Body Burden in Aquatic Systems

##### *Decabromodiphenyl Ether*

25 Limited information is available on the mechanisms of BDE-209 ADME in aquatic organisms;  
26 most studies to date have measured concentrations of PBDEs in tissues of aquatic organisms to estimate  
27 body burdens. BDE-209 and the lower brominated congeners BDE-206, BDE-207, and BDE-208 were  
28 experimentally shown to accumulate in the liver of juvenile lake whitefish (*Coregonus clupeaformis*) as a



1 result of exposure to BDE-209 via the diet ([Kuo et al., 2010](#)). Fish exposed to 2 µg/g diet BDE-209 for  
2 30 days accumulated a mean of 5.80 nmol/g lipid in the liver, compared to 0.208 nmol/g lipid for the rest  
3 of the body and 0.183 nmol/g lipid in the liver of control fish. Liver concentrations of BDE-206,  
4 BDE-207, and BDE-208 also were higher compared to control, although concentrations were less than  
5 0.01 nmol/g lipid for each congener ([Kuo et al., 2010](#)).

6 Similarly, juvenile lake trout (*Salvelinus namaycush*) exposed to various PBDE congeners for  
7 56 days accumulated measurable PBDE concentrations, and depuration half-lives ranged from 26 to  
8 346 days ([Tomy et al., 2004](#)). When BDE-209 was present in the diet at 3.4 ng/g dry weight, the uptake  
9 rate constant was calculated as 132 g/day. When the concentration of BDE-209 in the diet was raised to  
10 27.5 ng/g dry weight, the uptake rate constant was much lower—6.1 g/day. Study authors determined a  
11 half-life for BDE-209 of 26 ± 5 days, and a BMF of 0.3 ([Tomy et al., 2004](#)). BMFs of other congeners  
12 ranged from 1.6 to 45.9.

13 Body burdens of PBDEs in aquatic organisms have been studied in top predators such as  
14 piscivorous birds of prey and top-level fish and in lower-level organisms like insects and crabs  
15 ([Environment Canada, 2010](#); [U.S. EPA, 2010b](#); [Environment Canada, 2006](#)) (see Section E.2 of  
16 Appendix E). Bottom feeders and bivalves often have the lowest PBDE body burdens, eels and higher  
17 level fish like sole and flounder have the highest body burdens, and shrimp have mid-range body burdens  
18 ([U.S. EPA, 2010b](#)). Studies have shown accumulation of BDE-209 (exceeding 100 ng/g) in top predators,  
19 including sharks in coastal Florida and marine mammals such as harbor porpoise and white-beaked  
20 dolphin ([Environment Canada, 2010](#)). Although BDE-209 likely only accumulates at low levels in lower  
21 trophic-level organisms, biomagnification can lead to relatively greater concentrations in higher trophic  
22 levels.

23 Bioaccumulation rates of BDE-209 and other PBDE congeners are affected by significant  
24 biotransformation and debromination ([Tomy et al., 2004](#)), so determining the level or pattern of PBDE  
25 uptake from the environment and accumulation in biota is difficult. Laboratory-based studies that control  
26 the exposure rates and measure tissue concentrations allow for calculations of uptake rates, depuration  
27 rates, and BMFs. For example, in a study by Kierkegaard et al. ([1999](#)), juvenile rainbow trout  
28 (*Oncorhynchus mykiss*) were exposed to technical-grade decaBDE via diet for 120 days, and then  
29 observed for 71 days postexposure. The level of decaBDE in the diet ranged from 7.5 to 10 mg/kg body  
30 weight per day. Study authors determined that the total uptake in muscle was between 0.02 and 0.13% of  
31 the exposure level. Fish tissue concentrations of BDE-209 increased over the course of the exposure  
32 period, reaching 38 ng/g fresh weight in muscle and 870 ng/g fresh weight in the liver at Day 120.  
33 Concentrations declined during the 71-day depuration period to 9.5 ng/g fresh weight in muscle tissue and  
34 30 ng/g fresh weight in the liver ([Kierkegaard et al., 1999](#)).

1 Bioavailability and bioaccumulation of BDE-209 are limited by the high molecular weight of  
2 BDE-209 and its strong sorption to soils and sediments ([Kierkegaard et al., 2004](#)). In general, PBDEs can  
3 bioaccumulate and biomagnify in the aquatic food web ([Agrell et al., 2004](#)). Their propensity to  
4 bioaccumulate and biomagnify depends in large part on their level of bromination. Highly brominated  
5 congeners like BDE-209 have a tendency to sink into aquatic sediments and are a minor congener found  
6 in aquatic biota. Benthic sediments are a major sink for PBDEs, but BDE-209 does not appear to be  
7 readily available to benthic organisms for uptake, although some movement through the food web does  
8 occur ([Ciparis and Hale, 2005](#)). To what extent BDE-209 can be transformed in the environment to lower  
9 brominated congeners like BDE-47 and BDE-99 is uncertain; BDE-47 and BDE-99 have been identified  
10 as the congeners frequently found in biota ([Watanabe and Sakai, 2003](#)).

11 Studies analyzing tissue levels and body burdens of PBDEs in organisms having various roles in  
12 a specific ecosystem and food web best illustrate biomagnification, as they quantify the body burdens of  
13 different organisms and relate these to food web relationships. In a study by Law et al. ([2006a](#)), authors  
14 illustrated biomagnification of brominated flame retardants (including PBDEs) in Lake Winnipeg, Canada  
15 by determining trophic structure, assessing trophic transfer, and quantifying the magnitude of  
16 biomagnification. Samples of water, sediment, plankton, mussels, and six fish species were collected over  
17 a four-year period and analyzed for whole-body (in invertebrates) or muscle-tissue (in vertebrates)  
18 concentrations of contaminants (see Appendix E, Table E-8). As Table 4-3 shows, biomagnification of  
19 various PBDE congeners in individual species predator-prey relationships ranged from very positive  
20 (BDE-209 concentration in emerald shiner was 33 times higher than in zooplankton) to negative (BDE-99  
21 concentration in emerald shiner was 10 times lower than in zooplankton) ([Law et al., 2006a](#)). The general  
22 trend illustrates, however, that higher level predators generally have higher body burdens of PBDEs than  
23 lower level prey. The authors determined a trophic magnification factor (which represents the average  
24 predator-prey transfer through a food web, as opposed to a BMF, which represents a transfer for a single  
25 predator-prey relationship) of 3.7 for total PBDEs in the system, and congener-specific trophic  
26 magnification factors of 5.2 for BDE-47 (tetraBDE), 1.5 for BDE-99 and 3.0 for BDE-100 (pentaBDEs),  
27 and 10.4 for BDE-209 (decaBDE) ([Law et al., 2006a](#)).

Table 4-3. Biomagnification factors of select PBDE congeners in an aquatic ecosystem.<sup>a</sup>

Predator	Prey	BDE-47	BDE-99	BDE-100	BDE-153	BDE-209
<b>System: zooplankton → emerald shiner → walleye, burbot</b>						
Walleye	Emerald shiner	0.3	1.2	0.2	0.3	0.6
Burbot	Emerald shiner	0.7	9.5	1	1.7	2.4
Emerald shiner	Zooplankton	5.2	0.1	2.2	1.2	33
<b>System: zooplankton, mussels → white sucker → walleye</b>						
Walleye	White sucker	0.2	2.1	0.1	0.2	2
White sucker	Zooplankton	6.1	0.1	3.4	2.2	9.9
White sucker	Mussels	3.4	0.1	2.9	1.5	0.2
<b>System: zooplankton, mussels → goldeye → walleye</b>						
Walleye	Goldeye	0.2	0.1	0.1	0.1	0.6
Goldeye	Zooplankton	7.2	6.5	4.9	5.5	34
Goldeye	Mussels	4	4.4	4.2	3.9	0.8
<b>System: zooplankton → whitefish → walleye</b>						
Walleye	White fish	8.9	1.7	3.9	4.6	6.8
White fish	Emerald shiner	0.1	0.7	0.1	0.1	0.1
White fish	Zooplankton	0.2	0.1	0.1	0.1	2.9

<sup>a</sup>Trophic levels: mussel → zooplankton, whitefish → goldeye, emerald shiner, white sucker → burbot, walleye.

Note: Biomagnification factor (BMF) is the lipid-corrected BDE concentration in predators / lipid-corrected BDE concentration in prey. BMF >1 indicates concentration in predator higher than in prey; BMF <1 indicates concentration in prey higher than in predator. Gray shading highlights where BMF >1, indicating that biomagnification has occurred as one moves up trophic levels.

Source: Law et al. (2006a).

### ***Multiwalled Carbon Nanotubes***

- 1 Limited information is available on MWCNT ADME and body burdens in aquatic organisms. As
- 2 mentioned in Section 3.3, CNTs are likely to attract lipophilic molecules in aqueous media (Wu et al.,
- 3 2006), and association of MWCNTs with lipophilic molecules could affect uptake in aquatic ecosystems.
- 4 One study exposed a species of water flea (*Ceriodaphnia dubia*) to MWCNTs stabilized in suspended
- 5 natural organic matter and demonstrated that absorption of carbon materials can occur in the gut
- 6 (Kennedy et al., 2008), suggesting that water-dwelling organisms could take up MWCNTs. Surface

1 functionalization by lipophilic molecules in the natural environment could further affect uptake by aquatic  
2 organisms by altering the binding between particles and body tissues ([Li and Huang, 2011](#)).

3 A few studies have shown that MWCNTs can be taken up by aquatic invertebrates, but are not  
4 bioaccumulated over time ([Petersen et al., 2011](#)). For example, Peterson et al. (2010) determined tissue  
5 concentrations of MWCNTs in the freshwater sediment blackworm (*Lumbriculus variegatus*) exposed to  
6 MWCNTs via soil for 30 days. The authors calculated BAFs between 0.1 and 1, indicating that retention  
7 of MWCNTs by this species is approximately one-tenth the concentration in the sediment ([Petersen et al.,](#)  
8 [2010](#)). Although this suggests that MWCNTs will not continue to build up in the tissues of some aquatic  
9 invertebrates over time, the small concentrations in these species might be better retained by larger  
10 predator species, leading to net accumulation in those species through dietary sources. Additionally,  
11 suggestions have been made that current methods for measuring bioaccumulation and calculating  
12 bioconcentration factors are not sufficient for nanomaterials ([Handy et al., 2012](#)). These methods rely on  
13 an evenly dispersed aqueous solution of the compound that achieves a steady-state concentration between  
14 external media and biological tissues, which is potentially incompatible with the dynamic behavior of  
15 nanomaterials in environmental media and the challenges associated with dispersion of MWCNTs, in  
16 particular. Further, traditional bioaccumulation assumes that the processes of uptake and elimination  
17 follow well-characterized kinetics and diffusive flux models, which are based on underlying biological  
18 mechanisms of solute transporter channels. Pathways of uptake and elimination for nanomaterials,  
19 including MWCNTs, are not well understood, and the degree to which the bioaccumulation pathways  
20 might differ from those of conventional materials is unclear ([Handy et al., 2012](#)).

21 Despite the lack of studies directly investigating uptake, absorption efficiency, and  
22 bioaccumulation of MWCNTs in aquatic food webs, the high persistence and hydrophobicity of  
23 MWCNTs are characteristics generally associated with bioaccumulative substances ([Petersen et al., 2010](#);  
24 [Helland et al., 2007](#)). Based on these characteristics alone, MWCNTs are expected to accumulate in  
25 aquatic food webs under some conditions. Which additional material, environmental, or biological  
26 characteristics determine whether and to what degree bioaccumulation occurs are unknown ([Handy et al.,](#)  
27 [2012](#)).

#### 4.3.4. Exposure Pathways in Terrestrial Systems

28 Although PBDEs are detected commonly in terrestrial ecosystems, exposure levels are higher for  
29 terrestrial organisms with diets that consist of animals from the aquatic system than for herbivorous  
30 organisms or organisms with diets consisting of animals from the terrestrial system ([Mikula and](#)  
31 [Svobodová, 2006](#)). As discussed in Section 3.2, long-range transport can result in exposure to terrestrial

1 organisms far from the initial source of release ([de Wit et al., 2010](#); [Su et al., 2009](#); [Breivik et al., 2006](#);  
2 [Agrell et al., 2004](#)).

3 Limited information is available regarding exposure pathways and ecological uptake of  
4 MWCNTs in terrestrial environments. As also discussed in Section 3.2, limited evidence exists that  
5 airborne MWCNTs can quickly (approximately two weeks) transform to amorphous carbon ([Zhu et al.,  
6 2011](#)), thus limiting exposures to terrestrial organisms. Other data suggest that MWCNTs might stabilize  
7 in ambient conditions, however, which would serve to increase exposures ([Yang et al., 2009](#)). If  
8 MWCNTs are present in soils, plant roots could interact with those in soil or pore water ([Navarro et al.,  
9 2008](#)). Pure MWCNTs are reportedly lipophilic, so they could accumulate in root lipids and other plant  
10 tissues ([Helland et al., 2007](#)).

## Toxicokinetics and Body Burden in Terrestrial Systems

### *Decabromodiphenyl Ether*

11 Limited information is available on the mechanisms of BDE-209 ADME in terrestrial organisms;  
12 most studies to date have measured concentrations of PBDEs in specific tissues of terrestrial organisms to  
13 estimate body burdens. Body burdens of PBDEs in terrestrial organisms have been studied in top  
14 predators such as piscivorous and carnivorous mammals and birds of prey. DecaBDE studies have shown  
15 high accumulation (exceeding 100 ng/g) in the liver and muscle tissues of top predators, including kestrel  
16 and sparrowhawk in China, the United Kingdom, and Sweden; peregrine falcon in the United Kingdom,  
17 Sweden, and Greenland; and buzzards and red fox in Belgium ([Environment Canada, 2010](#)). An EPA  
18 ([2010b](#)) review reported total PBDE concentrations in tissues of predatory birds ranged from below  
19 detection limits in some tissue types to greater than 12,000 ng/g weight in some muscle and liver tissues  
20 (see Appendix E, Table E-7).

21 As previously discussed, the high molecular weight and strong sorption of BDE-209 to soils and  
22 sediments would suggest that bioavailability and bioaccumulation is limited in terrestrial systems. Body  
23 burdens of BDE-209, however, have been identified in some—but not all—terrestrial organisms,  
24 suggesting that biomagnification does sometimes occur. The complexity of food web interactions that  
25 cross aquatic and terrestrial systems makes it challenging to determine whether the source of BDE-209 in  
26 terrestrial food webs stems from contaminated abiotic media in the aquatic environment (e.g., sediments,  
27 interstitial waters), the terrestrial environment (e.g., soils, pore water), or a combination of both.

### *Multiwalled Carbon Nanotubes*

28 Limited information is available on MWCNT ADME and body burdens in terrestrial organisms.  
29 MWCNTs present in soils could be absorbed or consumed by biota; MWCNTs taken up by plant roots  
30 and plant tissues also could be consumed. Few studies have attempted to measure tissue concentrations of

1 MWCNTs in biota. One laboratory study was identified that determined tissue concentrations of  
2 MWCNTs in earthworms (*Eisenia foetida*) exposed to MWCNTs via soil for 30 days. The authors  
3 calculated BMFs between 0.01 and 0.1, indicating that tissue concentrations of MWCNTs in this species  
4 is approximately 1/100<sup>th</sup> to 1/10<sup>th</sup> the concentration in the sediment ([Petersen et al., 2010](#)). In another  
5 study using <sup>14</sup>C-labeled pure MWCNTs and MWCNTs with various polyethyleneimine surface coatings,  
6 Petersen et al. ([2011](#)) assessed the extent to which modified MWCNTs concentrate in earthworms.  
7 Results indicated that surface coating did not significantly affect MWCNT uptake or elimination rates  
8 over a 28-day period. The BAF remained less than 0.12 throughout the study regardless of MWCNT type  
9 (purified or modified with surface coatings), indicating that accumulation of MWCNTs from soil by  
10 earthworms is low ([Petersen et al., 2011](#)). As discussed in Section 4.3.1, despite the lack of studies  
11 directly investigating uptake, absorption efficiency, and bioaccumulation of MWCNTs in food webs, the  
12 high persistence and hydrophobicity of MWCNTs are characteristics generally associated with  
13 bioaccumulative substances ([Petersen et al., 2010](#); [Helland et al., 2007](#)). And, as with decaBDE, the  
14 complexity of food web interactions that cross aquatic and terrestrial systems makes determining the  
15 source of MWCNTs in terrestrial food webs difficult.

## 4.4. Aggregate Exposures

16 Assessing aggregate exposures involves characterizing exposures to a single chemical across  
17 multiple exposure routes. Due to the range of applications for which decaBDE and MWCNTs can be  
18 used, release from multiple products and subsequent exposure via multiple routes is anticipated.

### *Decabromodiphenyl Ether*

19 BDE-209 and the other PBDEs are ubiquitous in the environment ([Daso et al., 2010](#)). The  
20 average daily intake of PBDEs from various routes has been evaluated, and inhalation of dust provides  
21 the highest contribution to body burden of PBDEs. As discussed in Section 4.1.2.5, levels of BDE-209 in  
22 household dust are orders of magnitude higher than in other matrices, by weight. BDE-209 is also the  
23 main PBDE contaminant in household dust ([Daso et al., 2010](#)). Data are not available on the relative  
24 contribution to household dust of BDE-209 from textile sources.

25 Measurable levels of BDE-209 are found in various types of food worldwide, including milk,  
26 fish, shellfish, eggs, beef, chicken, cheese, butter, and other dairy products. The highest concentrations in  
27 food have been reported for cod liver, with fish generally making up the highest dietary source of  
28 BDE-209 ([Daso et al., 2010](#); [Frederiksen et al., 2009](#)).

29 As a result of exposure from various sources, BDE-209 has been detected in breast milk, serum  
30 samples, umbilical cord blood, and the placenta of humans ([Daso et al., 2010](#); [Frederiksen et al., 2009](#)).

1 Ingestion of food, ingestion of dust, inhalation of dust, and dermal contact with soil/dust are the known  
2 pathways by which humans are primarily exposed to BDE-209. One review estimates that exposure to  
3 BDE-209 from ingestion and dermal contact with soil and dust represents more than 29% of total PBDE  
4 exposure from these exposure routes, and that exposure through those routes accounts for 82% of total  
5 PBDE exposure from all routes ([Lorber, 2008](#)).

***Multiwalled Carbon Nanotubes***

6 As described in Text Box 4-2, the properties of MWCNTs are easily altered through manipulation  
7 of material characteristics such as size, bundling affinity, and surface treatments, and the degree to which  
8 these specific changes affect the overall exposure profile is unclear. Moreover, the composition of  
9 MWCNT formulations can vary with differences in synthesis techniques and remaining impurities from  
10 manufacturing stock. If small changes in MWCNT characteristics result in measurable changes in the  
11 nature and extent of exposure, each MWCNT formulation might be considered a unique substance;  
12 therefore, MWCNTs produced by different manufacturers using different techniques might introduce  
13 discrete sets of aggregate exposures. No consensus has been reached on which physicochemical  
14 characteristics drive changes in exposure potential or what magnitude of change to any specific  
15 characteristic or property is necessary to elicit a measureable change in exposure.

16 In addition to different material designs, MWCNTs can be used in a wide range of possible  
17 applications, including in coatings, electronics, adhesives, polymer composites, thermoplastics, and  
18 others. MWCNT applications can then be used in textiles, aerospace, construction, sporting goods,  
19 medical applications, and many other types of products ([Aschberger et al., 2010](#)). Thus, the potential for  
20 exposure to MWCNTs exists where humans interact with any of these products as producers or  
21 consumers or when CNTs are released to environmental media.

22 Exposure to MWCNTs is likely to occur through inhalation of MWCNT bundles and MWCNTs  
23 sorbed to dust produced during the manufacture and processing of MWCNTs and composites containing  
24 MWCNTs. A secondary pathway is through dermal exposure, which could occur in occupational settings  
25 from dust settling on work surfaces. For consumers, exposure could occur from the abrasion or wear of  
26 products containing MWCNTs. The general public could be exposed to MWCNTs via drinking water,  
27 contact with contaminated soil, ingestion and inhalation of household dust, dermal contact with surfaces  
28 upon which MWCNTs and dust have settled, and other pathways as a result of their release from product  
29 matrices. MWCNT releases from composite materials, such as those used in sporting goods, plastics,  
30 touchscreens, and batteries are expected to be minimal, if not negligible, during consumer use because  
31 MWCNTs used for these products are bound in relatively strong matrices. End-of-life product  
32 dismantling, land-filling, and incineration, however, might offer greater potential for release of  
33 constituent materials to environmental compartments because many of the processes involved in end-of-

1 life practices are intended to break down the strong matrices in which the MWCNTs are embedded  
2 ([Aschberger et al., 2010](#)). What the implications of these releases will be on exposures and impacts to  
3 human health, ecological receptors, and other receptors is not yet known.

4 The anticipated market trend for production of MWCNTs is strong growth in the near future,  
5 especially as production costs drop and a wider variety of applications is discovered ([Lam et al., 2006](#)).  
6 Strong market growth and diverse applications could lead to a greater diversity and number of exposure  
7 scenarios, thus increasing the aggregate exposure potential for MWCNTs.

## 4.5. Cumulative Exposures

8 As stated in *The Exposure Factors Handbook* ([U.S. EPA, 2011](#)), “Cumulative exposure is defined  
9 as the exposure to multiple agents or stressors via multiple routes.” For the purpose of this case study, the  
10 “multiple agents or stressors” considered to contribute to cumulative exposure include those substances  
11 that are produced or released as a result of the product life cycles of decaBDE or MWCNT flame-  
12 retardant upholstery textile coatings, facilitate uptake of decaBDE or MWCNTs into humans and biota,  
13 are taken up as a result of decaBDE or MWCNT exposures, or induce effects in humans or biota through  
14 a comparable or synergistic mode of action. As mentioned in Section 4.4, different characteristics of  
15 different MWCNT formulations could result in the necessity to consider different formulations as unique  
16 stressors, in which case each formulation might represent a contribution to cumulative exposures.

### *Decabromodiphenyl Ether*

17 As discussed in Section 4.4 on aggregate exposure, PBDEs are ubiquitous in the environment due  
18 to their widespread use and physicochemical characteristics. The lower brominated congeners can be  
19 metabolites of higher congeners such as BDE-209, and subsequent exposure to lower congeners is likely  
20 when BDE-209 is released to the environment. Like BDE-209, many of the lower brominated congeners  
21 such as BDE-47 and BDE-99 can bioaccumulate, and the lower brominated congeners generally are more  
22 toxic than BDE-209. Exposure to the lower brominated metabolites of BDE-209 is also likely following  
23 environmental degradation or aging of composites or textiles containing BDE-209 ([Lagalante et al., 2011](#);  
24 [Christiansson et al., 2008](#)).

25 Manufactured textiles treated with decaBDE could include impurities from the synthesis process  
26 such as PBDDs and PBDFs ([Ren et al., 2011](#)). Breakdown or aging of flame-retardant textiles could  
27 contribute trace amounts of these pollutants to the environment. In addition, disposal or incineration of  
28 these textiles might generate more impurities.

29 Synergistic and antagonistic reactions have been observed in composites. Antimony compounds,  
30 which are typically used in the formulation of flame retardants containing decaBDE, tend to act



1 synergistically with halogenated flame retardants to produce highly corrosive hydrogen chloride gas or  
2 hydrogen bromide gas, for example ([Textile Exchange, 2012](#)). These exposures likely would be limited to  
3 manufacturing activities. The decomposition or incineration of manufactured textiles, however, might  
4 release other gases that could cause synergistic reactions.

### *Multiwalled Carbon Nanotubes*

5 Depending on which feedstocks are used in the manufacturing process, by-products might differ;  
6 therefore, coexposures to MWCNTs and other compounds might differ. Although the generation of  
7 impurities is likely during the manufacturing process, MWCNTs are typically purified after synthesis  
8 with varying degrees of success (see Appendix C). As described in Section 2.2.2.2, Plata et al. ([2009](#))  
9 observed production of 45 side-products of CVD synthesis of MWCNTs, including polycyclic aromatic  
10 hydrocarbons, methane, and volatile organic carbons. Single-walled carbon nanotube production can  
11 result in by-products of sodium hydroxide, ethanol, water, filtrate, and scrap membrane ([Healy et al.,](#)  
12 [2008](#)), but whether these by-products also will be generated by MWCNT synthesis is unclear.

13 Functionalization, which involves covalent attachment of submolecular components to the  
14 MWCNTs, is required before MWCNTs can be dispersed into polymers or organic solvents.  
15 Functionalization can involve several different reagents, depending on the process used, as listed in Table  
16 2-3. Any of the MWCNT-containing textiles could include small amounts of the reagents. No data were  
17 found, however, on the by-products or impurities in textiles treated with MWCNT flame-retardant  
18 coatings.

19 CNTs released to the environment might bind or sequester pollutants in a form that is not  
20 bioavailable, thus reducing the impact of other toxic substances. For example, when MWCNTs are added  
21 to sewage sludge, seed germination and root growth increased, which could be because the MWCNTs  
22 bound pollutants (e.g., heavy metals, organic compounds) present in the sludge ([Oleszczuk et al., 2011](#)).  
23 On the other hand, MWCNTs might facilitate transport of these pollutants through environmental  
24 compartments, across biological boundaries, and into cells, where they could react with cell machinery  
25 ([Johnston et al., 2010](#)).

26 Increasing production and market growth for products containing CNTs likely will lead to  
27 increasing levels of CNTs, by-products, and related compounds in the environment, as well as an increase  
28 in exposures. Due to the heterogeneous nature of MWCNTs, the various manufacturing processes used,  
29 exposure to a wide variety of CNTs and by-products from many different sources is possible. In addition,  
30 the environmental persistence of CNTs could lead to long-term exposures or consecutive exposures in  
31 multiple receptors.

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# Chapter 5. Potential Human Health, Ecological, and Other Impacts

1           The final step of compiling information into the comprehensive environmental assessment (CEA)  
2 framework is to link the information described in the previous chapters on the product life cycle;  
3 transport, transformation, and fate; and exposure-dose with potential impacts to receptors. The CEA  
4 framework includes information relevant to impacts on human health and ecological receptors, similar to  
5 what might be investigated in traditional risk assessment processes, as well as other plausible impacts that  
6 might be considered in life-cycle-focused assessments (e.g., socioeconomics, climate change, resource  
7 depletion).

8           Section 5.1 discusses potential impacts of exposure to decabromodiphenyl ether (decaBDE),  
9 multiwalled carbon nanotubes (MWCNTs), and related contaminants on human health. This section relies  
10 heavily on evidence from experimental studies with laboratory animals, the results of which could be  
11 extrapolated to humans using established quantitative toxicity assessment techniques. As discussed in  
12 Chapter 4, humans could be exposed to decaBDE, MWCNTs, or related contaminants from flame-  
13 retardant upholstery textiles through a variety of pathways, reaching receptors through dermal deposition,  
14 oral ingestion, or inhalation of these contaminants. This section discusses potential health impacts from  
15 these exposure routes; data are grouped to illustrate the types of impacts (e.g., pulmonary toxicity, skin  
16 irritation, reproductive effects) observed in studies with laboratory animals exposed to decaBDE or  
17 MWCNTs and sub-grouped by exposure routes for each impact.

18           Section 5.2 discusses the potential impacts of environmental media contaminated with decaBDE  
19 and MWCNTs on ecological health, which encompasses impacts on the organism, population, and  
20 ecosystem levels. This section is therefore approached from an ecosystem perspective (aquatic vs.  
21 terrestrial), and data on groups of organisms within those ecosystems are summarized. The discussion of  
22 impacts to ecological health focuses on identifying and comparing data on exposure levels that might  
23 cause significant mortality, delayed growth or development, reproductive defects, or other impacts that  
24 could alter community structure and potentially cause ecosystem collapse.

25           Finally, Section 5.3 discusses other plausible impacts resulting from the product life cycles of  
26 decaBDE and MWCNTs in flame-retardant upholstery textiles. The section includes a consideration of  
27 the energy input requirements for synthesis of the two compounds, the economic impacts related to the

1 cost of material production, and the potential for disproportionate impacts on populations with lower  
2 socioeconomic status.

3 As noted throughout this document, MWCNTs are not a single material, but rather a mixture of  
4 materials with different physicochemical properties. Text Box 5-1 provides introductory-level detail on  
5 how changes in physicochemical properties might influence toxicity. For the purpose of this case study,  
6 however, MWCNTs are generally regarded as a single class of materials. Throughout this chapter, where  
7 physicochemical properties can be related to effects on particular outcomes (e.g., fiber length on  
8 inhalation endpoints), these properties are described and their potential influences on effects are  
9 discussed. Additionally, Appendix F presents detailed toxicokinetic and toxicological study summaries in  
10 which the MWCNT characteristics and components of test designs that influence toxicological outcomes  
11 are provided.

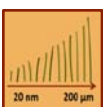
## 5.1. Human Health Effects

12 This section discusses the potential human health effects resulting from exposures to decaBDE  
13 and MWCNTs. As noted in Chapter 4, exposure to both of these materials from aggregate sources is  
14 likely; no studies were found that investigate impacts to human health that can be attributed directly to  
15 exposure to decaBDE, MWCNTs, or related compounds released during the life cycles of decaBDE and  
16 MWCNT flame-retardant upholstery textile coatings. Toxicology studies presented for decaBDE  
17 generally were conducted using BDE-209. As discussed in Chapter 3 (see Text Box 3-1), environmental  
18 degradation and debromination of decaBDE results in contamination of media with lower polybrominated  
19 diphenyl ether (PBDE) congeners. These lower PBDEs have toxicological relevance, as they are more  
20 bioavailable than decaBDE and potentially more toxic; toxicity of PBDEs generally decreases with  
21 increased number of bromine atoms ([Rahman et al., 2001](#)). Primary literature on MWCNTs was identified  
22 for most endpoints discussed in the following sections. If primary literature was not identified on  
23 MWCNTs, however, literature on single-walled carbon nanotubes (SWCNTs) was considered.

24 Toxicology studies conducted on animals comprise much of the information discussed in this  
25 chapter because studies on humans in the literature are limited. Effects observed in animal studies are  
26 typically extrapolated to humans when conducting quantitative toxicity assessments (e.g., when  
27 calculating a reference dose [RfD] or reference concentration [RfC]; see Section 4.2.5). Potential health  
28 effects associated with all routes of exposure (dermal, inhalation, and oral) are presented in this section  
29 because each is plausible for humans (see Chapter 4 for additional exposure scenario information).

### Text Box 5-1. Specific Physicochemical Properties of Multiwalled Carbon Nanotubes Shown to Influence Toxicity

As introduced in Text Box 1-1, not all multiwalled carbon nanotubes (MWCNTs) possess the same physicochemical characteristics or behave in a similar manner. And many physicochemical characteristics of MWCNTs are interrelated, making isolating one characteristic and determining how it influences toxicity difficult. For example, ground MWCNTs have been observed to induce more inflammation than their unground counterparts, but whether this response results from reduced fiber length or reduced bundling, which is itself related to a change in surface properties introduced by the grinding process (Muller et al., 2005), is unclear. Further, general assumptions about the toxicity of CNTs are rarely made without also presenting several exceptions. Dispersion state (and the characteristics that influence it, such as morphology and functionalization), for example, appears to be a driving factor behind granuloma formation, with more highly bundled CNTs inducing large intraluminal granulomas localized in the bronchi ground, and better dispersed CNTs inducing granulomas in the interstitial tissue of the alveolar spaces and interstitium. The following physicochemical characteristics have been identified as contributing to changes in the toxicity of CNTs in vitro and in vivo [as summarized by Johnston et al. (2010)].



**Morphology.** Aspects of morphology, such as the diameter, length, and bundled state of CNTs might influence toxicity. Following peritoneal injection, long, relatively straight CNTs can induce asbestos-like effects (i.e., mesotheliomas), whereas bundles of shorter CNTs do not. Longer MWCNTs also have been associated with a greater inflammatory response than shorter MWCNTs following dermal exposure. Cells might attempt to take up CNTs that are too long and straight to be fully engulfed, thereby resulting in high reactive oxygen species and pro-inflammatory cytokine release due to frustrated phagocytosis. In contrast, shorter bundled CNTs that are more easily engulfed by cells produce little inflammatory response. Most toxicological studies use shorter CNTs (typically only a few microns in length), and many studies do not characterize the length of the CNTs used due to the tendency of the CNTs to bundle, so the role of length in toxicity is not well understood. Diameter might play a role in toxicity; as studies have shown that thin MWCNTs (diameters of 50 nm or less) are less toxic than thick MWCNTs (diameters of 70 nm or more) (Fenoglio et al., 2012; Nagai et al., 2011). Kim et al. (2011) reported that while aspect ratio (the ratio of the CNT diameter and CNT length) did not impact the direct genotoxicity of MWCNTs, aspect ratio could impact other aspects of toxicity such as oxidative stressor inflammation that could indirectly induce genotoxicity; similarly, others have suggested that aspect ratio plays a large role in toxicity (e.g., structural similarities with asbestos fibers) (Stella, 2011; Johnston et al., 2010; Pacurari et al., 2010; Saeed, 2010).



**Surface Functionalization.** Alterations of surface chemistry can both enhance and reduce toxicity. Some surface modifications, such as nitrogen-doping, result in less toxicity than pure CNTs because the modification makes CNTs more biocompatible. Other surface modifications, such as oxidation, result in greater toxicity than pristine CNTs presumably because the modification promotes better dispersion of the CNTs and greater interaction with cells. Some surface modifications can result in altered shape or form of the CNTs, for example prolonged oxidation treatment results in shorter and straighter CNTs with different surface chemistry than nontreated CNTs. In a study by Jain et al. (2011), authors found that toxicity of MWCNTs critically depended on functionalization density; a higher density of surface carboxyl groups resulted in lower toxicity to male Swiss mice over a 4-week period.



**Contaminants.** Higher levels of metal impurities in CNTs are associated with an increase in toxicity. For example, cobalt and nickel catalysts that remain in trace concentrations after CNT purification are likely responsible for delayed hatching observed in zebrafish exposed as embryos to CNTs. Other potential contaminants remaining after the manufacturing process include iron, amorphous carbon, hydrocarbons, and endotoxins, all of which can induce unique toxic impacts. Although unpurified CNTs generally induce higher levels of toxicity (as evidenced by higher levels of cytotoxicity, morphological changes in cells, release of pro-inflammatory cytokines, and glutathione depletion, among other effects), many purification processes are known to result in structural changes to the CNTs, making it difficult to attribute increases in toxicity to contaminant content alone. Further, excluding certain unavoidable contaminants that are integral to an MWCNT's life cycle from consideration in toxicity studies might not be appropriate (Johnston et al., 2010).



**Wall Number.** Several studies have illustrated that single-walled CNTs (SWCNTs) are potentially more toxic than MWCNTs (Inoue et al., 2008; Tian et al., 2006; Jia et al., 2005; Radomski et al., 2005; Warheit et al., 2004); however, other physicochemical properties likely varied between the SWCNTs and MWCNTs used in these studies, making conclusions on the impact of number of walls difficult to decipher (Johnston et al., 2010).

1 Dermal and oral exposures to decaBDE in dust seem to be the primary routes of exposure for  
2 consumer populations, but whether this is true for MWCNTs is unclear (see Section 4.2.2). Because of  
3 higher levels of decaBDE contamination in dust and on other particles, the oral and dermal routes might  
4 also be expected to be prominent for general public exposures, but again, whether this is true for  
5 MWCNTs is unclear (see Section 4.2.3). Available data for decaBDE and MWCNTs indicate that the  
6 inhalation exposure route appears to dominate for workers (see Section 4.2.1). Although inhalation is a  
7 possible route of exposure, especially for workers, many inhalation toxicology studies identified were  
8 conducted by administering the test material (decaBDE or MWCNTs) via intratracheal instillation and  
9 pharyngeal aspiration; these routes of administration require an invasive delivery of chemicals or particles  
10 and are not as physiologically relevant for risk assessment purposes, but could provide biological  
11 information useful for qualitative, mode-of-action determinations.

12 Available information on these exposure routes in experimental animal studies is grouped by the  
13 main types of health impacts observed in the literature, namely, in vivo and in vitro data on systemic  
14 toxicity, pulmonary toxicity, eye irritation, skin irritation, reproductive effects, developmental effects,  
15 immune system effects, genotoxicity/mutagenicity, carcinogenicity, and susceptible populations.  
16 Toxicology studies were reviewed and determined to be key if the following criteria were met:

- 17 • appropriate species and test system were used,
- 18 • appropriate dose levels were used,
- 19 • route of exposure was appropriate for humans,
- 20 • control groups were appropriate, and
- 21 • the study was consistent with standard principles and practices.

22 In some cases, multiple studies investigating the same endpoint were available, and the most  
23 robust study or the study that most closely aligned with current guidelines for toxicity testing was chosen  
24 as key. In other cases, no studies were available that met all the criteria provided above; available studies  
25 were then summarized with deficiencies noted in the text. If the study was considered key, a written  
26 summary was included in the appropriate section of this chapter. Key studies and supporting nonkey  
27 studies are summarized in Table F-3 through Table F-11 in Appendix F. Because a large amount of  
28 published data is available for decaBDE, key studies presented in text are primarily those summarized by  
29 reviews or agency reports, and only a representative subset of studies are included in Appendix F.

30 The paragraph and summary tables that follow (see Table 5-1) provide an overview of the  
31 findings for human health effects of decaBDE and MWCNTs, after which a detailed discussion of the  
32 available data is presented.

**Table 5-1. Summary of effects observed after dermal, oral, and inhalation exposure to decaBDE and MWCNTs.**

Route of exposure	Observed effect	DecaBDE			MWCNTs		
		Yes	No	No data	Yes	No	No data
<b>Dermal</b>							
Local effects	Skin irritation		X		X (weak <sup>1</sup> )		
	Skin sensitization		X			X	
	Ocular irritation		X		X (weak <sup>2</sup> )		
Other effects	Acute toxicity		X				X
	Subchronic toxicity			X			X
	Chronic toxicity			X			X
<b>Inhalation</b>							
Local effects	Inflammation			X	X <sup>3</sup>		
	Respiratory sensitization			X	X <sup>3</sup>		
Other effects	Acute toxicity		X				X
	Subchronic toxicity			X		X	
	Chronic toxicity			X			X
	Immunotoxicity			X	X <sup>4</sup>		
<b>Oral</b>							
Effects	Acute toxicity		X				X
	Subchronic toxicity	X <sup>5</sup>					X
	Chronic toxicity	X <sup>5</sup>					X
	Reproductive/developmental	X <sup>6</sup>					X (weak) <sup>7</sup>

<sup>1</sup>Exposure resulted in a primary irritation index (PII) of 0.6 (calculated by mean dermal response score at 24 hr + mean dermal response score at 48h + mean dermal response score at 72 hr divided by 3; a PII score greater than 5 is considered positive) when animals were exposed to 1% Nikkiso-MWCNTs in an OECD 406-compliant study ([Ema et al., 2011](#)).

<sup>2</sup>Conjunctival redness and blood vessel hyperemia at 1 hr, but not at 24 hr ([Ema et al., 2011](#)).

<sup>3</sup>Inflammation was found in three OECD-compliant studies ([Pauluhn, 2010b](#); [Ellinger-Ziegelbauer and Pauluhn, 2009](#); [Ma-Hock et al., 2009](#)); respiratory sensitization was found in Park et al. ([2009](#)).

<sup>4</sup>Immunosuppressive results were found in Mitchell et al. ([2009](#); [2007](#)) and Nygaard et al. ([2011](#); [Nygaard et al., 2009](#)).

<sup>5</sup>Effects included changes to thyroid and liver observed in subchronic and chronic oral studies ([NTP, 1986](#); [Norris et al., 1975](#); [Norris et al., 1973](#)).

<sup>6</sup>Effects reported in response to neonatal exposure include changes in sperm parameters ([Tseng et al., 2006](#)) and changes in locomotor activity or altered expression of proteins in the central nervous system ([Johansson et al., 2008](#); [Viberg et al., 2008](#); [Viberg et al., 2007](#); [Viberg et al., 2003](#)).

<sup>7</sup>Effects reported in response to neonatal exposure (via intraperitoneal injection) included external and skeletal malformations ([Fujitani et al., 2012](#)); an oral study did not report any developmental effects ([Lim et al., 2011](#)).

### *Overview of Decabromodiphenyl Ether*

1 Most toxicological studies for decaBDE involve the oral route of exposure (see Section 4.2.2 for  
2 discussion on why the oral route appears to be a primary exposure pathway for decaBDE), with thyroid  
3 and liver changes observed in rats and mice in subchronic and chronic studies ([NTP, 1986](#); [Norris et al.,  
4 1975](#)). Several studies ([Johansson et al., 2008](#); [Viberg et al., 2008](#); [Viberg et al., 2007](#); [Tseng et al., 2006](#);  
5 [Viberg et al., 2003](#)) also reported effects of neonatal exposure, including changes in sperm parameters  
6 ([Tseng et al., 2006](#)) and changes in locomotor activity or altered expression of proteins in the central  
7 nervous system ([Johansson et al., 2008](#); [Viberg et al., 2008](#); [Viberg et al., 2007](#); [Viberg et al., 2003](#)). An  
8 RfD of 0.007 mg/kg/day was calculated in 2008 ([U.S. EPA, 2008b](#)) by the U.S. Environmental Protection  
9 Agency (EPA) based on the developmental neurobehavioral effects observed in the Viberg et al. ([2003](#))  
10 study (see Section 5.1.1.1 for details on RfD derivation).

11 With regard to carcinogenicity, the National Toxicology Program (NTP) stated that there was  
12 “some evidence of carcinogenicity” for male and female rats based on significantly increased incidences  
13 of neoplastic nodules of the liver, and “equivocal evidence of carcinogenicity” for male mice based on a  
14 significantly increased incidence of hepatocellular tumors in only the low-dose group and non-statistically  
15 significant increases in thyroid follicular cell tumors in both dose groups ([NTP, 1986](#)). Additionally, the  
16 International Agency for Research on Cancer determined that decaBDE is not classifiable as a human  
17 carcinogen (Group 3) based on limited evidence in animals ([IARC, 1998](#)). In 2008, EPA used the  
18 descriptor “suggestive evidence of carcinogenic potential” for decaBDE ([U.S. EPA, 2008b](#)) under  
19 relevant guidelines ([U.S. EPA, 2005b](#)) (see Section 5.1.11).

### *Overview of Multiwalled Carbon Nanotubes*

20 Most toxicological studies for MWCNTs involve the dermal and inhalation routes of exposure  
21 (see Section 4.2.2 for discussion of why dermal and inhalation might be primary exposure pathways for  
22 MWCNTs in occupational settings); effects were predominantly localized and included irritation (both  
23 skin and ocular), sensitization (respiratory), and inflammation (respiratory). When determining the  
24 toxicity of MWCNTs for humans, the following factors should be considered:

- 25 • Numerous in vitro and in vivo studies have shown that carbon nanotubes (CNTs) (both  
26 SWCNTs and MWCNTs) might induce prominent pulmonary inflammation ([Pauluhn, 2010b](#);  
27 [Ellinger-Ziegelbauer and Pauluhn, 2009](#); [Ma-Hock et al., 2009](#)) (see Section 5.1.3).
- 28 • At least some CNTs were found to contain a large proportion of metal catalyst (iron and  
29 nickel), which contributes significantly to oxidative stress, indicated by the formation of free  
30 radicals and accumulation of peroxidative products, depletion of total antioxidant reserve, and  
31 a loss of cell viability ([Shvedova et al., 2003](#)). Transition metals such as iron can be important  
32 in the toxicity of a range of pathogenic dusts because of their ability to cause oxidative stress  
33 ([Pulskamp et al., 2007](#); [Ghio et al., 1999](#); [Donaldson et al., 1996](#); [Kennedy et al., 1989](#)).



1 Although no subchronic inhalation studies were identified for systemic toxicity (i.e., toxic effects  
2 resulting from absorption and distribution of a toxicant at a site distant from its entry point) in animals  
3 (see Section 5.1.2.2), exposure to MWCNTs altered immunological function after acute inhalation  
4 exposure ([Mitchell et al., 2009](#); [Mitchell et al., 2007](#)) (see Section 5.1.8). The carcinogenicity of  
5 MWCNTs following inhalation is unknown because no studies were identified using the inhalation route  
6 of exposure. Several studies using methods such as instillation and intraperitoneal injection ([Sakamoto et  
7 al., 2009](#); [Poland et al., 2008](#); [Takagi et al., 2008](#)), however, demonstrate that certain forms of MWCNTs  
8 could behave in a manner similar to asbestos and induce mesotheliomas, indicating that the inhalation  
9 route of exposure might be of toxicological concern.

### 5.1.1. Quantitative Toxicity Assessment

10 In a quantitative toxicity assessment, appropriate toxicity information is collected and evaluated.  
11 These data then are used to derive toxicity values, such as an RfD for oral exposure or RfC for inhalation  
12 exposure. Similar to an RfD (as defined in Section 4.2.5), an RfC is an estimate of a continuous inhalation  
13 exposure for a given duration to the human population (including susceptible subgroups) that is likely to  
14 be without an appreciable risk of adverse health effects over a lifetime. Both values, an RfC and an RfD,  
15 are derived from a benchmark dose lower confidence limit, no-observed-adverse-effect level (NOAEL), a  
16 lowest-observed-adverse-effect level (LOAEL), or another suitable point of departure, with  
17 uncertainty/variability factors applied to reflect limitations of the data used. Other types of toxicity values  
18 also can be derived to provide exposure limit values for other exposure durations (e.g., acute or  
19 subchronic), more specific populations (e.g., healthy workers), or specific exposure contexts (e.g.,  
20 emergency response or occupational exposure; see Section 4.2.5). The sections that follow discuss the  
21 derivation of an RfD for decaBDE; due to limited data, an RfC for decaBDE has not been determined.  
22 EPA has not evaluated MWCNTs to derive an RfD or an RfC. The only toxicologically based reference  
23 value for MWCNTs derived by a government agency is the draft recommended exposure limit (REL)  
24 proposed by the National Institute for Occupational Safety and Health (NIOSH) for CNTs ([NIOSH,  
25 2010](#)), as discussed in Section 4.2.5. In addition, acute and subchronic human no-effect levels for general  
26 public inhalation exposures also have been proposed in the open literature; derivation of these values is  
27 briefly discussed in the sections that follow.

### 5.1.1.1. Health Reference Values

#### *Decabromodiphenyl Ether*

1 As mentioned in Section 4.2.5, an RfD of 0.007 mg/kg/day was calculated by EPA ([2008b](#)) based  
2 on developmental neurobehavioral effects observed in the Viberg et al. ([2003](#)) study (see Section 5.1.7).  
3 The NOAEL of 2.22 mg/kg from this study was used as the point of departure. A total uncertainty factor  
4 of 300 was applied to account for interspecies differences (10×), intraspecies differences (10×), and acute-  
5 to-chronic extrapolation (3×). As mentioned previously, due to the limited toxicity data available, an RfC  
6 for decaBDE has not been determined.

#### *Multiwalled Carbon Nanotubes*

7 To date, MWCNTs have not been evaluated by EPA to establish an RfD or RfC. As discussed in  
8 Section 4.2.5, NIOSH ([2010](#)) conducted a risk analysis for CNTs and established a draft REL of 7 µg/m<sup>3</sup>  
9 (the high estimate of the limit of quantification for NIOSH Method 5040) for elemental carbon, based on  
10 a working lifetime inhalation exposure of 0.2–2 µg/m<sup>3</sup> (8-hour time-weighted average) associated with a  
11 10% excess risk of early-stage adverse lung effects (95% lower confidence limit estimates). The REL was  
12 derived using two subchronic (90-day) animal inhalation studies ([Pauluhn, 2010b](#); [Ma-Hock et al., 2009](#)).

13 Although not derived by a government agency, Aschberger et al. ([2010](#)) estimated human no-  
14 effect levels for the general public of 0.25 µg/m<sup>3</sup> based on a LOAEL ([Ma-Hock et al., 2009](#)) and a  
15 NOAEL ([Pauluhn, 2010b](#)) of 0.1 mg/m<sup>3</sup> for MWCNTs from the two subchronic studies NIOSH ([2010](#))  
16 used in their derivation of an REL. Aschberger et al. ([2010](#)) also calculated a human no-effect level for  
17 acute exposure of 0.15 mg/m<sup>3</sup> from a LOAEL of 11 mg/m<sup>3</sup> based on the absence of inflammatory effects  
18 in an MWCNT rat study ([Ellinger-Ziegelbauer and Pauluhn, 2009](#)). Although both values were calculated  
19 based on the guidance provided by Registration, Evaluation, Authorisation and Restrictions of Chemicals  
20 for chemical safety assessment ([ECHA, 2008](#)), the relatively limited and often conflicting database of  
21 currently available toxicological values for MWCNTs suggests that these values are preliminary estimates  
22 associated with a high degree of uncertainty.

23 The two subchronic animal inhalation studies ([Pauluhn, 2010b](#); [Ma-Hock et al., 2009](#)) that were  
24 used to derive both the draft NIOSH ([2010](#)) REL and the subchronic human no-effect levels proposed by  
25 Aschberger et al. ([2010](#)) are described in detail in Section 5.1.3.

## 5.1.2. Systemic Toxicity

### 5.1.2.1. Acute

#### *Decabromodiphenyl Ether*

1 Acute toxicity studies for all routes of exposure were identified for decaBDE. Results indicate  
2 that, for all routes of exposure, decaBDE exhibits low acute toxicity. No mortality occurred after a 1-hour  
3 inhalation exposure in rats (5 animals/sex/group) to 200 mg/L BDE-209; no gross pathological changes  
4 were observed during the 2-week observation period ([CPTC, 1978](#)).

5 The low acute oral toxicity of decaBDE ([Zhou et al., 2001](#); [Kierkegaard et al., 1999](#); [Norris et al.,  
6 1973](#)) might be due in part to poor gastrointestinal absorption. No clinical signs of toxicity or death were  
7 observed when a single dose (up to 5000 mg/kg) of BDE-209 was administered to rats via gavage ([Great  
8 Lakes Chemical Corporation, 1994](#); [IRDC, 1990](#)).

9 The low acute dermal toxicity of decaBDE is presumed based on lack of treatment-related effects  
10 in rabbits following single administrations of 200 or 2000 mg/kg BDE-209 to clipped intact skin for  
11 24 hours (14-day observation period) ([IRDC, 1990](#); [Great Lakes Chemical Corporation, 1977](#)).

#### *Multiwalled Carbon Nanotubes*

12 No data were identified on the acute systemic toxicity of MWCNTs following inhalation  
13 exposure (see Section 5.1.8 for Immune System Effects). Acute inhalation studies identified for  
14 MWCNTs, including key studies, are presented in Section F.1.2 in Appendix F.

15 No data were identified on the acute toxicity of MWCNTs following oral or dermal exposure (see  
16 Section 5.1.5 for discussion of skin irritation). One oral acute toxicity study on SWCNTs was identified in  
17 which single doses of 1000 mg/kg body weight (bw) of three different types of SWCNTs  
18 (raw: 1 nm × 1–2 μm, 25% Fe; purified: 1 nm × 1–2 μm, <4% Fe; ultrashort: 1 nm × 20–80 nm, <1.5%  
19 Fe) were administered to mice ([Kolosnjaj-Tabi et al., 2010](#)). No signs of toxicity (such as reduced  
20 survival, delayed growth, behavioral abnormalities, or clinical chemistry changes) were observed for any  
21 type of SWCNT. An acute dermal exposure study was not identified for SWCNTs.

22 One acute intraperitoneal toxicity study was identified for MWCNTs. Patlolla et al. ([2011](#))  
23 observed decreased body-weight gain, and increased markers of oxidative stress and hepatotoxicity  
24 (increased reactive oxygen species in liver, enhanced activity of liver enzymes such as serum  
25 aminotransferases and alkaline phosphatases) in mice injected with 0.25, 0.5, or 0.75 mg/kg/day of  
26 purified, carboxylated MWCNTs for 5 days (see Table F-8 in Appendix F).

### 5.1.2.2. Subchronic

#### *Decabromodiphenyl Ether*

1 In humans, an increase in primary hyperthyroidism and a significant reduction in calf sensory and  
2 fibula motor nerve velocities were observed in workers exposed to decaBDE during manufacturing  
3 [(Bahn et al. (1980) as cited in NTP ([1986](#)); Bialik (1982), as cited in HSDB ([2011](#))]]; whether these  
4 effects are due to decaBDE or polybrominated biphenyls is unclear, however, because only  
5 polybrominated biphenyls were detected in blood.

6 Numerous subchronic oral studies were identified for decaBDE, and all studies considered,  
7 including those summarized below, are presented in Section F.1.2 in Appendix F. DecaBDE-related  
8 thyroid and liver changes were observed in male rats when administered a lower purity (77.4%) form of  
9 decaBDE ([Norris et al., 1975](#); [Norris et al., 1973](#)). Effects included thyroid hyperplasia, increased liver  
10 weight, and hepatic centrilobular cytoplasmic enlargement and vacuolation ([Norris et al., 1975](#); [Norris et](#)  
11 [al., 1973](#)).

#### *Multiwalled Carbon Nanotubes*

12 No data were identified on the subchronic systemic toxicity of MWCNTs following exposure by  
13 any route. See Section 5.1.3 for discussion of pulmonary effects and Section 5.1.8 for discussion of  
14 immune system effects following subchronic exposure.

### 5.1.2.3. Chronic

#### *Decabromodiphenyl Ether*

15 Numerous chronic oral studies were identified for decaBDE, and all studies considered, including  
16 those summarized below, are presented in Section F.1.2 in Appendix F. In a chronic study conducted by  
17 NTP ([1986](#)), a dose-dependent increase in thyroid follicular cell hyperplasia was observed in male mice  
18 fed BDE-209 (purity 94–97%) in the diet for 103 weeks ([NTP, 1986](#)); these effects were not observed in  
19 female mice or female and male rats that were similarly exposed to BDE-209. Centrilobular hypertrophy  
20 (consisting of enlarged hepatocytes with frothy vacuolated cytoplasm) also was observed in male mice,  
21 but not in female mice or in male and female rats ([NTP, 1986](#)). Incidences of thrombosis and  
22 degeneration of the liver were increased in male rats at the LOAEL (2240 mg/kg/day), but not at  
23 1120 mg/kg/day (NOAEL); these hepatic effects were not observed in female rats or in mice of either sex.  
24 The NTP ([1986](#)) studies were considered for the basis of the EPA ([2008b](#)) quantitative cancer assessment  
25 (see Section 5.1.11). Observed changes in liver weight and hepatocytomegaly might have been due to  
26 enzyme induction, as supported by recent studies conducted by Van der Ven et al. ([2008](#)) and Bruchajzer  
27 et al. ([2010](#)) (see Table F-7 in Appendix F).

### *Multiwalled Carbon Nanotubes*

1 No data were identified on the chronic systemic toxicity of MWCNTs following exposure by any  
2 route.

## 5.1.3. Pulmonary Toxicity

### *Decabromodiphenyl Ether*

3 When BDE-209 was administered to rats via a single intratracheal injection of 20 mg BDE-209  
4 dust (purity 77.4%) suspended in rat serum ([Dow Chemical Co, 1990b](#)), minimal histopathological  
5 changes (scattered focal aggregates of alveolar macrophages) occurred, consistent with retention of large  
6 dust particles that would not normally reach the lungs during inhalation. Rats exposed to 2000 or  
7 48,000 mg/m<sup>3</sup> BDE-209 for 1 hour exhibited dyspnea at both dose levels ([Great Lakes Chemical  
8 Corporation, 1994](#); [IRDC, 1990](#)); all animals survived until study termination and were normal at the end  
9 of the 14-day observation period (see Table F-5 in Appendix F).

### *Multiwalled Carbon Nanotubes*

10 The material characteristics and study details associated with the acute and subchronic inhalation  
11 studies identified for MWCNTs are presented in Section F.1.2, Table F-6 in Appendix F. No chronic  
12 inhalation studies were identified for MWCNTs. Inhalation studies (intratracheal, aspiration, or  
13 inhalation) generally have shown consistent toxicological responses, with exposed animals exhibiting  
14 pulmonary inflammation and fibrosis. Results reported for animals exposed to MWCNTs via intratracheal  
15 instillation ([Park et al., 2009](#); [Muller et al., 2008a](#); [Muller et al., 2008b](#); [Muller et al., 2005](#)), however,  
16 generally resulted in more severe effects than those observed for inhalation ([Pauluhn, 2010b](#); [Ellinger-  
17 Ziegelbauer and Pauluhn, 2009](#); [Li et al., 2009](#); [Li et al., 2007](#); [Mitchell et al., 2007](#)).

18 Pulmonary inflammation was observed in three Organisation for Economic Co-operation and  
19 Development-compliant animal inhalation studies (acute and subchronic) ([Pauluhn, 2010b](#); [Ellinger-  
20 Ziegelbauer and Pauluhn, 2009](#); [Ma-Hock et al., 2009](#)), with granulomas observed in both subchronic  
21 studies ([Pauluhn, 2010b](#); [Ma-Hock et al., 2009](#)). In the study conducted by Ma-Hock et al. ([2009](#)), a dose-  
22 related increase in the incidence of granulomatous inflammation in the lung and lung-associated lymph  
23 nodes was observed in dosed rats (head-nose exposure). At the mid and high exposures (0.5 and  
24 2.5 mg/m<sup>3</sup>, respectively), increased lung weights, pronounced multifocal granulomatous inflammation,  
25 diffuse histiocytic and neutrophilic inflammation, and intra-alveolar lipoproteinosis were observed in lung  
26 and lung-associated lymph nodes. Similar effects were observed in a study by Pauluhn ([2010b](#)), in which  
27 Wistar rats were exposed (nose only) to MWCNTs (0.1, 0.4, 1.5, 6 mg/m<sup>3</sup>); inflammatory changes in the  
28 distal nasal cavities were observed at all concentrations except the low dose. Additionally, dose-related

1 lesions of the upper respiratory tract (e.g., goblet cell hyperplasia or metaplasia, eosinophilic globules,  
2 and focal turbinate remodeling) and lower respiratory tract (e.g., inflammatory changes in the  
3 bronchioloalveolar region and increased interstitial collagen staining) were observed at higher doses. A  
4 study conducted by Kim et al. ([In Press](#)) showed that pulmonary DNA damage is initiated after very short  
5 exposure periods; a Comet assay performed on lung cells from rats exposed to 0.94 mg/m<sup>3</sup> MWCNTs  
6 6 hours per day for 5 days showed a significant increase in DNA damage compared to controls  
7 immediately and one month following the last exposure.

### 5.1.4. Eye Irritation

8 All in vivo eye irritation studies considered are presented in Sections F.1.2 (Tables F-3 and F-4  
9 for decaBDE and MWCNTs, respectively). Key studies are summarized below.

#### *Decabromodiphenyl Ether*

10 DecaBDE does not appear to be an eye irritant. Ocular exposure to dry solid decaBDE caused  
11 transient conjunctival irritation in washed and unwashed rabbit eyes when 100 mg of decaBDE was  
12 administered via instillation to the conjunctival sac ([NRC, 2000](#); [IRDC, 1990](#)). Effects in some rabbits  
13 included very slight conjunctival redness and chemosis and slight or moderate discharge ([Great Lakes  
14 Chemical Corporation, 1994](#)). Investigators concluded that the effects were not serious enough to be  
15 considered primary eye irritation ([IRDC, 1990](#); [Norris et al., 1975](#)). Pharmakon ([1994](#)) similarly reported  
16 that decaBDE (Saytex 102) did not cause primary eye irritation when instilled once (100 mg/eye) into the  
17 eyes of rabbits. Rats exposed to 2000 or 48,000 mg/m<sup>3</sup> BDE-209 dust in the ambient air for 1 hour,  
18 however, exhibited ocular porphyrin discharge at both dose levels, and eye squint at the high  
19 concentration ([IRDC, 1990](#)); all animals survived until study termination and were normal at the end of  
20 the 14-day observation period.

#### *Multiwalled Carbon Nanotubes*

21 With regard to ocular effects, one of two types of MWCNTs administered via instillation to the  
22 conjunctival sac resulted in conjunctival redness and blood vessel hyperemia at 1 hour, but not at 24 hours  
23 in an in vivo study conducted with rabbits. Differences in purity, diameter, and surface area (see  
24 Appendix F, Table F-4) between the two types of MWCNT tested may explain why effects were observed  
25 with only one of the two types of administered MWCNTs ([Ema et al., 2011](#)).

## 5.1.5. Skin Irritation

1           The material characteristics and study details associated with the in vivo dermal studies  
2 considered for decaBDE and MWCNTs are presented in Section F.1.2. in Appendix F.

### *Decabromodiphenyl Ether*

3           DecaBDE does not appear to be a skin irritant based on observations from a human skin irritation  
4 study ([Dow Chemical Co, 1990a](#); [Norris et al., 1975](#); [Norris et al., 1973](#)), a skin irritation study in rabbits  
5 ([IRDC, 1990](#); [Norris et al., 1975](#); [Norris et al., 1973](#)), and an acne-genesis study in rabbits ([Pharmakon](#)  
6 [Research International, 1994](#)). Dermal studies were conducted with BDE-209.

### *Multiwalled Carbon Nanotubes*

7           Based on the information available, the most irritating of several MWCNTs tested appears to be a  
8 weak skin irritant when tested on healthy intact skin ([Ema et al., 2011](#); [Kishore et al., 2009](#)). Data on  
9 dermabraded or damaged skin were not identified, but the available studies were done in accordance with  
10 accepted standard practices for conventional skin irritation tests, which involve use of healthy, intact skin  
11 exposed for 4 hours under semioccluded conditions.

## 5.1.6. Reproductive Effects

### *Decabromodiphenyl Ether*

12           In general, studies found that decaBDE was not a reproductive toxicant at doses up to and  
13 exceeding 1000 mg/kg/day ([Tseng et al., 2008](#); [Hardy et al., 2002](#); [Dow Chemical Co, 1990c](#); [NTP,](#)  
14 [1986](#)). Van der Ven et al. ([2008](#)) reported significant, decaBDE dose-related changes in epididymis and  
15 seminal vesicle weight for male rats and decreased activity of CYP17, a key enzyme in the androgen  
16 synthesis pathway, for female rats administered 1.9–60 mg/kg by oral gavage. No corresponding  
17 histopathological changes, sperm counts, or morphology of epididymal sperm, however, were observed.  
18 Based on these results, the authors concluded that BDE-209 might represent a hazard to reproductive  
19 health.

### *Multiwalled Carbon Nanotubes*

20           No in vivo reproductive studies were identified for MWCNTs.

## 5.1.7. Developmental Effects

### *Decabromodiphenyl Ether*

1 Several studies reported no developmental effects for decaBDE at doses up to and exceeding  
2 1000 mg/kg/day ([Hardy et al., 2009](#); [Tseng et al., 2008](#); [Hardy et al., 2002](#); [Dow Chemical Co., 1990c](#)). A  
3 significant increase in CYP450 activity in adult male CD-1 mouse offspring was noted in the study  
4 conducted by Tseng et al. ([2008](#)) at doses of 1500 mg/kg/day; this dose level, however, exceeds the  
5 current dose limit (e.g., 1000 mg/kg/day) recommended by international toxicity testing guidance  
6 documents ([OECD, 2007](#); [U.S. EPA, 1998](#)). Another study found significant increases in numbers of rat  
7 litters with subcutaneous edema and delayed ossification of skull bones at 1000 mg/kg/day ([Norris et al.,](#)  
8 [1975](#)); dams for this study were administered BDE-209 (77.4% containing 21.8% nonabromodiphenyl  
9 oxide and 0.8% octabromodiphenyl oxide) via gavage at dose levels of 0, 10, 100, or 1000 mg/kg/day.  
10 Consequently, the NOAEL and LOAEL for fetal effects in this study were 100 and 1000 mg/kg/day,  
11 respectively; the NOAEL for maternal effects was 1000 mg/kg/day.

12 In contrast, several studies did observe adverse effects when neonatal mice or rats were exposed  
13 orally to decaBDE at lower doses ([Johansson et al., 2008](#); [Viberg et al., 2008](#); [Viberg et al., 2007](#); [Tseng](#)  
14 [et al., 2006](#); [Viberg et al., 2003](#)). Effects of neonatal exposure included changes in sperm parameters  
15 ([Tseng et al., 2006](#)) and changes in spontaneous behavior or altered expression of proteins in the central  
16 nervous system ([Johansson et al., 2008](#); [Viberg et al., 2008](#); [Viberg et al., 2007](#); [Viberg et al., 2003](#)). Rice  
17 et al. ([2007](#)) orally exposed male and female mouse pups to decaBDE at doses of 0, 6, or 20 mg/kg/day  
18 from Postnatal Days (PNDs) 2 through 15. Treatment-related effects occurred only in the high-dose group  
19 and included a reduction in palpebral reflex on PND 14, a reduction in forelimb grip in males on PND 16,  
20 a change in the slope of the linear trend for serum T4 in males on PND 21, and a change in the linear  
21 slope of motor activity on PND 70. Of the available studies, Viberg et al. ([2003](#)) was selected for the  
22 derivation of the RfD (see Section 5.1.1.1).

### *Multiwalled Carbon Nanotubes*

23 One oral developmental study was identified in which MWCNTs were administered via gavage  
24 to pregnant Sprague-Dawley rat dams at doses of 0, 40, 200, and 1000 mg/kg/day on Gestation Days  
25 (GD) 6-19; dams were sacrificed on GD 20 ([Lim et al., 2011](#)). Minimal maternal toxicity was observed at  
26 1000 mg/kg/day. Although a dose-dependent decrease in thymus weight was observed, no effects were  
27 observed on maternal body weight, food consumption, and oxidant-antioxidant balance in the liver. No  
28 differences in gestation index, fetal death, fetal and placental weights, or sex ratio were observed as a  
29 result of MWCNT treatment. Therefore, the embryo-fetal NOAEL was 1000 mg/kg/day.



1 In a study by Fujitani et al. (2012), teratogenic effects were observed in fetuses when MWCNTs  
2 were administered via intraperitoneal or intratracheal injection to pregnant ICR mice in a single dose of  
3 0, 2, 3, 4, or 5 mg/kg on GD 9. Fetal examinations performed on GD 18 showed external and skeletal  
4 malformations such as short or absent tails, cleft palate, limb reduction deformities, fused ribs and  
5 vertebral bodies, and hypo/hyperphalangia (see Table F-8 in Appendix F).

## 5.1.8. Immune System Effects

### *Decabromodiphenyl Ether*

6 No immunology studies were identified for decaBDE.

### *Multiwalled Carbon Nanotubes*

7 Studies examining the immune system after administration of MWCNTs via inhalation are  
8 summarized in Section F.1.2 in Appendix F. Immunosuppression was observed in mice exposed to 0.3,  
9 1, or 5 mg/m<sup>3</sup> MWCNTs via inhalation for 14 days (Mitchell et al., 2007).<sup>15</sup> The immunosuppressive  
10 mechanism of MWCNTs could involve a signal originating in the lungs that activates cyclooxygenase  
11 enzymes in the spleen (Mitchell et al., 2009). Similarly, an acute inflammatory response was observed by  
12 Nygaard et al. (2009) following administration of MWCNTs via single intranasal injection to female  
13 BALB/cAnCrI mice at 200 or 400 µg/mouse (plus OVA).

14 Several studies were identified indicating that MWCNTs are respiratory sensitizers. In a study by  
15 Park et al. (2009), a potential allergic response in mice following intratracheal instillation of 50 mg/kg  
16 MWCNTs was observed. The authors noted that the significantly increased immunoglobulin E  
17 concentrations coupled with pro-inflammatory responses likely resulted from B-cell activation by IL-10.  
18 Inoue et al. (2009) similarly demonstrated a potential allergic response in mice following six weekly  
19 intratracheal instillations of 50 µg MWCNTs. The authors reported a significant increase in the number of  
20 total immune cells (including macrophages, neutrophils, eosinophils, and lymphocytes) in the bronchiolar  
21 lavage fluid, concurrent with infiltration of eosinophils, neutrophils, and mononuclear cells in the lung.  
22 Authors also noted a significant induction of goblet cell hyperplasia in the bronchial epithelial tissue,  
23 indicating that MWCNTs exacerbate metaplasia in the presence or absence of other allergens. Of note is  
24 that the Organisation for Economic Co-operation and Development currently has no guidelines for

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<sup>15</sup>This study was questioned after publication primarily because an image in the study indicated that nanofibers, not nanotubes, were used. Lison and Muller (2008) stated that although Mitchell et al. (2007) might be correct in their assertion, the results of these earlier installation experiments are “probably of little relevance to assess the hazard of MWCNT because they could not be reproduced upon inhalation exposure;” they maintain conclusions about immunological effects cannot be reached by Mitchell et al. (2007).

1 standardized respiratory sensitization studies, and the studies identified used intratracheal instillation, not  
2 inhalation, as the route of exposure.

3 One study was identified that used inhalation as the route of exposure. Ryman-Rasmussen et al.  
4 ([2009b](#)) exposed mice with allergic asthma to 100 mg/m<sup>3</sup> MWCNT aerosol for 6 hours (approximately 10  
5 mg/kg MWCNT total) and found that airway fibrosis differentially occurred in ovalbumin-sensitized mice  
6 versus nonsensitized mice. The authors concluded that airway fibrosis occurs as a result of MWCNT  
7 inhalation with preexisting inflammation, suggesting that individuals with preexisting allergic  
8 inflammation are susceptible. One study was identified suggesting immune effects from oral exposure to  
9 MWCNTs. As described in Section 5.1.7, Lim ([2011](#)) observed a decrease in thymus weight in dams  
10 following administration of MWCNTs at the highest dose tested (1000 mg/kg/day).

### 5.1.9. In Vitro Data

11 In vitro data can be used to make judgments on the toxic potential of stressors, but the relevance  
12 of in vitro data to predicting toxicological responses of “real-world” exposures is not always clear.

#### *Decabromodiphenyl Ether*

13 No in vitro data were identified for decaBDE.

#### *Multiwalled Carbon Nanotubes*

14 Multiple in vitro studies were identified for MWCNTs; a few were selected for discussion here  
15 and inclusion in Table F-9 in Appendix F to highlight the major themes and important concepts covered  
16 in the literature.

17 One in vitro study was identified on ocular effects of MWCNTs. The study produced negative  
18 results (i.e., no irritation was observed) when two sizes of MWCNTs were evaluated using hen’s egg test  
19 chorioallantoic membrane with white leghorn chicken eggs ([Kishore et al., 2009](#)).

20 Negative results also were observed in an in vitro dermal irritation study by Kishore et al. ([2009](#)),  
21 in which two sizes of MWCNTs were evaluated using the three-dimensional human epidermis model with  
22 human skin cells. The relevance of dermal in vitro studies to occupational, consumer, and general public  
23 exposures, however, depends on the capability of CNTs to penetrate the stratum corneum barrier in vivo,  
24 which is unknown at this time ([Monteiro-Riviere and Inman, 2006](#)).

25 Radomski et al. ([2005](#)) investigated effects of MWCNTs on platelet aggregation and found that  
26 MWCNTs were capable of promoting platelet aggregation. One possible mechanism for thrombus  
27 development following MWCNT exposure observed by the study authors was a change in the abundance  
28 of GPIIb/IIIa (glycoprotein integrin receptor), which triggers platelet adhesion.

1 Other in vitro studies have found that MWCNTs induce proinflammatory effects, generate  
2 reactive oxygen species and oxidative stress, inhibit phagocytosis, and induce apoptosis, as reported in a  
3 review article ([Donaldson et al., 2006](#)). Similarly, in human T cells, MWCNTs were found to decrease  
4 cell viability and increase programmed cell death in a dose- and time-dependent manner between 40 and  
5 400 µg/mL ([Bottini et al., 2006](#)). The study authors noted that the level of toxicity was significantly  
6 greater for oxidized MWCNTs compared to their pristine counterparts ([Bottini et al., 2006](#)).

## 5.1.10. Genotoxicity/Mutagenicity

### *Decabromodiphenyl Ether*

7 DecaBDE does not appear to be genotoxic and generally did not induce (1) gene mutations in  
8 bacteria (*Salmonella typhimurium*) in Ames assays ([Wagner and Klug, 1998](#); [GSRI, 1990](#); [Huntingdon](#)  
9 [Life Sciences, 1990](#); [NTP, 1986](#); [Haworth et al., 1983](#); [Litton Bionetics, 1976](#)), (2) gene mutations in  
10 mouse L5178Y lymphoma cells, (3) chromosomal aberrations in mouse bone marrow cells, or (4) sister-  
11 chromatid exchanges or cell transformation in Chinese hamster ovary cells ([Myhr et al., 1990](#); [McGregor](#)  
12 [et al., 1988](#)). These findings are consistent with those reported by EPA ([U.S. EPA, 2008b](#)). Because  
13 decaBDE has consistently failed to produce genotoxic or mutagenic responses, the aforementioned  
14 studies are not summarized in Appendix F.

### *Multiwalled Carbon Nanotubes*

15 Standard and modified in vitro genotoxicity tests have been conducted to investigate the  
16 genotoxic potential of CNTs. Genotoxic potential of CNTs is uncertain at this time, however, as available  
17 tests have shown contradictory results, which might be due to differences in composition and  
18 physicochemical characteristics of the CNTs (see Table F-9 in Appendix F).

19 MWCNTs were not found to be mutagenic when evaluated with the Ames test<sup>16</sup> using  
20 *S. typhimurium* with and without metabolic activation ([Di Sotto et al., 2009](#); [Wirmitzer et al., 2009](#)).  
21 Bacterial mutagenicity-based assays, however, might not be suitable for detecting genotoxicity induced  
22 by nanoscale materials because prokaryotes lack the ability to perform endocytosis, and the nanoscale  
23 materials might not be able to diffuse across the bacterial cell wall. This lack of uptake could lead to  
24 false-negative results ([Singh et al., 2009](#)). Similarly, purified MWCNTs did not show genotoxic activity  
25 in several other genotoxicity assays at different dose levels and in different test systems, including  
26 micronucleus and sister-chromatid exchange assays of human lymphocyte cells ([Szendi and Varga, 2008](#))  
27 and a chromosome aberration assay of Chinese hamster lung cells ([Asakura et al., 2010](#)). The MWCNTs  
28 used in these tests were predominantly of high purity and contained minimal metal impurities such as

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<sup>16</sup>The Ames test is a bacterial reverse mutation assay, designed to determine mutagenicity of the test compound.

1 metal catalysts, which are included in the commercial preparation as a result of the synthesis process.  
2 Such impurities could influence the genotoxic potential of MWCNTs.

3 In contrast, other micronucleus assays reported significant increases in micronuclei of rat lung  
4 epithelial cells, Chinese hamster lung cells, and human lung carcinoma A549 cells ([Asakura et al., 2010](#);  
5 [Muller et al., 2008a](#); [Kato et al., In Press](#)), and that MWCNTs acted as clastogen and aneugen agents  
6 simultaneously in human blood cells ([Cveticanin et al., 2010](#)). Similarly, Migliore et al. ([2010](#)) reported a  
7 significantly higher dose-related percentage of DNA in comet tails in a Comet assay and a significant  
8 cytotoxic effect in a Trypan blue test using murine macrophage cell line RAW 264.7. Cavallo et al.  
9 ([2012](#)) also reported a concentration-dependent, statistically significant induction of direct DNA damage  
10 in human lung epithelial A549 cells evidenced by percentage of DNA in comet tails in a Comet assay that  
11 corresponded with reduced cell viability; the authors noted, however, that oxidative DNA damage was not  
12 statistically significant. A statistically significant, dose-dependent increase in the percentage of DNA in  
13 comet tails in a Comet assay also was observed in normal human dermal fibroblast cells by Patlolla et al.  
14 ([2010b](#); [2010a](#)).

### 5.1.11. Carcinogenicity

15 Carcinogenicity studies considered for decaBDE and MWCNTs are presented in Table F-10 and  
16 Table F-11 of Appendix F, respectively. The target organs for decaBDE carcinogenicity appear to be the  
17 liver and thyroid; decaBDE was not, however, included on the most recent U.S. NTP list of carcinogens.<sup>17</sup>  
18 No studies have investigated carcinogenicity of MWCNTs following oral or inhalation exposures; several  
19 studies indicate, however, that certain forms of MWCNTs behave in a manner similar to asbestos,  
20 inducing mesotheliomas when administered using methods such as injection (e.g., intrascrotal,  
21 intraperitoneal). Therefore, the lung could be another target of MWCNT carcinogenicity.

#### *Decabromodiphenyl Ether*

22 Information on the carcinogenicity of decaBDE is available from three chronic feeding studies in  
23 rodents ([Kociba et al., 1994](#); [NTP, 1986](#); [Kociba et al., 1975](#)). In the NTP study ([1986](#)), a treatment-  
24 related increase in liver neoplastic nodules was observed in low- and high-dose male rats (7/50 and 15/49,  
25 respectively, compared to 1/50 in controls) and high-dose female rats (9/50 compared to 1/50 and 3/49 in  
26 control and low-dose groups, respectively). F344/N rats were fed BDE-209 (94–98% pure) at dietary  
27 concentrations of 0, 25,000, or 50,000 ppm for 103 weeks (equivalent to 0, 1120, and 2240 mg/kg/day in  
28 male rats; 0, 1200, and 2550 mg/kg/day in female rats). The increase in liver neoplastic nodules was not

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<sup>17</sup>The U.S. NTP 12<sup>th</sup> Report on Carcinogens (released June 2011) is available at  
<http://ntp.niehs.nih.gov/?objectid=03C9AF75-E1BF-FF40-DBA9EC0928DF8B15>

1 accompanied by an increase in hepatocellular carcinomas in rats. Hepatocellular adenomas or carcinomas  
2 (combined), however, were observed in low- and high-dose male mice (8/50 controls, 22/50 low-dose  
3 mice, 18/50 high-dose mice). Male mice also exhibited a marginal increase in thyroid gland follicular cell  
4 adenomas or carcinomas (combined) at the low and high doses (0/50 controls, 4/50 low-dose mice, 3/50  
5 high-dose mice). The possible significance of this finding was strengthened by increased incidences of  
6 follicular cell hyperplasia in the male mice (2/50 controls, 10/50 low-dose mice, 19/50 high-dose mice),  
7 but was weakened by increased mortality in control animals. Based on these results, the NTP study  
8 ([1986](#)) concluded that there was “some evidence of carcinogenicity” for male rats in the low-dose group  
9 and both male and female rats in the high-dose group based on significantly increased incidences of  
10 neoplastic nodules of the liver, and “equivocal evidence of carcinogenicity” for male mice based on a  
11 significantly increased incidence of hepatocellular tumors in only the low-dose group and non-statistically  
12 significant increases of thyroid follicular cell tumors in both dose groups. Although the International  
13 Agency for Research on Cancer ([1998](#)) reports that decaBDE is not classifiable as a human carcinogen  
14 (Group 3) based on limited evidence in animals, EPA, under the *Guidelines for Carcinogen Risk*  
15 *Assessment* ([U.S. EPA, 2005b](#)), determined that the descriptor “suggestive evidence of carcinogenic  
16 potential” is appropriate for decaBDE ([U.S. EPA, 2008b](#)) based on the data from NTP ([1986](#))  
17 demonstrating evidence of carcinogenicity in more than one species, sex, and site.

### ***Multiwalled Carbon Nanotubes***

18 Currently, the carcinogenic potential of MWCNTs is unknown because no carcinogenicity studies  
19 were identified that used the inhalation route of exposure. Several studies indicate that some MWCNTs  
20 behave in a manner similar to asbestos, inducing mesotheliomas when administered using methods such  
21 as injection (e.g., intrascrotal, intraperitoneal) ([Sakamoto et al., 2009](#); [Poland et al., 2008](#); [Takagi et al.,](#)  
22 [2008](#)). Varga and Szendi ([2010](#)) found, however, that peritoneal injection of 10 mg MWCNTs did not  
23 result in development of mesotheliomas in F-344 rats examined at 12 months postexposure, but did result  
24 in a granulomatous reaction. Similarly, Muller et al. ([2009](#)) found that a single 20-mg injection of  
25 MWCNTs did not produce mesotheliomas in male Wistar rats observed for 24 months postexposure.  
26 Intratracheal instillation studies are noted to be useful for evaluating respiratory toxicity for particles,  
27 such as MWCNTs, because they produce qualitatively similar results to inhalation studies for endpoints  
28 such as pulmonary inflammation and fibrosis; however, such studies also have limitations because  
29 treatment with bundled particles can produce artifactual granulomatous lesions ([Muller et al., 2005](#)). One  
30 possible reason for the mesotheliomas observed in some studies is that MWCNTs are more cohesive than  
31 asbestos; consequently, MWCNTs bundle easily into granules after instillation or injection into animals  
32 ([Schulte et al., 2010](#); [Sakamoto et al., 2009](#); [Takagi et al., 2008](#)). Currently, the mechanism by which  
33 MWCNTs reach and persist in the pleura, including retention time and the importance of factors such as

1 fiber length or bundle size, is not well enough understood to determine whether the outcome of  
2 mesotheliomas is possible after inhaling MWCNTs.

3 The carcinogenic potential of MWCNTs might also be influenced by the presence of metal  
4 contaminants, like iron or nickel. These contaminants could play a role in carcinogenicity by accelerating  
5 the generation of reactive oxygen species ([Johnston et al., 2010](#)).

## 5.1.12. Susceptible Populations

6 Sacks et al. ([2011](#)) defined susceptibility as “individual- and population-level characteristics that  
7 increase the risk of health effects in a population, including, but not limited to, genetic background, birth  
8 outcomes (e.g., low birth weight, birth defects), race, sex, life stage, lifestyle (e.g., smoking status,  
9 nutrition), preexisting disease, socioeconomic status (e.g., educational attainment, reduced access to  
10 health care), and characteristics that may modify exposure ... (e.g., time spent outdoors).” In this section,  
11 populations susceptible to decaBDE or MWCNT impacts based on characteristics such as age, genetic  
12 background, and disease are considered. Characteristics that could modify exposure and increase  
13 susceptibility were discussed previously in Section 4.2.4; for a discussion on impacts related to  
14 socioeconomic status, see Section 5.3.

### *Decabromodiphenyl Ether*

15 Results regarding developmental neurotoxicity studies are conflicting. Whether young children  
16 comprise a sensitive (i.e., more susceptible) population is therefore unclear. A few animal studies have  
17 indicated that BDE-209 might cause developmental neurotoxicity, affecting motor and cognitive domains;  
18 however, in discussing susceptible populations for decaBDE, EPA noted that differences in the effects of  
19 decaBDE on neurodevelopment are unclear and whether other targets (thyroid and liver) are more  
20 sensitive in children is unknown ([U.S. EPA, 2008b](#)). Disposition studies using pregnant rats indicate that  
21 fetuses are less exposed to decaBDE than mothers. Fetuses (whole litter) contained only 0.43% of the  
22 dose in a study by Riu et al. ([2008](#)). In a study by Inoue et al. ([2006](#)), higher brominated congeners like  
23 decaBDE transferred from blood to milk to a lesser degree than did lower brominated congeners. In a  
24 study by Fukata et al. ([2005](#)), BDE-209 was not detected in umbilical cord tissue, but was found at  
25 23 ng/g lipid weight in umbilical cord serum and 10 ng/g lipid weight in maternal serum. Exposure to  
26 decaBDE in infants, however, appears to be greater than in adults. Additional information regarding  
27 populations that are susceptible to greater levels of exposure can be found in Chapter 4. No sources  
28 indicating that specific genetic polymorphisms increase susceptibility were identified.

### *Multiwalled Carbon Nanotubes*

1 No information was identified regarding MWCNTs and susceptible populations. Because  
2 MWCNTs appear to induce inflammatory and fibrotic effects (see Sections 5.1.3 and 5.1.8), however,  
3 individuals with existing pulmonary disease and children with higher respiration rates could be  
4 susceptible populations.

## 5.2. Ecological Effects

5 This section presents a summary of data on the potential ecological impacts of environmental  
6 contamination with decaBDE and MWCNTs. Specific information from the studies reviewed for this case  
7 study can be found in Section F.2 in Appendix F. Considerations for ecological impact include the  
8 absolute and relative toxicity of the decaBDE and MWCNTs and other factors such as bioaccumulation  
9 and biomagnification potential (see Section 4.3.1). For aquatic ecosystems, more information was  
10 identified for decaBDE than for MWCNTs, primarily because decaBDE has been studied extensively in  
11 aquatic vertebrates. Conversely, more information was identified on the potential effects of MWCNTs in  
12 terrestrial ecosystems than for decaBDE. The terrestrial ecosystem studies focus on agriculturally relevant  
13 plants and soil microbes. In both aquatic and terrestrial ecosystems, studies for both compounds are  
14 predominantly laboratory-based experiments on single species. Few studies address how exposure and  
15 uptake of PBDEs relate to ecological health and effects in the field ([Vonderheide et al., 2008](#)). Some field  
16 studies show correlations between PBDE exposure, reproductive behavior, and immunosuppression, but  
17 ecological consequences and potential population-level impacts of environmental PBDE contamination in  
18 general, and decaBDE in particular, remain uncertain ([Vonderheide et al., 2008](#)). Similarly, limited  
19 research has been performed on the broad ecological impact of MWCNT exposure, which might be the  
20 result of limited data on its presence in the environment. As mentioned in Section 4.3.1, ecological  
21 receptors can be exposed to decaBDE and MWCNTs attached to textile fibers, embedded in polymers, or  
22 sorbed to other particles, all of which are more likely to occur in the environment than exposure to the  
23 pristine compound. Studies examining exposure to larger textile scraps, polymer particles, and other  
24 heterogeneous compounds containing decaBDE and MWCNTs, however, are lacking. The results of  
25 laboratory studies using pristine compounds must therefore be considered, recognizing that results might  
26 not translate directly into real-world exposure scenarios.

27 As discussed in Chapter 3 (see Text Box 3-1), environmental degradation and debromination of  
28 decaBDE result in contamination of media with lower PBDE congeners, which are generally more  
29 bioavailable and more toxic than decaBDE. Also as stated previously in Chapter 3, debromination of  
30 decaBDE is expected to contribute significantly to the environmental presence of BDE-47, a tetraBDE,

1 and BDE-100 and BDE-99, which are both pentaBDEs, among other congeners ([Gandhi et al., 2011](#);  
2 [Ross et al., 2009](#)). In this section, information is presented on the acute toxicity of decaBDE and other  
3 PBDEs, as appropriate. Considerations for negative ecological impacts from continual long-term  
4 exposures in an ecosystem are also discussed.

## 5.2.1. Aquatic Receptors

### *Overview of Decabromodiphenyl Ether*

5 DecaBDE has been shown not to be acutely toxic to species of fish or marine algae studied to  
6 date ([Hardy, 2002a](#)). Few studies were identified regarding the acute or chronic toxicity of decaBDE to  
7 marine or freshwater algae and benthic invertebrates (see Section 5.2.1.1). No information was identified  
8 regarding toxic effects on aquatic plants or water-dwelling invertebrates (see Section 5.2.1.1); some  
9 information was identified on toxicity to aquatic vertebrates (see Section 5.2.1.2).

10 DecaBDE is not expected to be chronically toxic to aquatic organisms at environmentally  
11 relevant concentrations due to its physicochemical properties, specifically high molecular weight and low  
12 water solubility ([Hardy, 2002a](#)) (see Section 1.3.1). These properties suggest that decaBDE accumulation  
13 directly from water into biota is unlikely; a more likely route of exposure is dietary ([Gandhi et al., 2011](#)).  
14 But as noted previously, the factors affecting bioavailability of decaBDE are not well understood.  
15 Comparatively, however, lower PBDEs such as pentaBDEs are known to have high potential for  
16 bioaccumulation ([U.S. EPA, 2010b](#)). Because these congeners are transformation products of decaBDE,  
17 their chronic toxicity is considered.

### *Overview of Multiwalled Carbon Nanotubes*

18 Limited information was identified on the toxicity of MWCNTs to algae and aquatic plants (see  
19 Section 5.2.1.1). Only a few studies have investigated toxicity of MWCNTs to aquatic invertebrates and  
20 aquatic vertebrates (see Sections 5.2.1.1 and 5.2.1.2). Although these studies provide information for  
21 acute effects, they vary with regard to endpoints, doses, functionalization, and other material  
22 characteristics (see Text Box 5-1). No information was identified regarding toxicity to benthic  
23 invertebrates, and most MWCNTs released to the aquatic environment are expected to accumulate in the  
24 benthic environment (see Sections 3.1 and 3.3). A limited amount of information was identified on  
25 ecosystem effects due to chronic MWCNT exposure.

26 As discussed in Sections 3.1 and 3.3, MWCNTs have low water solubility and are expected to  
27 partition to sediment where they might be available primarily to benthic organisms. Physicochemical  
28 properties of MWCNTs suggest potential for bioaccumulation in aquatic systems ([Kroll et al., 2011](#)), but



1 no studies were identified on this topic. The potential impact of bioaccumulation of MWCNTs in aquatic  
 2 systems is therefore uncertain.

### 5.2.1.1. Algae, Aquatic Plants, and Aquatic Invertebrates

3 Table 5-2 describes key toxicity values identified for the effects of decaBDE and MWCNTs on  
 4 algae, aquatic plants, and aquatic invertebrates. Table F-12, Table F-14, and Table F-15 in Appendix F  
 5 summarize details of the studies identified and reviewed for this section.

Table 5-2. Effects of decaBDE and MWCNTs on aquatic receptors: algae, plants, and invertebrates.

Organism	DecaBDE			MWCNTs		
	Effect	Effect level <sup>a</sup>	Citation	Effect	Effect level	Citation
Sediment oligochaetes	Acute NOEC	>5000 mg/kg	Hardy (2002a)	ND		
	28-day NOEC	>3841 mg/kg	ACC (2001a, b) <sup>b</sup>			
Algae	Growth inhibition, 96-hr EC <sub>50</sub>	>1 mg/L	Hardy (2002a)	Growth inhibition LOEC	1 mg/L	Wei et al. (2010)
Zebra mussels	DNA damage	0.1 to 10 µg/L	Riva et al. (2007)	ND		
Macrophytes	ND			Positive effects on recolonization and community structure after 3 months of exposure in sediment		Velzeboer et al. (2011)
Water fleas	<i>Daphnia magna</i> : 21-day LOEC (growth)	BDE-209: ND; pentaBDE: 9.8 µg/L	Chemical Manufacturers Association (1998) <sup>b</sup>	<i>Ceriodaphnia dubia</i> : acute LC <sub>50</sub>	2–100 mg/L	Li and Huang (2011)
	21-day EC <sub>50</sub> (survival, reproduction)	BDE-209: ND; pentaBDE: 14 µg/L	Chemical Manufacturers Association (1998) <sup>b</sup>	Subchronic growth inhibition EC <sub>50</sub>	50.9 mg/L	Kennedy et al. (2008)
				3-generation reproduction EC <sub>50</sub>	4–17 mg/L	Li and Huang (2011)

<sup>a</sup>Concentration in media (water [units µg/L or mg /L] or sediment [units mg/kg]).

<sup>b</sup>As cited in Environment Canada (2006).

ND = no data identified, NOEC = no-observed-effect concentration, EC<sub>50</sub> = median effective concentration

#### *Decabromodiphenyl Ether*

6 No studies were identified that investigated the effects of decaBDE on algae or on aquatic plants.  
 7 A single study on water-dwelling aquatic invertebrates was identified involving freshwater bivalve zebra  
 8 mussels (*Dreissena polymorpha*) exposed to technical-grade decaBDE at sublethal levels of 0.1, 2, or

1 10 µg/L. This study showed DNA damage that increased as levels of decaBDE exposure increased,  
2 indicating potential for genotoxicity ([Riva et al., 2007](#)). A review by Hardy ([2002a](#)) stated that decaBDE  
3 was nontoxic to marine algae and sediment oligochaetes, but no details on the derivation of these  
4 conclusions were provided. The review also investigates toxicity of octaBDE and pentaBDE, concluding  
5 that octaBDE is neither acutely toxic nor chronically toxic to a species of water flea, and pentaBDE is not  
6 acutely toxic to algae, up to the limit of their water solubility ([Hardy, 2002a](#)). Details on endpoints  
7 observed were not provided.

8 Environment Canada ([2006](#)) reviewed ecotoxicity studies for multiple PBDE mixtures. They  
9 report high (>5000 mg/kg) no-observed-effect levels and median (>50 mg/kg) effective concentration  
10 values for chronic survival and reproduction effects for a freshwater oligochaete (*Lumbriculus variegatus*)  
11 exposed to sediments that contained a mixture of 55% pentaBDE and 36% tetraBDE as well as a mixture  
12 containing 97% decaBDE. For water fleas (*Daphnia magna*), Environment Canada ([2006](#)) reported  
13 toxicity values in the low µg/L range for survival, growth, and reproduction following chronic exposure  
14 to a commercial pentaBDE mixture [(Chemical Manufacturers Association ([1998](#)) as cited in  
15 Environment Canada ([2006](#))]. Some water fleas are therefore more sensitive to PBDEs than oligochaete  
16 worms, but as mentioned in Section 3.3, decaBDE is not likely to remain in the water column; instead, it  
17 partitions to sediment, where benthic invertebrates are expected to be exposed.

### ***Multiwalled Carbon Nanotubes***

18 The effects of MWCNTs on marine algae, sediment macrophytes, and water-dwelling  
19 invertebrates have not been extensively studied; only four published studies were identified ([Li and](#)  
20 [Huang, 2011](#); [Velzeboer et al., 2011](#); [Wei et al., 2010](#); [Kennedy et al., 2008](#)). Because MWCNTs are  
21 likely to partition to sediment, benthic organisms are expected to be primary receptors ([Christian et al.,](#)  
22 [2008](#)). No studies that investigated the effects of MWCNTs on benthic invertebrates, however, were  
23 identified. In a study on macrophyte growth, experimental plots were cleared of all living organisms and  
24 MWCNTs were added to the sediment. After three months, researchers observed that the density of  
25 macrophytes that had recolonized the plots was positively correlated with MWCNT levels ([Velzeboer et](#)  
26 [al., 2011](#)). This result was counter to the authors' initial hypothesis based on previous laboratory  
27 experiments that macrophyte growth and species composition would be negatively affected by MWCNTs,  
28 indicating a level of complexity in community-level effects of MWCNTs in real-environment situations  
29 that is not well understood ([Velzeboer et al., 2011](#)).

30 Unicellular green algae (*Dunaliella tertiolecta*) exposed to carboxylated MWCNTs in sea water  
31 did not exhibit inhibited growth until concentrations reached 1 mg/L and above ([Wei et al., 2010](#)).  
32 Growth lagged up to 23 days behind the control, and exponential growth rates were reduced by 35% when

1 exposure was 10 mg/L, indicating mid-exponential growth phase cytotoxicity at high exposures ([Wei et](#)  
2 [al., 2010](#)).

3 Two studies provided a wide variety of data for another species of water flea than included in the  
4 decaBDE studies discussed above (*Ceriodaphnia dubia*) ([Li and Huang, 2011](#); [Kennedy et al., 2008](#)). The  
5 MWCNT studies describe an acute median lethal concentration in the mg/L range, the variation of which  
6 might be due to differences in functionalization treatment and diameter size of the MWCNTs ([Li and](#)  
7 [Huang, 2011](#)) (see Table F-15 in Appendix F for study-specific details and Text Box 5-1 for discussion of  
8 how physicochemical properties affect toxicity). Subchronic and chronic growth and reproduction tests  
9 show that MWCNTs that had been treated to increase dispersal and limit bundling (a common treatment  
10 in MWCNTs—see Section 2.2.3.1) are not likely to cause significant, population-level effects until high  
11 doses (1- to 100-mg/L range) ([Li and Huang, 2011](#)). Even though MWCNTs are expected to partition to  
12 sediment, functionalization and suspension in natural organic matter could improve dispersion and  
13 solubility of MWCNTs in aqueous media and might increase the exposure levels of MWCNTs to water-  
14 dwelling aquatic organisms ([O’Driscoll et al., 2010](#); [Kennedy et al., 2008](#)).

### 5.2.1.2. Aquatic Vertebrates

15 Table 5-3 describes key toxicity values identified for the effects of decaBDE and MWCNTs on  
16 aquatic vertebrates. Table F-13, Table F-16, and Table F-17 in Appendix F summarize details of the  
17 studies identified and reviewed for this section.

#### *Decabromodiphenyl Ether*

18 A review by Hardy ([2002a](#)) reports on acute toxicity of decaBDE, octaBDE, and pentaBDE,  
19 stating that all three congeners have a fish 48-hr median lethal concentration of greater than 500 mg/L,  
20 indicating that the congeners are not acutely toxic to fish up to the limit of their water solubility. No  
21 effects on egg mortality were observed in rainbow trout (*Oncorhynchus mykiss*) at doses up to 12 µg  
22 pentaBDE per egg, and no effects on reproduction or spawning success were observed in three-spined  
23 stickleback (*Gasterosteus aculeatus*) exposed to pentaBDE ([Hardy, 2002a](#)).

24 Tests conducted on frogs often measure low-dose, chronic thyroid disruption, because  
25 metamorphic development from tadpole to frog is controlled by thyroid hormones ([Qin et al., 2010](#)).  
26 African clawed frog (*Xenopus laevis*) tadpoles (Table 5-3) exposed to decaBDE in their water at sublethal  
27 doses ranging from 1 to 1000 ng/L experienced histopathological alterations in thyroid gland cell shapes  
28 and decreases in thyroid hormone expression in tail tissue during metamorphosis at all tested doses.  
29 Additionally, researchers observed a concentration-dependent trend of delay in time to metamorphosis  
30 with a statistically significant delay at 1000 ng/L ([Qin et al., 2010](#)).

Table 5-3. Effects of decaBDE and MWCNTs on aquatic receptors: aquatic vertebrates.

Organism	Exposure	Effect	Effect level	Citation
<b>DecaBDE</b>				
African clawed frog	Water	Thyroid effects LOAEL	1 ng/L	Qin et al. (2010)
Lake trout	Diet, chronic	Decreased thyroid hormones LOAEL	2.5 ng/g	Tomy et al. (2004)
Rainbow trout	Diet, chronic	Increased liver weight LOAEL	7.5 ng/kg	Kierkegaard et al. (1999)
	NR	Vitellogenin production	NR	Nakari and Pesala (2005)
Lake whitefish	Diet, chronic	Decreased growth LOAEL	2 µg/g	Kuo et al. (2010)
Chinese rare minnow	Water, chronic	Decreased growth LOAEL	10 µg/L	Li et al. (In Press)
	Water, chronic	Spermatogenesis inhibition LOAEL	10 µg/L	Li et al. (In Press)
	Water, chronic	Upregulation of thyroid hormones	Variably occurred at 0.1–10 µg/L	Li et al. (In Press)
<b>MWCNTs</b>				
Zebrafish	Water	Reduced blood circulation	70 µg/mL	Asharani et al. (2008)
	Water	Developmental effects	60 µg/mL	Asharani et al. (2008)
	Water	Increased mortality LOAEL	60 µg/mL	Asharani et al. (2008)
	Microinjection	Developmental effects NOEL	>2 ng/embryo	Cheng et al. (2009)
	Microinjection	Second-generation reduced survival	2 ng/embryo	Cheng et al. (2009)
Japanese medaka	Water	Developmental effects LOAEL	1500 µg/mL	Kim et al. (2012)

NR = Not reported, NOAEL = No-observed-adverse-effect level, LOAEL = Lowest-observed-adverse-effect level

1           Endocrine effects also have been studied in Chinese rare minnow (*Gobiocypris rarus*) and lake  
2 trout (*Salvelinus namaycush*) chronically exposed to decaBDE via water and diet, respectively (Tomy et  
3 al., 2004; Li et al., In Press). Expression of thyroid hormone-related genes was variably affected in both  
4 studies, indicating the potential for chronic endocrine disruption but not elucidating a mechanism for  
5 those effects or a clear effect level. Chronic toxicity of decaBDE in fish is complicated by biotic  
6 debromination of decaBDE, which can result in bioaccumulation of octa-, hepta-, hexa-, and pentaBDE  
7 congeners (Gandhi et al., 2011; Stapleton et al., 2004) (as discussed in Section 4.2.6.1). Most  
8 informative, therefore, are studies of multiple PBDEs or PBDE mixtures. In one such study, induction of  
9 vitellogenin production was observed in hepatocyte cell cultures of rainbow trout (*Oncorhynchus mykiss*)

1 exposed to PBDE mixtures ([Nakari and Pessala, 2005](#)). This estrogenic response raises concerns for  
2 population dynamic impacts due to endocrine disruption ([Mikula and Svobodová, 2006](#)).

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3 Four studies were identified that investigated the effects of MWCNTs on fish; three of these  
4 studies used common laboratory species—zebrafish (*Danio rerio*) and Japanese medaka (*Oryzias latipes*),  
5 while one used rainbow trout (*Oncorhynchus mykiss*).

6 In one zebrafish study, embryos acutely exposed to MWCNTs showed dose-dependent increased  
7 mortality rates, reduced blood circulation, and delayed development (hatching), and developmental  
8 defects (bent notochord) starting at 60 µg/mL ([Asharani et al., 2008](#)). The other zebrafish study ([Cheng et  
9 al., 2009](#)) examined embryos following a smaller yet more direct exposure—a single microinjection of  
10 MWCNTs—and observed changes in enzyme expression signifying an immune response. Although no  
11 increase in mortality or developmental defects were observed in the exposed zebrafish through adulthood,  
12 survival in the second generation was significantly decreased. Similarly, Kim et al. ([2012](#)) observed a  
13 statistically significant increase in heart abnormalities, absence of swim bladders, caudal fin  
14 malformation, and pericardial and peritoneal edemas in Japanese medaka embryos following 4 days of  
15 continual exposure to 2000 µg/L functionalized MWCNTs in the water. Increased mortality also occurred  
16 in response to exposures to 1500 and 2000 µg/L, and exposure to 1500 µg/L resulted in a hatching delay.

17 Klaper et al. ([2010](#)) further investigated the possibility of an immune response in fish with an in  
18 vitro study of rainbow trout. In this study, MWCNTs did not elicit an antiviral response at sublethal doses  
19 up to 10 µg/mL regardless of various types of functionalization. Investigators did, however, observe  
20 expression of IL-1beta, evident of macrophage stimulation, at 5 and 10 µg/mL ([Klaper et al., 2010](#)).

## 5.2.2. Terrestrial Receptors

### *Overview of Decabromodiphenyl Ether*

21 A limited amount of information was found regarding toxicity of decaBDE to soil microbes,  
22 plants, and terrestrial invertebrates (see Sections 5.2.2.1 and 5.2.2.2). No information was identified  
23 regarding toxicity to terrestrial vertebrates (see Section 5.2.2.3); nevertheless, some assumptions can be  
24 made for mammals based on toxicity studies intended for human health purposes presented in Section 5.1.  
25 Many studies of decaBDE in terrestrial ecosystems have focused on bioaccumulation and  
26 biomagnification, important considerations for potential ecological hazard (see Section 4.3.4). These  
27 studies, however, did not investigate occurrence of toxic effects.

## Overview of Multiwalled Carbon Nanotubes

1 Compared to other organism groups, a large amount of data was identified regarding toxicity of  
 2 MWCNT to soil microbes and plants (see Sections 5.2.2.1 and 5.2.2.2). No information was identified for  
 3 toxicity to terrestrial vertebrates (see Section 5.2.2.3), but some assumptions can be made for mammals  
 4 based on toxicity studies intended for human health purposes presented in Section 5.1.

### 5.2.2.1. Soil Microbes and Terrestrial Invertebrates

5 Changes in soil microbial activity result in changes to nutrient cycling; therefore, studying the  
 6 impact of contaminants on soil microbes can provide insight on how those contaminants might affect  
 7 ecosystem function ([Chung et al., 2011](#)). Similarly, effects on terrestrial invertebrates, such as worms, can  
 8 influence health and fertility of a soil ecosystem ([Xie et al., 2011](#)). Table 5-4 describes key toxicity values  
 9 identified for the effects of decaBDE and MWCNTs on soil microbes and invertebrates. Table F-18 and  
 10 Table F-19 in Appendix F summarize details of the studies identified and reviewed for this section.

Table 5-4. Effects of decaBDE and MWCNTs on terrestrial receptors: soil microbes and invertebrates.

Organism	DecaBDE			MWCNTs		
	Effect	Effect level	Citation	Effect	Effect level	Citation
Soil microbes	Acute NOEL	>2274 mg/kg	Sverdrup et al. (2006)	Acute NOEL (C. metallidurans)	>100 mg/L	Simon-Deckers et al. (2009)
				Acute LD <sub>50</sub> (E. coli)	100 mg/mL	Simon-Deckers et al. (2009)
	Chronic cytotoxicity LC <sub>50</sub> (6 months)	100 mg/kg	Liu et al. (2011b)	Chronic cytotoxicity NOEL; LOAEL	500 µg/g 5000 µg/g	Chung et al. (2011)
Invertebrate worms	Acute NOEL ( <i>Enchytraeus crypticus</i> )	>2274 mg/kg	Sverdrup et al. (2006)	ND		
	Chronic NOEL ( <i>Eisenia fetida</i> )	>4910 mg/kg	ACC (2001c) as cited in Environment Canada (2006)			
	Oxidative stress ( <i>E. fetida</i> )	0.1–10 mg/kg	Xie et al. (2011)			

ND = No data identified, NOEL = No-observed-effect level, LOAEL = Lowest-observed-effect level

### ***Decabromodiphenyl Ether***

1 Two studies were identified that investigated the toxicity of decaBDE to soil microbes. Although  
2 Sverdrup et al. (2006) showed no effects on nitrifying ability of bacteria following exposure to decaBDE  
3 at levels up to 2274 mg/kg in soil, Liu et al. (2011b) found that microbial cytotoxicity significantly  
4 increased at doses 10-fold lower (100 mg/kg), and community structure was altered following long-term  
5 exposure to decaBDE. The rate of community diversity increase over time was significantly slower from  
6 Day 90 through the last day of the study (Day 180) when soil contained 1–100 mg/kg decaBDE. After six  
7 months, the total bacterial count in the soil containing 100 mg/kg decaBDE was approximately half that  
8 of the control plot. Treatment soil microcosms were dominated by *Pseudomonas*, *Bacillus*, and  
9 uncultured bacteria types, and had significantly reduced cell counts for *alpha*, *beta*, and *gamma* type  
10 proteobacteria and the Cytophaga-Flavobacterium-Bacteroides group (Liu et al., 2011b).

11 Studies of oligochaete worms [*Enchytraeus crypticus* (a soil worm) and *Eisenia fetida*  
12 (earthworms)] showed that survival, reproductive behavior, and number of offspring are not affected by  
13 long-term exposure to decaBDE in soil in the g/kg range [Sverdrup et al. (2006); ACC (2001c) as cited in  
14 Environment Canada (2006)]. Earthworms, however, experienced a sublethal, dose-dependent increase in  
15 hydroxyl radical generation and subsequent oxidative stress after 1 week of exposure to 0.1–10 mg/kg  
16 decaBDE (Xie et al., 2011). Oxidative stress in earthworms is considered a biomarker indicative of  
17 potential for greater impacts of soil contaminants within terrestrial ecosystems (Xie et al., 2011).

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18 Multiple studies have shown that carbon nanotubes exhibit antimicrobial activity, suggesting that  
19 release of MWCNTs into soils could adversely affect soil microcosms. This possibility, however, has not  
20 yet been investigated outside of controlled lab experiments (Chung et al., 2011). A short, 1-hour exposure  
21 to low doses of MWCNTs (e.g., 5 µg/mL [5 ppm]) resulted in mortality rates of 20–50% in *Escherichia*  
22 *coli*, *Pseudomonas aeruginosa*, and *Staphylococcus epidermidis* cell cultures, which are 1.5–5 times  
23 higher than background mortality levels (Kang et al., 2009; Kang et al., 2008). An increase in exposure  
24 level or duration, however, does not drastically increase cytotoxicity, and species-specific responses vary.  
25 For example, exposure to 100 mg/mL (100,000 ppm) MWCNTs for 24 hours caused 50–60% cytotoxicity  
26 in *E. coli*, yet had no effect on *Cupriavidus metallidurans*, a more environmentally relevant bacterium  
27 (Simon-Deckers et al., 2009). In a chronic duration study (Chung et al., 2011), the authors showed that  
28 addition of MWCNTs at the high concentration of 5 mg/g soil (5000 ppm) resulted in an average of 34.2–  
29 60.5% decrease in microbial activity over 11 days; lower levels of MWCNTs (500 and 50 µg/g [ppm])  
30 did not cause significant cytotoxicity.

### 5.2.2.2. Terrestrial Plants

1 Table 5-5 describes key toxicity values identified for the effects of decaBDE and MWCNTs on  
 2 terrestrial plants. Table F-18 and Table F-20 in Appendix F summarize details of the studies identified  
 3 and reviewed for this section.

Table 5-5. Effects of decaBDE and MWCNTs on terrestrial receptors: plants.

Endpoint	DecaBDE			MWCNTs		
	Organism	Effect level	Citation	Organism	Effect level	Citation
Germination NOEL	Corn	penta/tetraBDE mix:>1000 mg/kg	Great Lakes Chemical Corporation (2000)	Corn, rapeseed, radish, ryegrass, lettuce, cucumber	>2000 mg/L	Lin and Xing (2007)
	Red clover	>2274 mg/kg	Sverdrup et al. (2006)	Brown mustard, blackgram	>40 µg/mL	Ghodake et al. (2010)
				Garden cress	0.01% w/w	Oleszczuk et al. (2011)
Germination LOAEL		ND		Garden cress	0.1% w/w	Oleszczuk et al. (2011)
Root growth NOAEL		ND		Corn, rapeseed, radish, ryegrass, lettuce, cucumber	>2000 mg/L	Lin and Xing (2007)
				Thale cress	>10 mg/L	Lin et al. (2009)
Root growth LOAEL		ND		Garden cress	0.01% w/w	Oleszczuk et al. (2011)
Shoot height LOAEL	Corn	penta/tetraBDE mix: 250 mg/kg	Great Lakes Chemical Corporation (2000)		ND	

ND = No data identified, w/w = weight-for-weight measurement, NOEL = No-observed-effect level, NOAEL = No-observed-adverse-effect level, LOAEL = Lowest observed adverse effect level

#### *Decabromodiphenyl Ether*

4 Few studies were identified that investigated effects of PBDEs on plants; those reviewed found  
 5 no adverse effects at environmentally relevant concentrations. No effects on seedling emergence were  
 6 observed in red clover (*Trifolium pretense*) exposed to decaBDE or corn (*Zea mays*) exposed to a PBDE  
 7 mixture (55% pentaBDE and 36% tetraBDE) at levels in the g/kg range (Sverdrup et al., 2006; Great  
 8 Lakes Chemical Corporation, 2000). In corn, mean shoot height was unaffected at concentrations up to  
 9 125 mg/kg, but was significantly reduced at 250 mg/kg and above [Great Lakes Chemical Corporation  
 10 (2000) as cited in Environment Canada (2006)]. As discussed in Section 3.4, soils are a major sink for



1 PBDEs in terrestrial systems, and uptake by plants is possible. Recent measured concentrations in soil  
2 have been in the ng/g (0.001 mg/kg) range (see Table E-5 in Appendix E).

### *Multiwalled Carbon Nanotubes*

3 Both beneficial and detrimental effects of nanoparticle exposures have been reported for plants.  
4 For example, water and fertilizer absorption is enhanced by nano-TiO<sub>2</sub> in soybeans, while root elongation  
5 is inhibited with nano-Al<sub>2</sub>O<sub>3</sub> exposure ([Lin and Xing, 2007](#)). Studies with MWCNTs have implied that  
6 exposure to high levels could have negative effects on seed germination and plant growth, as several  
7 studies show trends and a few show statistically significant impacts. For example, Lin and Xing ([2007](#))  
8 showed that exposure to MWCNTs with diameters 10–20 nm at a concentration of 2000 mg/L caused no  
9 significant differences in germination rates or root length for six different agriculturally relevant plant  
10 species, although a non-statistically significant decrease in germination was observed in four of the  
11 species ([Lin and Xing, 2007](#)). Conversely, Oleszczuk et al. ([2011](#)) found that MWCNTs added to sewage  
12 sludge<sup>18</sup> at concentrations of 0.01, 0.1, and 0.5% weight-for-weight significantly inhibited garden cress  
13 (*Lepidium sativum*) seed germination. The authors observed diameter-dependent responses, as root  
14 growth was inhibited at all three concentrations for the smaller diameter MWCNTs but was not affected  
15 at any concentration for the larger diameter MWCNTs ([Oleszczuk et al., 2011](#)) (see Text Box 5-1).  
16 Finally, no physical injury to cell morphology was observed in thale cress (*Arabidopsis thaliana*) cell  
17 suspensions exposed to 10 mg/L MWCNTs, but significant loss in cell viability as well as growth and  
18 chlorophyll inhibition were observed after 7 days of exposure. Cytotoxicity was more severe following  
19 exposure to fine, small bundles than to loose, large bundles of MWCNTs ([Lin et al., 2009](#)), indicating that  
20 dispersion state could play a role in toxicity (see Text Box 5-1 and Appendix F, Table F-20).

21 A study by Tan and Fugetsu ([2007](#)) provides some insight on the mechanism through which  
22 MWCNT exposure affects plant growth and the ecological relevance of the trend described above.  
23 Cultures of rice cells in an embryonic growth stage formed large associations with MWCNT; the cells  
24 that interacted with the MWCNTs experienced high cell death. Only a portion of cells within the culture  
25 associated with the MWCNTs, however, and clumps formed by this initial subset of the cells in the  
26 culture continued to attract other MWCNTs, forming larger associations over the course of the 4-day  
27 exposure period. Cells that did not form these associations with MWCNTs were not adversely affected by  
28 the MWCNTs as exposure continued. The authors stated that their results illustrate how some plants  
29 might be able to tolerate low levels of MWCNTs without major population-level effects due to a self-  
30 defense response ([Tan and Fugetsu, 2007](#)).

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<sup>18</sup>Sewage sludge samples were collected from four municipal industrial sewage treatment plants were analyzed and reported to contain heavy metals (e.g., Pb, Cr, Cd, Cu, Ni) and polycyclic aromatic hydrocarbons.

1 Ghosh et al. (2011) illustrated clastogenicity in *Allium cepa* (onion) bulbs exposed to 0, 10, 20,  
2 and 50 µg/mL MWCNTs using traditional cell culture tests. Chromosomal aberrations, DNA cross-  
3 linking, and induction of apoptosis led authors to conclude that MWCNTs might have a significant  
4 impact on genomic activities of plants.

### 5.2.2.3. Terrestrial Vertebrates

#### *Decabromodiphenyl Ether*

5 No studies were identified that specifically investigated the effects of decaBDE on terrestrial  
6 vertebrates outside the laboratory setting. Results from extensive testing performed in mammals for  
7 toxicological relevance to humans are reported in Section 5.1.

8 Chronic effects of PBDEs at environmentally relevant exposure concentrations are a possibility in  
9 terrestrial vertebrates, primarily due to assumed ecological impacts associated with high biomagnification  
10 rates, as discussed previously in Section 4.3.1.

#### *Multiwalled Carbon Nanotubes*

11 The impacts of oral exposure in mammals are uncertain (see Section 5.1). Testing performed in  
12 mammals for relevance to humans has focused on inhalation exposure routes; acute inhalation studies  
13 have found that MWCNTs or associated contaminants can induce oxidative stress, pulmonary  
14 inflammation, and fibrosis. MWCNTs might cause slight skin and eye irritation. No studies were  
15 identified that specifically investigated the ecological effects of MWCNTs on terrestrial vertebrates.

## 5.3. Other Impacts

16 As stated in Chapter 1, the CEA framework considers not only human and ecological health  
17 impacts, but also aesthetic, environmental, social, legal, ethical, and economic impacts. Such impacts  
18 might be associated with impacts on specific socioeconomic sectors (e.g., disparate impacts on  
19 environmental justice communities), the environment as a whole (e.g., climate change, depletion of  
20 natural resources, energy demand), or the built environment (e.g., damage to building facades).

21 Apart from the impacts discussed in Sections 5.1 and 5.2, the only other impacts considered in  
22 this case study are those for which a plausible premise can be developed to support assumptions that a  
23 discernible impact might occur as a result of the life cycles of decaBDE or MWCNTs flame-retardant  
24 upholstery textile coatings. Data from both decaBDE and MWCNTs on each of these impacts would be  
25 required for a thorough comparison; however, in all cases where other impacts were identified as being of  
26 concern for either decaBDE or MWCNTs, no data were available for the comparison material. For

1 decaBDE, empirical data have revealed a correlation between decaBDE body burdens and socioeconomic  
2 status, indicating that effects having environmental justice implications are plausible for decaBDE. No  
3 such empirical data exist relating MWCNTs to other impacts, but the background literature on processes  
4 involved in manufacturing similar materials (e.g., carbon nanofibers [CNFs] and SWCNTs) provides  
5 some basis for concerns regarding potential impacts of MWCNTs on energy demand, resource depletion,  
6 climate change, and economics.

### 5.3.1. Environmental Justice

7 Environmental justice is defined by EPA as the “fair treatment and meaningful involvement of all  
8 people regardless of race, color, national origin, or income with respect to the development,  
9 implementation, and enforcement of environmental laws, regulations, and policies.”<sup>19</sup> The goal of  
10 environmental justice is to give all people “...the same degree of protection from environmental and  
11 health hazards and equal access to the decision-making process...”<sup>20</sup> As a result, environmental justice  
12 impacts include those in which a particular group or geographic area experiences a disproportionate share  
13 of the impacts associated with an environmental contaminant.

#### *Decabromodiphenyl Ether*

14 Releases of decaBDE throughout the life cycle of a flame-retardant upholstery coating product  
15 could disproportionately impact certain communities. In a review by Zota et al. (2010), findings from  
16 several recent studies suggest that racial and ethnic minorities and populations having lower  
17 socioeconomic status (i.e., low income, low educational attainment) experience disproportionate  
18 exposures to PBDEs. For example, Rose et al. (2010) observed that body burdens of BDE-209, among  
19 other congeners, were significantly higher in children aged 2–5 years born to mothers of lower  
20 educational attainment compared to those born to mothers achieving a college degree or higher.

21 The causal pathway connecting low socioeconomic status to elevated PBDE exposure is not well  
22 understood, but Zota et al. (2010) hypothesized that furniture quality and the characteristics of the living  
23 spaces (e.g., size, ventilation, age), which populations of lower socioeconomic status might occupy,  
24 contribute to elevated exposure to PBDEs. Indeed, Rose et al. (2010) demonstrated that higher maternal  
25 education attainment is correlated with larger living spaces, and in turn, children living in larger homes  
26 had lower body burdens of BDE-209. Similarly, Stapleton et al. (2012) found that variation in PBDE  
27 serum concentrations in children could be explained by handwipe levels, house dust levels, father’s

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<sup>19</sup>U.S. EPA Compliance and Enforcement. Environmental Justice. <http://www.epa.gov/environmentaljustice/>

<sup>20</sup>ibid

1 education, breast feeding duration, age, and gender (different factors associated with different PBDE  
2 congeners).

### *Multiwalled Carbon Nanotubes*

3 No information was identified that examined the relationship between MWCNT exposures and  
4 socioeconomic status.

## 5.3.2. Energy Demand and Natural Resource Depletion

### *Decabromodiphenyl Ether*

5 No information was identified that examined impacts on energy demand and natural resource  
6 depletion associated with the production of decaBDE flame-retardant textile coatings.

### *Multiwalled Carbon Nanotubes*

7 No information was identified that examined impacts on energy demand and natural resource  
8 depletion associated with the production of MWCNT flame-retardant textile coatings. Various studies,  
9 however, have calculated a large range of minimum energy requirements for synthesis of CNTs ([Khanna  
10 et al., 2008](#); [Cipiriano et al., 2007](#); [Smalley et al., 2007](#)). Table 5-6 presents an overview of some  
11 estimated minimum energy requirements and process rates for CNT synthesis.

12 The differences in energy requirements are largely attributable to different synthesis processes,  
13 different process rates, different feedstocks, and process improvements as synthesis of CNTs has been  
14 optimized ([Gutowski et al., 2010](#); [Kushnir and Sanden, 2008](#)). Additionally, these energy requirements  
15 represent only the minimum for synthesis and do not consider the energy required for purification,  
16 additional infrastructure (e.g., equipment needed to regulate environmental conditions during synthesis  
17 and processing), and other related processes. Including these additional energy requirements, Gutowski et  
18 al. ([2010](#)) estimated that CNTs could be one of the most energy-intensive materials of all time. Although  
19 information regarding the energy requirements for MWCNT synthesis is limited, such energy  
20 requirements likely also would be sizeable and span a large range as synthesis processes are continually  
21 optimized.

22 One environmental impact assessment examined the water inputs required for two methods of  
23 continuous synthesis of SWCNTs via chemical vapor deposition (CVD) ([Kolosnjaj-Tabi et al., 2010](#)).  
24 These results indicated that production of SWCNTs can require significant amounts of water (almost  
25 65,000 kg/hour at a manufacturing rate of about 595 kg/hour of SWCNTs). The relationship between  
26 water requirements for SWCNT synthesis and MWCNT synthesis, however, is unclear.

Table 5-6. Estimated minimum energy requirements and process rates for synthesis of CNTs.

Synthesis process	Material	Process rate (kg/hr)	Synthesis energy requirements (J/kg)	Estimated energy per hour (J/hr)	Reference
CVD	CNF (methane-based)	$1.30 \times 10^{-2}$	$3.13 \times 10^9$	$4.07 \times 10^7$	Khanna et al. (2008)
	CNF (ethylene-based)	$1.80 \times 10^{-2}$	$2.22 \times 10^9$	$3.96 \times 10^7$	
Arc discharge	SWCNT	$8.10 \times 10^{-5}$	$8.73 \times 10^{10}$	$7.07 \times 10^6$	Healy et al. (2008)
HiPCO®	SWCNT	$4.50 \times 10^{-4}$	$2.41 \times 10^{10}$	$1.08 \times 10^7$	Smalley et al. (2007)
HiPCO®	SWCNT	$4.50 \times 10^{-4}$	$3.18 \times 10^{10}$	$1.43 \times 10^7$	Healy et al. (2007)
Floating catalyst CVD <sup>1</sup>	MWCNT	NR	$2.95 \times 10^8$ (thermal)	NR	Kushnir and Sanden (2008)
			$1.87 \times 10^8$ (electric)		
Laser ablation <sup>2</sup>	MWCNT	NR	$2.11 \times 10^8$ (thermal)	NR	Kushnir and Sanden (2008) <sup>3</sup>
			$9.4 \times 10^9$ (electric)		

<sup>1</sup>Benzene gas feedstock.

<sup>2</sup>Graphite feedstock.

<sup>3</sup>Authors report both baseline (shown above) and "efficient" estimates (not shown).

CVD = chemical vapor deposition; CNF = carbon nanofiber; HiPCO® = a high pressure carbon monoxide synthesis process; NR = not reported.

Source: Gutowski et al. (2010).

1 A life-cycle assessment of CNF production via CVD calculated potential impacts on acidification,  
2 eutrophication, and ozone layer depletion (Khanna et al., 2008). The results of this analysis are presented  
3 in Table 5-7. The authors found that CNF production of both methane-based and ethylene-based CNFs  
4 has minor impacts on acidification, eutrophication, and ozone layer depletion. This study did not  
5 incorporate CNF emissions into its calculations, however, due to a lack of data on fate, transport, and  
6 impacts of CNFs (Khanna et al., 2008). The authors noted that the lack of models to predict endpoint  
7 effects of some emissions (e.g., CNF emissions) renders these calculations uncertain. Plata et al. (2009)  
8 found that release of gases such as methane, volatile organic compounds, and polycyclic aromatic  
9 hydrocarbons from MWCNT synthesis is possible. Methane release would likely have a negligible impact  
10 on local air pollution and ozone depletion compared to existing methane sources; however, release of  
11 volatile organic compounds such as 1,3-butadiene and benzene, could be significant on a local scale  
12 (Plata et al., 2009).

Table 5-7. Environmental assessment of production of 1 kilogram of carbon nanofibers.<sup>a</sup>

Impact category	Impact <sup>b</sup>		Unit
	Methane-based CNF	Ethylene-based CNF	
Acidification	5.5	4.0	Kg SO <sub>2</sub> Equivalent
Eutrophication	4.0	3.0	Kg PO <sub>4</sub> Equivalent
Ozone layer depletion potential	2.8 × 10 <sup>-5</sup>	2.8 × 10 <sup>-5</sup>	Kg CFC-11 Equivalent

<sup>a</sup>Environmental impacts of production of 1 kilogram of carbon nanofibers (CNFs) using chemical vapor deposition calculated by SimaPro™ Eco-Indicator 1999 (EI99) method, hierarchist perspective (long-term; substances included if there is consensus regarding their effect; damages avoidable by good management; fossil fuels assumed not easily substituted).

<sup>b</sup>Normalized and weighted impacts.

Source: Khanna et al. (2008).

1           Eckelman et al. (2012) developed a life-cycle framework to compare the impact on ecological  
2 (and specifically aquatic) organisms of CNT production versus CNT releases to environmental media  
3 during the product life cycle. This assessment used existing data and a recently established consensus  
4 model for life-cycle impact assessments, USEtox, to estimate ecotoxicity from emissions during CNT  
5 production and CNT releases during product use and disposal for “realistic” and “worst case” scenarios.  
6 They calculated the potentially affected fraction of aquatic organisms per unit mass of CNTs released and  
7 “comparative toxic units for ecosystems” for different methods of synthesis and projected scale-up  
8 results. The theoretical framework was useful for comparing the relative impacts of different synthesis  
9 methods, what proportion of potential ecotoxicity is due to the synthesis process compared to required  
10 purification methods, and also made projections based on future increased scale of production. The  
11 authors concluded that the greatest ecotoxicity impacts do not result from release of CNTs during the  
12 product life cycle or from unused reagents or synthesis products during production, but rather from the  
13 emission of metals due to the combustion of fossil fuels necessary to generate electricity for CNT  
14 synthesis or production of various inputs.

15           Another study analyzed a broad range of environmental impacts from the production of one  
16 SWCNT polymer mesh (a transistor/electromagnetic interference-shielding application) (Dahlben and  
17 Isaacs, 2009). The study examined both the energy requirements for raw material extraction and  
18 manufacturing and emissions from these processes (excluding SWCNT emissions due to the current lack  
19 of consensus on its effects). The authors found that manufacturing this CNT application could damage  
20 ecosystems and resource quality, as shown in Table 5-8. Damage to ecosystems (due to  
21 acidification/eutrophication and land use) was expressed as the loss of species over a certain area in a  
22 given time. Damage to resource quality was expressed as the surplus energy needed for future extractions

1 of minerals and fossil fuels (due to the resources needed to extract these materials for SWCNT polymer  
2 mesh production).

3 The authors found that production of SWCNT polymer mesh generated larger fossil fuel impacts  
4 relative to other measured environmental impacts. The authors also found that fossil fuel impacts were  
5 dominated by processes requiring energy-intensive equipment (e.g., furnace for synthesis, wet bench for  
6 cleaning, and spinner for coating). Although the impact measures were reported to be low for all  
7 categories, they represent the resource impacts of producing a single SWCNT polymer mesh. The level of  
8 aggregation required to compile these metrics, however, coupled with the lack of models to predict  
9 endpoint effects of some emissions (e.g., from nanotubes), render these metrics highly uncertain ([Khanna  
10 et al., 2008](#)). Additionally, this study did not include impacts of SWCNT emissions in its overall

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Table 5-8. Environmental assessment of production of one SWCNT polymer mesh.<sup>a</sup>

Impact category	Impact <sup>b</sup>	Unit
Acidification/Eutrophication	$1.229 \times 10^{-2}$	PDF*m <sup>2</sup> yr
Land use	$4.440 \times 10^{-3}$	PDF*m <sup>2</sup> yr
Minerals	$1.117 \times 10^{-3}$	MJ Surplus
Fossil fuels	$7.531 \times 10^{-1}$	MJ Surplus

<sup>a</sup>Environmental impacts of production of one SWCNT polymer mesh by high-pressure carbon monoxide synthesis (a form of chemical vapor deposition) calculated by SimaPro™ Eco-Indicator 1999 (EI99) method, hierarchist perspective (long-term; substances included if there is consensus regarding their effect; damages avoidable by good management; fossil fuels assumed not easily substituted).

<sup>b</sup>Normalized and weighted impacts.

PDF\*m<sup>2</sup>yr = potentially disappeared fraction per area (m<sup>2</sup>) per year; MJ Surplus = Additional megajoules of energy required for future extraction of the resource.

Source: Dahlben and Isaacs ([2009](#)).

11 calculations of environmental impact. How the environmental impacts of SWCNT polymer mesh  
12 production differ from the impacts of flame-retardant textiles using MWCNTs or other alternative  
13 materials, such as decaBDE, is unclear.

### 5.3.3. Climate Change

#### *Decabromodiphenyl Ether*

14 No information was identified that examined climate change impacts due to decaBDE flame-  
15 retardant textile coatings.

### *Multiwalled Carbon Nanotubes*

1 No information was identified that directly examined climate change impacts due to MWCNT  
2 flame-retardant coatings. Empirical data suggest, however, that release of greenhouse gases such as  
3 methane, volatile organic compounds, and polycyclic aromatic hydrocarbons from MWCNT synthesis is  
4 possible ([Plata, 2009](#); [Plata et al., 2009](#)). The authors concluded, however, that for commercial-scale  
5 production the contribution of MWCNT synthesis to atmospheric methane will be negligible compared to  
6 existing methane sources, and that volatile organic compound emissions might be significant only on the  
7 local scale ([Plata et al., 2009](#)). Singh et al. ([2009](#)) calculated emissions of 4 kg CO<sub>2</sub>/kg SWCNT from one  
8 method of CVD synthesis. Altering CNT synthesis methods might minimize formation of these or other  
9 hazardous by-products. For example, Plata ([2009](#)) found that by identifying select thermally generated  
10 compounds correlated with CNT growth rate, such compounds could be delivered to the catalyst without  
11 thermal treatment and thereby eliminate the need to heat reactant gases.

12 On the other hand, a life-cycle assessment of CNF production calculated that manufacture of 1 kg  
13 of methane-based CNFs equals at least 700 kg of CO<sub>2</sub> equivalents, and 1 kg of ethylene-based CNFs  
14 equals at least 400 kg of CO<sub>2</sub> equivalents ([Khanna et al., 2008](#)). In other words, the authors calculated that  
15 production of 1 kg of methane-based CNFs is equivalent to CO<sub>2</sub> emissions from 78.5 gallons of gasoline  
16 consumed, while production of 1 km of ethylene-based CNFs is equivalent to CO<sub>2</sub> emissions from  
17 44.8 gallons of gasoline consumed.<sup>21</sup> The relationship between climate change effects due to synthesis of  
18 SWCNTs, CNFs, and MWCNTs is unclear.

## 5.3.4. Economics

### *Decabromodiphenyl Ether*

19 No information was identified that calculated the cost of manufacturing decaBDE or decaBDE  
20 flame-retardant textiles.

### *Multiwalled Carbon Nanotubes*

21 No information was identified that calculated the cost of manufacturing MWCNTs or MWCNT  
22 flame-retardant textiles. Isaacs et al. ([2010](#)) estimated, however, that the cost of manufacturing 1 g of  
23 SWCNTs by arc discharge, CVD, and HiPCO® (a type of CVD commonly used to manufacture  
24 SWCNTs) is roughly \$1906, \$1706, and \$485, respectively. These estimates include all materials, labor,  
25 and equipment necessary for synthesis, dispersion, filtration, inspection, and packaging of SWCNTs.  
26 MWCNTs are generally thought to be less expensive to produce than SWCNTs, and further optimization  
27 of MWCNT manufacturing is likely to decrease manufacturing costs further.

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<sup>21</sup>EPA GHG Calculator available at <http://www.epa.gov/cleanenergy/energy-resources/calculator.html>.



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# Chapter 6. Identifying and Prioritizing Research Needs to Support Risk Assessment and Risk Management

## 6.1. Context for Identifying and Prioritizing Research

1 Previous chapters in this case study represent the assembly of information through the vertical  
2 continuum of the comprehensive environmental assessment (CEA) framework (Figure 1-1); as introduced  
3 in Chapter 1, however, this step is merely the first in the CEA process (Figure 1-2). The next step is for a  
4 diverse group of expert stakeholders to consider the compiled information, in the context of their own  
5 knowledge of multiwalled carbon nanotubes (MWCNTs) and flame-retardant materials, to identify and  
6 prioritize research needs for future risk assessment efforts that inform risk management practices for  
7 MWCNTs in flame-retardant textile coatings. This step then supports subsequent efforts within the CEA  
8 process to facilitate an iterative communication flow across the horizontal spectrum of research, risk  
9 assessment, and risk management.

10 Several recommendations have been made recently to improve risk assessment and risk  
11 management approaches. These include calls for greater transparency and increased stakeholder  
12 engagement in assessment efforts for evaluating options to mitigate the exposures or hazard(s) associated  
13 with an agent ([NRC, 2009](#)). Greater transparency and broader stakeholder input promote informed  
14 evaluations of the various trade-offs between individual risk management options ([NRC, 2009](#)). More  
15 recently the need to consider longer term consequences of alternative options in a broader context, which  
16 would encompass social, environmental, and economic indicators, has been recognized ([NRC, 2011](#)). All  
17 of these recommendations stress the need to address the cumulative effects from multiple exposures to  
18 one or more stressors, vulnerability of susceptible populations, and potential for impacts throughout the  
19 product life cycle in risk assessments ([NRC, 2011, 2009](#)). A shift toward this more holistic, systems-  
20 based approach would provide more complete information to risk assessors to better inform risk managers  
21 in making decisions that support long-term, sustainable management practices ([NRC, 2011](#)).

22 Many efforts are underway to gather information and develop approaches that support the  
23 implementation of such recommendations [e.g., ([Anastas, 2012](#); [Lavoie et al., 2010](#); [Rossi et al., 2006](#))].  
24 The CEA approach represents one such effort by recognizing that to use risk assessments effectively and

1 efficiently for evaluating risk management options and understanding the longer term consequences of a  
2 broad scope of complex information (e.g., cumulative risk, life-cycle analyses), research supporting such  
3 evaluations must be transparently planned and promptly executed. The use of this document in the next  
4 step of the CEA process is an effort to plan such research for MWCNTs in flame-retardant textile  
5 coatings. Specifically, a group of expert stakeholders representing a variety of technical backgrounds  
6 (e.g., material characterization, environmental fate and transport, life-cycle analysis) and sectors (e.g.,  
7 industry, academia, nongovernmental organizations) will use this document as a starting point for  
8 identifying and prioritizing research needs to support assessments that inform near-term risk management  
9 goals.

10 In planning research to support assessments, reviewing risk management goals to understand the  
11 types of analyses and assessments that would inform management efforts is useful. Such a review is  
12 consistent with the connections highlighted in the CEA process diagram (Figure 1-2). Research outcomes  
13 feed back into the CEA framework to provide additional information necessary for assessing risk-related  
14 trade-offs and, subsequently, developing adaptive risk management plans. Various risk management goals  
15 could be selected for the application of MWCNTs in flame-retardant textile coatings; as discussed in  
16 Chapter 1, the selection of any one goal for a comparative CEA would depend on the needs of risk  
17 managers at the time. One particular scenario, however, based on what might occur for this specific  
18 nanoenabled product, is used here as an example to provide context to the formulation of priority research  
19 needs. The use of this scenario is not meant to imply actual assessment or risk management  
20 recommendations, but rather to illustrate how specific research needs to support future evaluations of  
21 MWCNTs might be identified. Additional considerations and examples of risk assessment and  
22 management decisions are discussed in Section 6.2.

23 As outlined in Chapter 1, the use of MWCNTs in flame-retardant textile coatings is not common,  
24 although evidence suggests they could be used more extensively in the future as conventional flame  
25 retardants are phased out due to concerns surrounding environmental persistence and human health  
26 effects ([Binetruy and Boussu, 2010](#); [Environment Canada, 2010](#); [U.S. EPA, 2010a, b](#); [Laoutid et al., 2009](#);  
27 [Cipiriano et al., 2007](#); [Kashiwagi et al., 2005b](#); [Kashiwagi et al., 2005a](#); [Kashiwagi et al., 2004](#);  
28 [Rahman et al., 2001](#)). Should a flame-retardant textile coating containing MWCNTs be developed for use  
29 in the United States, the manufacturer or importer likely would be required to submit a premanufacturing  
30 notice (PMN) to the U.S. Environmental Protection Agency (EPA) ([U.S. EPA, 2008c](#)). Information in a  
31 PMN includes the chemical identity (i.e., name and structure), anticipated production volume, use and  
32 disposal methods, human exposure estimates, and any readily available test data ([U.S. EPA, 2010g](#)). After  
33 receiving a PMN, EPA has 90 days to identify and control any unreasonable risks by evaluating  
34 information related to environmental health, exposure and release, and economic impacts ([U.S. EPA,](#)

1 [2010f](#)). Thus, one of the first risk management decisions for MWCNT flame-retardant textile coatings  
2 could be to determine whether the material should be (1) produced without restriction or regulations, (2)  
3 imported, produced, or used with limitations, or (3) prohibited from import, production, or use ([U.S. EPA,](#)  
4 [2010f](#)). The third outcome, prohibition, could result from several determinations, including that  
5 information on potential impacts of the material is insufficient ([U.S. EPA, 2010f](#)).

6 To support this and other risk management decisions about the use of MWCNTs in flame-  
7 retardant textile coatings, information must be readily available to decision-makers to enable a considered  
8 determination within the relevant time constraints. The research objectives identified and prioritized in  
9 this CEA application ideally would provide such information within three to five years of initiating the  
10 research. Notably, completion of all research is not feasible within this time frame due to practical (e.g.,  
11 budget) and other (e.g., other research should be completed first) constraints. For these reasons, the CEA  
12 approach emphasizes the prioritization of information gaps in the next step of this process.

13 Considerations when prioritizing information gaps might include aspects of the material  
14 described in the case study, the context of making risk management decisions, and the potential for  
15 unforeseen consequences that are inadequately addressed in the literature. For instance, as discussed in  
16 Chapter 1, Chapter 3, Chapter 4, and Chapter 5 of this document, the specific physicochemical  
17 characteristics of MWCNTs influence their behavior in environmental media, subsequent exposure in  
18 human and ecological populations, as well as potential impacts on humans, ecological populations, and  
19 the environment. Although various approaches are used to understand the relationship between  
20 physicochemical characteristics and behavior as an initial indicator of risk for some conventional  
21 materials (such as structure activity relationships, test data on the substance or analogs, quantitative  
22 structure activity relationships), the applicability of these approaches for nanoscale materials  
23 (nanomaterials) is still developing ([Burello and Worth, 2011](#); [Fourches et al., 2011](#)). Notably,  
24 understanding this relationship for engineered nanomaterials provides not only an opportunity to predict  
25 adverse effects in relevant receptors, but also to apply green chemistry methods to mitigate, through  
26 material design, potential exposure to or effects of the material and its by-products ([Balakrishnan et al.,](#)  
27 [2011](#); [Albrecht et al., 2006](#)).

28 The potential for unintended consequences of a material is another important aspect to consider in  
29 the prioritization process. For example, as described in Chapter 3 and Chapter 4, current data suggest that  
30 the debromination of decabromodiphenyl ether (decaBDE) has led to environmental fate and exposure of  
31 the material and by-products that differ from initial expectations based on material properties. Although  
32 the risk management concerns associated with decaBDE will differ from those for MWCNTs in flame-  
33 retardant textile coatings, information on decaBDE can provide context for the type of considerations that  
34 might be involved in evaluating such coatings. Such information is intended also to demonstrate the need

1 to identify potential, unintended consequences early in the continuum of planning research, executing risk  
2 assessments, and informing risk management practices.

3 As discussed in Section 6.2 below, the next step of the CEA process results in a prioritization of  
4 components of the CEA framework and specific research questions for those components considered by  
5 the diverse expert stakeholder group as important to include in assessments, but lacking information to  
6 support future risk management decisions. If these research questions are pursued, the knowledge gained  
7 could support a variety of risk assessments and other analyses that then inform risk management  
8 decisions. Examples of such decisions are determinations of whether particular MWCNTs in flame-  
9 retardant coatings are preferable to conventional flame retardants, or whether altering certain material  
10 characteristics to mitigate potential exposures or hazards would be prudent before allowing the material to  
11 be placed on the market.

12 Such research fits within the overall research paradigm at EPA, the principles of which include  
13 sustainability; systems thinking; integrated transdisciplinary research; and relevant, responsive, and rapid  
14 research ([Anastas, 2012](#)). Within this research paradigm, known as the “Path Forward,” are six national  
15 research programs ([Anastas, 2012](#)). Research specific to nanomaterials falls within the Chemical Safety  
16 for Sustainability program and themes within this program are oriented toward addressing priority  
17 research questions that might arise in the CEA process for MWCNTs. For example, questions related to  
18 physicochemical properties might be investigated under the Program’s theme on inherent chemical  
19 properties. Yet, the integrated transdisciplinary nature of CEA and the Path Forward suggests that some  
20 research questions could be addressed by multiple national programs working collaboratively. Notably,  
21 some of the identified research objectives might best be addressed by other government agencies,  
22 academic institutions, or others in the scientific community. The research priorities identified in the CEA  
23 process are thus intended not only to inform EPA research, but also to serve as a resource for the broader  
24 scientific community.

## 6.2. Carrying Out Identification and Prioritization of Research Needs

25 With the above context for identifying and prioritizing research needs to support future  
26 assessments and risk management decisions for MWCNT, the lingering question is: How? As discussed  
27 in the previous section and in Chapter 1, a diverse group of expert stakeholders will participate in a  
28 structured collective judgment process that supports equal representation of each individual’s input.  
29 Specifically, participants will use a software-based tool, which supports stakeholder engagement

1 remotely, to consider each component of the CEA framework in relation to potentially relevant risk  
2 factors associated with the product life cycle of MWCNT flame-retardant textile coatings. Stakeholders  
3 will use this tool in a series of exercises to rate: (1) the importance of CEA framework components for  
4 future assessments of MWCNTs in flame-retardant textile coatings, and (2) the current state of the science  
5 of the components in terms of supporting risk management initiatives. These exercises are intended to  
6 actively engage stakeholders in identifying critical research needs based on each stakeholder's perception  
7 of the information presented in the case study, their own individual experience and expertise, and the  
8 expert opinion of other stakeholders. This approach thus avoids simply asking stakeholders to review and  
9 prioritize a predetermined list of data gaps, which could exclude important data gaps a priori. This  
10 collective judgment exercise, coupled with a subsequent structured, face-to-face workshop, will provide a  
11 well-informed set of specific research needs. This early step in the risk assessment process establishes the  
12 goals, scope, focus, and potential options to consider in decision-making ([NRC, 2009](#); [Van Leeuwen et  
13 al., 1998](#)). The problem formulation step helps establish the type of analyses, and associated uncertainty  
14 and variability, that will be useful to a risk manager in making a decision about the material, chemical, or  
15 technology of focus ([NRC, 2009](#); [Van Leeuwen et al., 1998](#)). A parallel concept is establishing the type of  
16 research that will be useful for the analyses that inform a risk manager about a particular material, such as  
17 MWCNT flame-retardant textile coatings. As discussed in Chapter 1, this particular CEA case study was  
18 not developed with a specific risk management objective in mind; rather, the case study uses the CEA  
19 framework to structure information such that expert stakeholders can consider what types of risk  
20 management decisions might be needed, and thus what information would support assessments that  
21 inform those decisions. Problem formulation at this early, research-orientated stage is focused then on  
22 thinking through the types of future risk-based decisions that could arise for MWCNTs in flame-retardant  
23 textile coatings. This is followed by identifying and prioritizing information to enable such risk-based  
24 decisions through the collective judgment step described above.

25 Placing a greater focus on problem formulation is recognized as an important step toward  
26 improving risk assessment ([NRC, 2009](#)) but the preceding step—anticipating what information to  
27 research in order to support problem formulation in future assessments—has received less attention.  
28 Placing more emphasis on deciding which information to research would engage stakeholders early in the  
29 assessment planning process to ensure that major factors they consider important are included, as well as  
30 making sure that risk assessors and managers have the information they need to develop management  
31 plans that include those considerations. This approach is consistent with recent NAS recommendations  
32 ([NRC, 2011, 2009](#)).

33 As discussed in the previous section, a variety of types of risk management decisions may be  
34 relevant to MWCNTs in flame-retardant textile coatings in the future. One of these was discussed in the

1 previous section and is presented along with other examples in Table 6-1. The questions in Table 6-2 are  
 2 examples of those that could be asked during the problem formulation phase of an assessment to evaluate  
 3 whether data are available and useful [e.g., consider relevant endpoints, relevant exposure routes, doses  
 4 and timing, acceptable levels of uncertainty in assay(s) selected, data variability] to support an assessment  
 5 that informs risk management decisions, such as those in Table 6-1. The answers to these questions can  
 6 help formulate an appropriate assessment approach or facilitate the identification of data gaps that must  
 7 be filled before the assessment can proceed. In the context of this case study, the extent to which these  
 8 questions, or other questions that stakeholders identify, can be answered could indicate which  
 9 components of the CEA framework are high priorities for developing specific research questions that  
 10 support future assessments and risk management decisions.

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**Table 6-1. Examples of Risk Management Decisions**

Area of Decision-Making	Directed At	Example Decisions
Product environmental health and safety	New chemicals Existing chemicals Biotechnology	Pre-manufacturing notices Pesticide re-evaluations Permits to release genetically modified organisms
Site management	Risk avoidance Risk mitigation Site location	Accidental releases Cleanup of hazardous waste landfills Degree of contamination, presence of endangered species
Natural Resource Use	Habitat integrity Species introductions	Land use (e.g., road construction, mining, agriculture, logging) Integrated pest management

Adapted from van Leeuwen (1998).

**Table 6-2. Example Questions for Problem Formulation**

General Areas	Specific Questions
What are the characteristics of the stressor of concern?	<p>Is the stressor of concern chemical, physical, or biological?</p> <p>What are the physicochemical characteristics of the stressor?</p> <p>What are the locations and quantities of releases of the stressor to different media?</p>
What are the characteristics of the exposure setting?	<p>What are the known concentrations of the stressor in different media?</p> <p>What processes move the stressor through the environment?</p> <p>How does the stressor change as it moves through the environment?</p> <p>What is the spatial scale over which exposures to the stressor are likely to occur?</p>
What are the characteristics of the exposed populations?	<p>Which individuals, populations, or population segments are expected to be exposed?</p> <p>Which species and trophic-level relationships are present in exposed ecosystems?</p> <p>What are the probable exposure routes and pathways for the population(s) of interest?</p> <p>Is exposure to the stressor expected to occur only during a single event or will exposures be episodic or continuous?</p> <p>What is the time scale over which exposures to the stressor are likely to occur?</p>
What are the assessment endpoints?	<p>What adverse effects have been observed in the population(s) of interest?</p> <p>What are the most sensitive species and measured endpoints?</p> <p>What processes affect the behavior of the stressor within the receptor?</p> <p>How does the stressor change as it moves through the receptor?</p> <p>What biological mechanisms are involved in the formation of adverse effects?</p> <p>What social conditions or impacts might result from the stressor?</p> <p>What economic conditions or impacts might result from the stressor?</p> <p>What natural resources might be affected and how?</p> <p>What ecosystem services might be altered and how?</p>



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**Nanomaterial Case Study:  
A Comparison of Multiwalled Carbon Nanotube and  
Decabromodiphenyl Ether Flame-Retardant Coatings  
Applied to Upholstery Textiles (DRAFT)**

**Appendices (A–F)**

*July 2012*

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U.S. Environmental Protection Agency  
Washington, DC



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# Appendix A: Case Study Candidate Evaluation and Selection Process

# Appendix A. Case Study Candidate Evaluation and Selection Process

1 Appendix A describes the process of evaluating and selecting carbon-based nanomaterials in  
2 specific applications as candidates on which to focus in the current case study. Specifically, it outlines the  
3 process by which the candidate carbon-based nanomaterial applications were identified and highlights  
4 factors relevant to the suitability of each candidate for a Nanomaterial Case Study. This information was  
5 used to support an informed selection of the nanomaterial and application for this case study by U.S.  
6 Environmental Protection Agency (EPA) program offices, labs, and centers in the Office of Research and  
7 Development, and regional offices during September 2011.

## A.1. Background

8 As discussed in Chapter 1, the EPA ([2007](#)) Nanotechnology White Paper called for the use of  
9 nanomaterial case studies and multidisciplinary expert workshops as a means to inform research planning  
10 to support the risk assessment process for nanomaterials. In response to the recommendations of the  
11 Nanotechnology White Paper, EPA has been developing case studies of selected nanomaterials in specific  
12 applications, including *Nanoscale Titanium Dioxide in Water Treatment and Topical Sunscreen*<sup>1</sup> and  
13 *Nanoscale Silver in Disinfectant Spray*.<sup>2</sup> To continue this series of case studies, five carbon-based  
14 nanomaterial applications were identified as candidates for the next Nanomaterial Case Study (presented  
15 in alphabetical order by material and application):

- 16 • Carbon nanofibers in cement/concrete
- 17 • Carbon nanotubes (multi-walled) in flame-retardant coatings and composites
- 18 • Carbon nanotubes (multi-walled) in rubber tires
- 19 • Carbon nanotubes (single-walled) in textiles
- 20 • Nanocrystalline cellulose in biodegradable packaging

---

<sup>1</sup> <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=230972>

<sup>2</sup> <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=226723>

1 This appendix outlines the process by which the candidate carbon-based nanomaterial  
2 applications were identified, briefly summarizes the state of the science for each of the identified  
3 candidates, and highlights factors relevant to the suitability of each candidate for a Nanomaterial Case  
4 Study. The following criteria were used as guides in judging the candidates:

- 5 • “Nano-ness” of the material (i.e., whether the material is intentionally engineered at the  
6 nanoscale and has properties that distinguish it from conventional forms of the material);
- 7 • Potential for exposure throughout the product life cycle (in humans, both occupational and  
8 general public, as well as in other biota);
- 9 • Availability of data (whether directly related or inferred from other materials/products);
- 10 • Feasibility of comparing the nano-enabled application to a non-nano-enabled application; and
- 11 • Relevance to EPA programs.

12 Despite the wealth of information on carbon-based nanomaterials, EPA had previously  
13 encountered difficulties in identifying an appropriate carbon-based nanomaterial application as a  
14 candidate for a case study. These difficulties arose in part due to the following factors:

- 15 • Few data are available on the actual commercial use of carbon-based nanomaterials in  
16 products.
- 17 • Little to no information is available on release of carbon-based nanomaterials from  
18 applications during normal use.
- 19 • Small loadings (<5% by weight or volume) of carbon-based nanomaterials are generally  
20 required to confer desirable properties.
- 21 • Compared to other types of nanomaterials, the applications for carbon-based nanomaterials  
22 appear to have a smaller exposure potential outside of occupational and disposal scenarios.

23 Although these challenges are still present, the recent increase in carbon-based nanomaterial  
24 research has produced new data, and new applications have been proposed that offer greater potential for  
25 widespread exposure. As a result, the selection of a carbon-based nanomaterial application for the next in  
26 the Nanomaterial Case Study series appears to be feasible.

## A.2. Candidate Identification Process

27 The process by which the five nanomaterial application candidates were identified is summarized  
28 in Figure A-1. Overall, the process began with a systematic approach to the identification of  
29 nanomaterials and applications for investigation. This preliminary phase of the process utilized strategic  
30 literature and Internet searches to identify supporting scientific literature, relevant news reports, and  
31 nanomaterial information aggregation websites. Certain basic literature search statistics (e.g., number of



1 total hits, number of hits in scientific databases) were then evaluated to provide an initial metric of overall  
2 data availability and interest within the nanotechnology community for each candidate  
3 nanomaterial/application combination. After the “long list” of material/application combinations was  
4 identified and narrowed down using this systematic approach, a more judgment-based approach was used  
5 to evaluate the suitability of a “medium list” of potential candidates and identify the most feasible  
6 candidates for a case study. In this phase of the process, a list of suitability questions was used to step  
7 through the life cycle of a specific nano-enabled product and evaluate the characteristics of that product  
8 that might affect release, exposure, environmental fate, and impact on humans, ecological receptors, and  
9 the environment. A professional judgment as to whether a case study feasibly could be conducted for each  
10 candidate then was determined based on the answers to the suitability questions, and a “short list” of five  
11 feasible candidates was developed based on professional judgment of suitability.

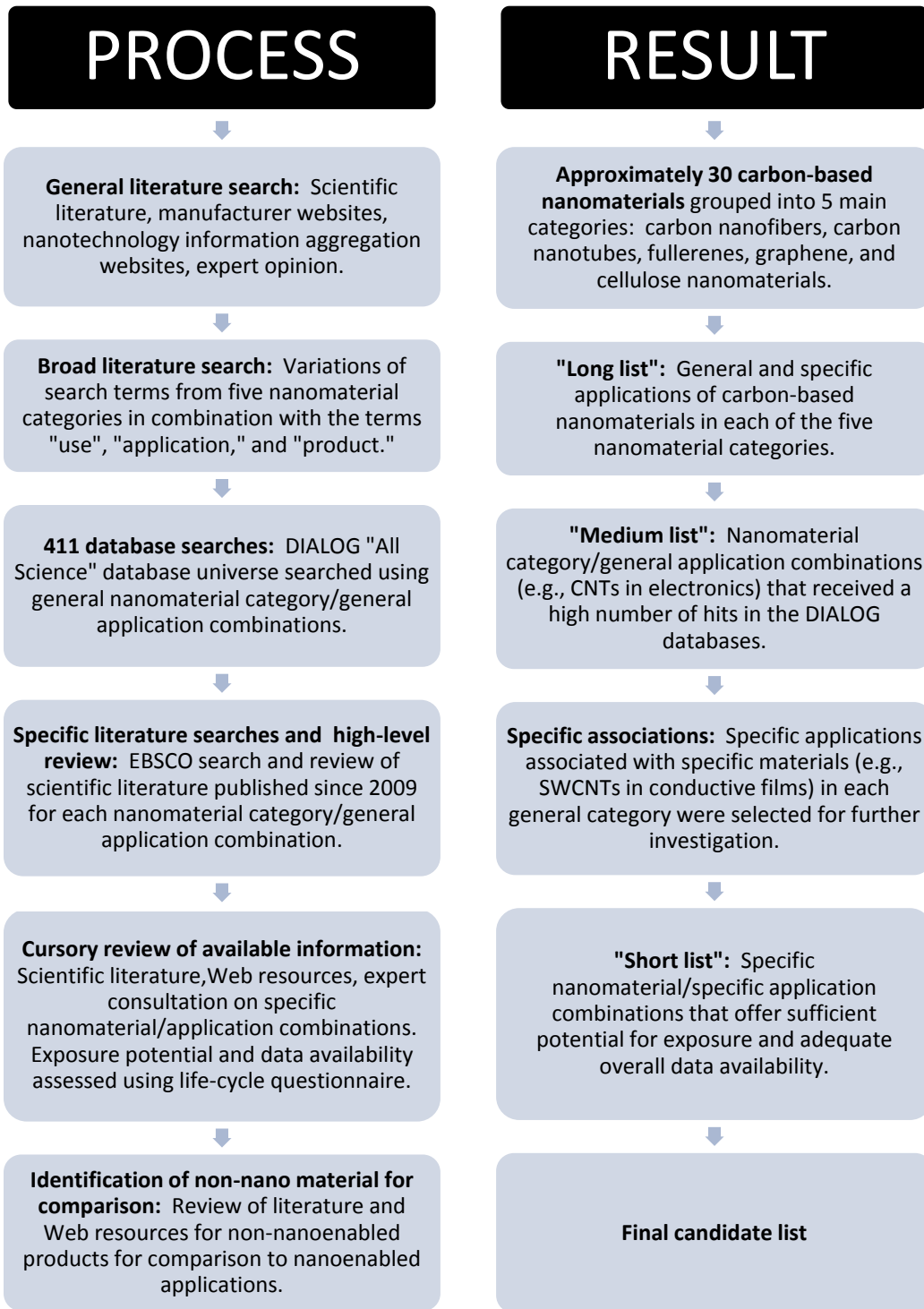


Figure A-1: Candidate Identification Process

## A.3. Nanomaterial Application Candidates

1           The candidate identification process yielded five nanomaterial applications for consideration as  
2 the subject of a new case study. The nanomaterial application candidates and proposed non-nanoenabled  
3 products for comparison are presented in Table A-1 below. As discussed in Chapter 1, the non-  
4 nanoenabled product is intended to provide a frame of reference against which the ecological, human  
5 health, and other implications of the selected nanomaterial application can be compared.

---

**Table A-1. Nanomaterial application candidates and non-nano-enabled products for comparison in a case study.**

---

Nanomaterial	Application	Proposed Non-Nano-Enabled Product for Comparison
Carbon nanofiber (CNF)	Cement/concrete (CNF-reinforced)	Steel- or glass-fiber reinforced cement/concrete
Multi-walled carbon nanotubes (MWCNTs)	Flame-retardant coatings and composites	Polybrominated diphenyl ether (PBDE) flame-retardant materials
MWCNT	Rubber tires (MWCNT as filler)	Carbon black and silica filler in tires
Single-walled CNTs (SWCNTs)	Textiles (SWCNT-reinforced/impregnated)	Traditional textiles reinforced with carbon fiber polymer composites
Nanocrystalline cellulose (NCC)	Biodegradable packaging (NCC-polymer composite)	Packaging containing polylactic acid (PLA) resin alone

---

## A.4. Summary of Factors Affecting Suitability

6           Key considerations of the suitability of each candidate for development into a case study were  
7 summarized in a suitability chart (Table A-2). Based on the initial findings of this analysis (which should  
8 not be considered exhaustive or comprehensive), four of five applications appeared to still be in the  
9 research stage and unavailable for the commercial market in the United States or internationally.  
10 Although carbon nanotubes have been incorporated into military textiles, carbon nanotube flame-retardant  
11 coating is the only application identified as being currently available on the consumer market.

Table A-2. Factors for consideration in selecting a candidate for case study.

Selection Factors		Candidates				
		CNF Cement/Concrete	MWCNT Flame-Retardant Coatings and Composites	MWCNT Rubber Tires	SWCNT Textiles	NCC Biodegradable Packaging
		■ = High    ■ = Medium    □ = Low				
Data Availability	Nanomaterial production volume	■	■	■	■	■
	Nanomaterial manufacturing processes	■	■	■	■	■
	Nanomaterial characterization	■	■	■	■	■
	Nanomaterial release from application	□	□	□	■	□
	Nanomaterial fate and transport in the environment	□	■	■	□	□
	Human exposure to nanomaterial	□	■	■	■	□
	Ecological exposure to nanomaterial	□	■	■	■	□
	Human health effects of nanomaterial	□	■	■	■	□
	Ecological effects of nanomaterial	□	■	■	■	□
	Nano-product data (i.e., nanomaterial application data)	■	■	□	□	□
	Conventional (i.e., non-nano) product data for comparison	■	■	■	■	■
	<b>Data Availability Qualifiers.</b>					
High (■) = The database appears to contain a large quantity of good quality, diverse literature on the topic.						
Medium (■) = The database contains some literature specific to the topic, but substantial data gaps were observed.						
Low (□) = Little to no information was identified on the topic.						
		● = Yes    ● = Possibly    ○ = No				
Suitability Questions	Is there presumptive potential for exposure:					
	During manufacturing?	●	●	●	●	●
	During use?	●	●	●	●	●
	At end of life?	●	●	●	●	●
	Will extrapolation from other applications/materials be necessary?	●	●	●	●	●
	Is the nanomaterial currently produced in quantities >5 tons/year?	●	●	●	●	○
	Is material production expected to increase in the near future?	●	●	●	●	●
	Will the nanomaterial be used in the product at levels >5% by weight?	○	○	●	●	●
	Is the product already on the market?	○	●	○	○	○
	Is there evidence that the nanomaterial is hazardous:					
To humans?	●	●	●	●	○	
To eco receptors?	●	●	●	●	○	
<b>Answers to Suitability Questions.</b>						
Yes (●) = Initial findings suggest that an affirmative answer can be given with relatively high confidence.						
Possibly (●) = Initial findings from the preliminary literature review were conflicting.						
No (○) = Initial findings suggest that a negative answer can be given with relatively high confidence.						

## A.5. U.S. EPA Program Involvement in Final Selection

1           The selection of which of the five nano-carbon product candidates to use in this case study  
2 document involved representatives from EPA program offices, labs and centers within the Office of  
3 Research and Development, and regional offices. To facilitate distributing and discussing information  
4 relevant to the selection, an internal online forum was developed using a commercially available product  
5 ([www.IdeaScale.com](http://www.IdeaScale.com)). The forum included brief introductory material on this nanomaterial case study  
6 series, instructions on using the website to nominate nano-carbon product candidates, links to tables  
7 summarizing life-cycle information on five candidate nano-carbon products (i.e., the applications in Table  
8 A-2), and a more detailed report summarizing the state of the science for each candidate.

9           A link to the forum was sent to EPA representatives along with a request to share the link with  
10 colleagues in their organization. Representatives and others in the Agency could then use the forum to  
11 discuss the candidates informally and nominate candidates for selection. Representatives were asked to  
12 submit a formal vote that reflected input from their colleagues through the IdeaScale forum and other  
13 communication channels they wished to use, as well as consideration of their own knowledge, the  
14 information provided on the forum, and the consideration of the criteria listed in Section A.1.

15           The candidates receiving the most votes were SWCNTs in textiles and MWCNTs in flame-  
16 retardant coatings and composites; thus, a hybrid option (MWCNTs in flame-retardant coatings applied to  
17 textiles) was selected. This choice reflected comments that, although the textile application was  
18 preferable, MWCNTs were perhaps of greater interest based on indications that they will contain a higher  
19 level of contaminants and are currently more widely produced.

## Appendix A References

U.S. EPA (U.S. Environmental Protection Agency). (2007). Nanotechnology white paper [EPA Report]. (EPA 100/B-07/001). Washington, DC. <http://www.epa.gov/osa/pdfs/nanotech/epa-nanotechnology-whitepaper-0207.pdf>.

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# Appendix B. Analytical Methods for Detecting, Measuring, and Characterizing BDE-209 and Multiwalled Carbon Nanotubes



# Appendix B. Analytical Methods for Detecting, Measuring, and Characterizing BDE-209 and Multiwalled Carbon Nanotubes

1           This appendix provides a brief overview of some of the available techniques to detect, quantify,  
2 and characterize polybrominated diphenyl ethers (PBDEs; specifically BDE-209) and multiwalled carbon  
3 nanotubes (MWCNTs) in laboratory, biological, and environmental settings, along with current  
4 challenges to making such measurements. This information is not intended to be exhaustive in reporting  
5 every applicable method and associated challenges or to be comprehensive in describing available  
6 methods; rather, it is a summary of relatively common or known methods for characterizing BDE-209 and  
7 MWCNTs based on information available at the time this case study was developed.

## B.1. Measuring and Characterizing PBDEs and MWCNTs

8           Accurately measuring BDE-209 or MWCNTs in relevant biological or environmental media is  
9 critical for evaluating any potential impacts of either material on human health, ecological populations, or  
10 environmental resources ([Alcock et al., 2011](#); [Lehman et al., 2011](#)). The choice of which measurement  
11 technique to use for either BDE-209 or MWCNT samples will ultimately involve a consideration of trade-  
12 offs related to cost, time, selectivity, and sensitivity ([Alcock et al., 2011](#); [Lehman et al., 2011](#); [Stapleton,  
13 2006](#)). In evaluating which analytical technique(s) to use, having an understanding of the challenges  
14 related to quantifying and characterizing BDE-209 and MWCNTs is useful. For both materials, multiple  
15 techniques might be required to characterize all of the physicochemical properties of interest in a single  
16 sample (e.g., molecular composition, purity, shape, surface charge) ([Alcock et al., 2011](#); [Lehman et al.,  
17 2011](#)). Moreover, the training of personnel and the capital cost associated with some of these tools can  
18 impede the analysis of materials by multiple laboratories ([Alcock et al., 2011](#)). In addition, the  
19 standardization and validation of methods, availability of material standards, and the consistent reporting  
20 of material characteristics in peer-reviewed literature have proven difficult for both BDE-209 and  
21 MWCNTs ([Alcock et al., 2011](#); [Lehman et al., 2011](#)). Distinguishing the sample from background  
22 concentrations or other materials of similar composition (e.g., nonaBDE congeners versus decaBDE,

1 single-walled CNTs versus MWCNTs) is also a challenge for both materials ([Lehman et al., 2011](#);  
2 [Stapleton, 2006](#)).

3 For BDE-209, gas chromatography coupled with mass spectrometry is the most prevalently used  
4 method; however, a number of variations in this approach exist ([Stapleton, 2006](#)). Even small differences  
5 in analytical techniques can result in significant variation in results ([Alcock et al., 2011](#); [Stapleton, 2006](#)).  
6 Recent efforts to standardize methods and develop techniques that minimize material degradation have  
7 improved interlaboratory variation, but continue to be the subject of study, particularly for measuring  
8 samples in complex milieus ([Stapleton, 2006](#)). Detection and characterization of BDE-209 has proven  
9 more difficult than lower brominated compounds due in part to degradation at high temperatures and with  
10 ultraviolet light exposure ([Stapleton, 2006](#)).

11 For MWCNTs, transmission electron microscopy is generally used to characterize structural  
12 properties of the material, which is the first step in differentiating between MWCNTs, SWCNTs, or other  
13 materials; however, using this tool in tandem with others is necessary to characterize the material  
14 ([Lehman et al., 2011](#)) more completely. Challenges related to characterizing and quantifying MWCNTs  
15 include their propensity to agglomerate or otherwise transform (e.g., surface oxidize) during the process  
16 of production, purification, or exposure, as well as interference from experimental artifacts (e.g., metal  
17 catalysts used in material production) ([Petersen and Henry, 2012](#); [Lehman et al., 2011](#)). The challenge of  
18 combining multiple techniques (e.g., gas chromatography and mass spectrometry) for BDE-209 analyses  
19 is amplified for MWCNTs in that a multitude of measurements and sampling techniques are generally  
20 required to fully characterize nanomaterials ([Lehman et al., 2011](#)).

## B.2. Summary Tables

21 The tables below highlight techniques for detecting, measuring, and characterizing PBDEs and  
22 MWCNTs. Table B-1 briefly outlines advantages and disadvantages of individual approaches to gas  
23 chromatography and spectrometry, as well as a few alternative techniques that are available for studying  
24 PBDEs. Table B-2 provides a brief overview of available methods to characterize a range of MWCNT  
25 properties. More detail on each approach can be found in the references listed at the end of this appendix,  
26 particularly the recent review by Lehman et al. ([2011](#)).

Table B-1. Analytical techniques for detecting, measuring, and characterizing PBDEs.†

Citation(s)	Technique	Application(s)	Advantages	Disadvantages
Stapleton et al. (2006)	Atmospheric pressure photoionization (APPI)-coupled liquid chromatography (LC)/MS-MS <sup>b, c</sup>	<ul style="list-style-type: none"> <li>Determination of congener ratios in environmental and biological media</li> </ul>	<ul style="list-style-type: none"> <li>Relatively soft ionization technique compared to electrospray ionization</li> </ul>	<ul style="list-style-type: none"> <li>Limited chromatographic resolution relative to gas chromatography</li> </ul>
Stapleton et al. (2006)	Gas chromatography (GC)/electron capture detection <sup>c</sup>	<ul style="list-style-type: none"> <li>Determination of congener ratios in environmental media</li> </ul>	<ul style="list-style-type: none"> <li>Inexpensive</li> <li>Ability to detect halogenated organic compounds</li> </ul>	<ul style="list-style-type: none"> <li>Relative imprecision compared to GC/ECNI</li> </ul>
Stapleton et al. (2006) La Guardia et al. (2006)	GC/electron capture negative ionization mass spectrometry (ECNI-MS) <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Determination of congener ratios in environmental and biological media</li> </ul>	<ul style="list-style-type: none"> <li>Low limit of detection</li> </ul>	<ul style="list-style-type: none"> <li>Selectivity</li> </ul>
Stapleton et al. (2006) La Guardia et al. (2006)	GC/electron ionization (EI) MS <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Determination of congener ratios in environmental and biological media</li> </ul>	<ul style="list-style-type: none"> <li>Selectivity</li> </ul>	<ul style="list-style-type: none"> <li>Interference may occur with methoxylated PBDEs</li> </ul>
Stapleton et al. (2006)	GC/high resolution mass spectrometry (HRMS) <sup>b, c</sup>	<ul style="list-style-type: none"> <li>Determination of congener ratios in environmental and biological media</li> </ul>	<ul style="list-style-type: none"> <li>Selectivity</li> <li>Sensitivity</li> <li>Can detect relatively high molecular weight analytes</li> </ul>	<ul style="list-style-type: none"> <li>Necessary equipment is not commonly found in laboratories</li> <li>Expensive</li> </ul>
Stapleton et al. (2006)	GC/HR time of flight (TOF) MS <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Determination of congener ratios in environmental media</li> </ul>	<ul style="list-style-type: none"> <li>Spectral data can be obtained over a wide mass range with little sacrifice in sensitivity</li> </ul>	<ul style="list-style-type: none"> <li>Expensive</li> <li>Low sample concentration required for accuracy</li> </ul>
Stapleton et al. (2006)	On-column injection GC <sup>a, c</sup>	<ul style="list-style-type: none"> <li>Separation and detection of PBDE congeners</li> <li>Determination of molecular weight</li> </ul>	<ul style="list-style-type: none"> <li>Necessary equipment commonly present in laboratories</li> <li>Precise discrimination, particularly of BDE-209</li> </ul>	<ul style="list-style-type: none"> <li>Small injection volume</li> <li>Sample must be free of impurities</li> </ul>

Table B-1, cont. Analytical techniques for detecting, measuring, and characterizing PBDEs.<sup>†</sup>

Citation(s)	Technique	Application(s)	Advantages	Disadvantages
Stapleton et al. (2006)	Programmable temperature vaporization (PTV) injection GC <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Separation and detection of PBDE congeners</li> <li>Determination of molecular weight</li> </ul>	<ul style="list-style-type: none"> <li>Relatively large injection volume compared to other GC techniques</li> <li>Separation can be performed on human serum</li> </ul>	<ul style="list-style-type: none"> <li>Requires significant optimization to perform separation</li> </ul>
Stapleton et al. (2006)	Split/splitless injection gas chromatography (GC) <sup>a, c</sup>	<ul style="list-style-type: none"> <li>Separation and detection of PBDE congeners</li> <li>Determination of molecular weight</li> </ul>	<ul style="list-style-type: none"> <li>Can be used on environmental samples</li> <li>Necessary equipment commonly present in laboratories</li> </ul>	<ul style="list-style-type: none"> <li>Injection volume must be small</li> <li>High injection temperature</li> </ul>

<sup>a</sup> Used for chemical (*in vitro*) analysis as reported in reference document  
<sup>b</sup> Used to analyze *in vivo* samples as reported in reference document  
<sup>c</sup> Used to analyze environmental samples as reported in reference document  
<sup>†</sup> Techniques listed in alphabetical order

Table B-2. Analytical techniques for detecting, measuring, and characterizing MWCNTs.<sup>†</sup>

Citation(s)	Technique	Application(s)	Advantages	Disadvantages
Petersen et al. (2012)	Atomic force microscopy <sup>a</sup>	<ul style="list-style-type: none"> <li>Size (diameter and length) and shape</li> </ul>		<ul style="list-style-type: none"> <li>Limited to samples in aqueous phase</li> </ul>
Lehman et al. (2011) Johnston et al. (2010) Petersen et al. (2012)	Centrifugation <sup>a</sup>	<ul style="list-style-type: none"> <li>Dispersion in solution</li> <li>Length distribution</li> <li>Size of nanoparticle aggregates</li> </ul>	<ul style="list-style-type: none"> <li>Centrifugation equipment commonly present in laboratories</li> </ul>	<ul style="list-style-type: none"> <li>Dispersion difficult; requires extensive sonication</li> <li>Accuracy may be affected by dispersion</li> </ul>
Petersen et al. (2012)	Chemothermal oxidation <sup>c</sup> (at 375°C)	<ul style="list-style-type: none"> <li>Measurement of MWCNT concentration in environmental samples</li> </ul>	<ul style="list-style-type: none"> <li>Allows for quantitative determination of MWCNT concentration</li> </ul>	<ul style="list-style-type: none"> <li>Inaccurate</li> </ul>
Petersen et al. (2012)	Cryotransmission electron microscopy (CEM) <sup>a</sup>	<ul style="list-style-type: none"> <li>Properties of MWCNTs in aqueous phase</li> </ul>		<ul style="list-style-type: none"> <li>Limited to samples in aqueous phase</li> </ul>
Petersen et al. (2012)	Fluorescence microscopy (FLM) <sup>b, c</sup>	<ul style="list-style-type: none"> <li>Detection of MWCNT in environmental media or tissue from biological specimens</li> </ul>	<ul style="list-style-type: none"> <li>Can detect single MWCNTs</li> </ul>	<ul style="list-style-type: none"> <li>Necessary equipment is not common in laboratories</li> </ul>

Table B-2, cont. Analytical techniques for detecting, measuring, and characterizing MWCNTs.†

Citation(s)	Technique	Application(s)	Advantages	Disadvantages
Lehman et al. (2011)	Fourier transform infrared spectroscopy (FTIR) <sup>a</sup>	<ul style="list-style-type: none"> <li>Nanoparticle functionalization</li> <li>CNT orientation (parallel or perpendicular to beam)</li> </ul>	<ul style="list-style-type: none"> <li>Reliable detector of carboxylic acids</li> </ul>	<ul style="list-style-type: none"> <li>Sample preparation may result in water contamination or altered surface functionalization</li> </ul>
Petersen et al. (2012)	Dynamic light scattering (DLS) <sup>a</sup>	<ul style="list-style-type: none"> <li>Size of aggregates in aqueous phase</li> </ul>	<ul style="list-style-type: none"> <li>Useful for detecting changes in MWCNT size at various points during synthesis or experimentation</li> </ul>	<ul style="list-style-type: none"> <li>Estimation of size by DLS based on spherical molecular structure and cannot be used for absolute calculation of aggregate size</li> </ul>
Lehman et al. (2011)	Gas pycnometry <sup>a</sup>	<ul style="list-style-type: none"> <li>Density</li> </ul>	<ul style="list-style-type: none"> <li>Can be used to determine both bulk and skeletal densities</li> </ul>	<ul style="list-style-type: none"> <li>Sample must be powder</li> </ul>
Lehman et al. (2011) Johnston et al. (2010) Petersen et al. (2012) Revel and Ayrault (2000)	ICP mass spectrometry (ICP-MS) <sup>b, c</sup>	<ul style="list-style-type: none"> <li>Metal concentration in environmental samples</li> </ul>	<ul style="list-style-type: none"> <li>Can be used to study health effects of MWCNT exposure by detecting changes in protein expression or structure</li> <li>Faster than instrumental neutron activation analysis</li> </ul>	<ul style="list-style-type: none"> <li>Necessary equipment is not commonly found in laboratories</li> </ul>
Petersen et al. (2012) Revel and Ayrault (2000)	Instrumental neutron activation analysis <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Metal concentrations</li> </ul>	<ul style="list-style-type: none"> <li>Can be more accurate than ICP-MS</li> </ul>	<ul style="list-style-type: none"> <li>Safety risk associated with radioactivity</li> <li>Lower sample throughput than ICP-MS</li> <li>Requires equipment not commonly found in laboratories</li> </ul>
Petersen et al. (2012) Johnston et al. (2010)	Light microscopy <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Identification of large MWCNT aggregates</li> </ul>	<ul style="list-style-type: none"> <li>Necessary equipment is common in laboratories</li> </ul>	<ul style="list-style-type: none"> <li>Technique provides qualitative, non-specific information</li> <li>Detection limited to large aggregates</li> </ul>

Table B-2, cont. Analytical techniques for detecting, measuring, and characterizing MWCNTs.†

Citation(s)	Technique	Application(s)	Advantages	Disadvantages
Lehman et al. (2011)	N <sub>2</sub> gas adsorption <sup>a, c</sup>	<ul style="list-style-type: none"> <li>• Surface area determination</li> </ul>		<ul style="list-style-type: none"> <li>• Permanent quadrupole inhibits N<sub>2</sub> adsorption to some substrates</li> <li>• Model of N<sub>2</sub> adsorption based on homogeneity across adsorption surface</li> <li>• May not be suitable for characterization of ecotoxicity</li> </ul>
Lehman et al. (2011) Johnston et al. (2010)	Nitrogen and phosphorous doping <sup>a, b</sup>	<ul style="list-style-type: none"> <li>• Structural defects</li> </ul>	<ul style="list-style-type: none"> <li>• Can detect non-carbon atoms present in MWCNT</li> <li>• Can differentiate between pentagonal and hexagonal structure</li> </ul>	<ul style="list-style-type: none"> <li>• Interaction between donor molecules and pentagonal and hexagonal structures on nanoparticle surface have not yet been quantified</li> </ul>
Lehman et al. (2011) Petersen et al. (2012) Johnston et al. (2010)	Optical density (UV-vis absorbance) <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>• MWCNT concentration in solution</li> </ul>	<ul style="list-style-type: none"> <li>• Necessary equipment is common in laboratories</li> </ul>	<ul style="list-style-type: none"> <li>• Results sensitive to presence of other compounds in solution</li> </ul>
Petersen et al. (2012) Johnston et al. (2010)	Radioactive labeling <sup>b, c</sup>	<ul style="list-style-type: none"> <li>• Detection of MWCNTs in environmental media</li> </ul>	<ul style="list-style-type: none"> <li>• Quantitative</li> <li>• Versatile (can be used in many forms of environmental media)</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive</li> <li>• Inherent danger of radioactivity</li> </ul>
Lehman et al. (2011) Johnston et al. (2010)	Raman spectroscopy <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>• Analysis of MWCNT purity</li> <li>• Detection of defects in MWCNT structure</li> <li>• Tube alignment</li> <li>• Tube diameter</li> </ul>	<ul style="list-style-type: none"> <li>• Relatively high resolution information about structure</li> </ul>	<ul style="list-style-type: none"> <li>• Complex interpretation of spectra for MWCNT</li> </ul>
Lehman et al. (2011)	Scanning electron microscopy (SEM) <sup>a</sup>	<ul style="list-style-type: none"> <li>• Surface morphology</li> <li>• Surface purity</li> </ul>	<ul style="list-style-type: none"> <li>• Repeatable</li> </ul>	<ul style="list-style-type: none"> <li>• Does not provide information on internal morphology</li> </ul>

Table B-2, cont. Analytical techniques for detecting, measuring, and characterizing MWCNTs.†

Citation(s)	Technique	Application(s)	Advantages	Disadvantages
Petersen et al. (2012)	Thermal optical transmittance <sup>c</sup>	<ul style="list-style-type: none"> <li>Loss of mass at various temperatures</li> </ul>	<ul style="list-style-type: none"> <li>Samples can contain dissolved environmental material</li> </ul>	<ul style="list-style-type: none"> <li>Only useful for MWCNTs in aqueous phase</li> <li>Necessary equipment is uncommon in laboratories</li> </ul>
Lehman et al. (2011)	Thermogravimetric analysis (TGA) <sup>a</sup>	<ul style="list-style-type: none"> <li>MWCNT purity analysis</li> </ul>	<ul style="list-style-type: none"> <li>Necessary equipment is common in laboratories</li> </ul>	<ul style="list-style-type: none"> <li>Sample size requirements may be large for certain applications (3-10 mg)</li> <li>Multiple measurements needed to ensure accuracy of data</li> </ul>
Lehman et al. (2011) Petersen et al. (2012) Johnston et al. (2010)	Transmission Electron Microscopy (TEM) <sup>a, b, c</sup>	<ul style="list-style-type: none"> <li>Surface morphology</li> <li>Crystallinity</li> </ul>	<ul style="list-style-type: none"> <li>Provides high resolution information about nanotube structure</li> </ul>	<ul style="list-style-type: none"> <li>Difficult sample preparation; preparation may damage sample</li> <li>requires expert personnel</li> <li>Images susceptible to excessive beam exposure</li> <li>Difficult to analyze large volumes in timely manner</li> </ul>
Lehman et al. (2011)	X-ray diffraction <sup>a</sup>	<ul style="list-style-type: none"> <li>Skeletal density</li> </ul>		<ul style="list-style-type: none"> <li>Cannot be used to determine bulk density</li> </ul>
Lehman et al. (2011) Echlin (1998)	X-ray microanalysis <sup>a, b</sup>	<ul style="list-style-type: none"> <li>Purity</li> </ul>	<ul style="list-style-type: none"> <li>Narrowing of incident beam allows greater resolution</li> </ul>	
Lehman et al. (2011) Petersen et al. (2012)	X-ray photoelectron spectroscopy (XPS) <sup>a</sup>	<ul style="list-style-type: none"> <li>Surface chemical composition</li> <li>Presence of functional groups</li> </ul>		<ul style="list-style-type: none"> <li>May be inaccurate without fluorine tagging</li> </ul>

<sup>a</sup>Used for chemical (*in vitro*) analysis as reported in reference document

<sup>b</sup>Used to analyze *in vivo* samples as reported in reference document

<sup>c</sup>Used to analyze environmental samples as reported in reference document

†Techniques listed in alphabetical order

## Appendix B References

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# Appendix C. Efficacy of Various Methods of Carbon Nanotube Purification

# Appendix C. Efficacy of Various Methods of Carbon Nanotube Purification

1           Appendix C provides a comparative overview of various purifications methods for carbon  
2 nanotubes reported in the literature, and as summarized by Hou et al. ([2008](#)). This information is  
3 organized to demonstrate the relative effectiveness of each method at removing each of the specified  
4 carbonaceous or metallic impurities. Each method is ranked as effective, partially effective, or not  
5 effective (✓= effective; ○= partially effective; ✗= not effective) for removing each impurity specified in  
6 Table C-1 below.

Table C-1. Purification methods for carbon nanotubes.

Purification methods			Yield (wt%)	Carbonaceous impurities				Metallic impurities		
				Amorphous carbon	Graphite	Carbon impurity on walls	Soluble carbon in solution	Exposed metal	Metal covered in polyhedral carbon	Metal encapsulated by CNT
Chemical methods	Gas phase	Air (Plus HCl)	~2-35	✓ <sup>a</sup>	✗	○	✗	✓	○	○
		Cl <sub>2</sub> , H <sub>2</sub> O, HCl	~15	✓	✗	○	✗	✓	○	○
		H <sub>2</sub> O, Ar, O <sub>2</sub> (Plus HCl)	~30	✓	✗	○	✗	✓	○	○
		O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> F <sub>4</sub> , SF <sub>6</sub>	25-48	✓	✗	○	✗	✓	✓	○
	Liquid phase	HNO <sub>3</sub>	~30-50	✓	✗	○	✗	✓	○	○
		H <sub>2</sub> O <sub>2</sub> , HCl	10-75	✓	✗	○	✗	✓	○	○
		Mixture of acid or KMnO <sub>4</sub>	30-75	✓	○	○	✗	✓	✓	○
		Microwave in inorganic acid	10-60	○	✗	○	✗	✓	○	○
Electrochemical	Alkali or acid solution (Plus HCl)	~80	○	✗	✗	✗	✓	✗	○	
Physical methods	Filtration	~30-84	○	○	✗	✓	○	○	✗	
	Centrifugation	~10-40	○	○	✗	✓	○	○	✗	
	Solubilization with functional groups	~17-50	○	○	✗	✓	✗	○	✗	
	High temperature annealing	~70-90	✗	✗	✗	✗	✓	✓	✓	
	Other physical techniques	~10-	✗	✗	✗	✗	✓	✓	✓	
	Chromatography, electrophoresis, FFF <sup>b</sup>	?	✓	✓	✗	✗	○	○	✗	
Multistep methods	HIDE <sup>c</sup> , wet grinding, filtration, oxidation, sonication, centrifugation	~2	✓	✓	○	✓	✓	○	○	
	Filtration/magnetic filtration, oxidation, annealing	~9-20	✓	✗	✓	✓	✓	✓	○	
	Sonication in H <sub>2</sub> O <sub>2</sub> , HNO <sub>3</sub> /HF/SDS, filtration	~25	✓	○	○	✓	✓	○	○	
	High temperature annealing extraction	~90	○	○	✓	✓	✓	✓	✓	

<sup>a</sup>✓ = effective; ○ = partially effective; ✗ = not effective

<sup>b</sup>Field-flow fractionation

<sup>c</sup>Hydrothermally initiated dynamic extraction

Source: Hou et al. (2008). Purification of carbon nanotubes. Carbon 46: 2003-2025. <http://dx.doi.org/10.1016/j.carbon.2008.09.009>.

## References for Appendix C

Hou, PX; Liu, C; Cheng, HM. (2008). Purification of carbon nanotubes. Carbon 46: 2003-2025.  
<http://dx.doi.org/10.1016/j.carbon.2008.09.009>.

# Appendix D. Study Summaries on the Transport, Transformation, and Fate of Decabromodiphenyl Ether and Multiwalled Carbon Nanotubes in Environmental Systems

# Appendix D. Study Summaries on the Transport, Transformation, and Fate of BDE-209 and MWCNTs in Environmental Systems

1           The following tables provide details from studies related to fate, transport, or transformation of  
2 decabromodiphenyl ether [(decaBDE) specifically the single isomer of decaBDE, BDE-209] or  
3 multiwalled carbon nanotubes (MWCNTs) in environmental media. Study information that provides  
4 support for the transformation (debromination) of BDE-209 in environmental media is included in Table  
5 D-1. Table D-2 provides study summaries related to the behavior of MWCNTs in aqueous media. Table  
6 D-3 and  
7           Table D-4 present information from studies conducted in terrestrial ecosystems for BDE-209 and  
8 MWCNTs, respectively.

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Table D-1. Relevant studies of transformation (debromination) of BDE-209.

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Citation	Relevant Study Information <sup>a</sup>
<b>Biotic Debromination</b>	
Deng et al. (2011)	<ul style="list-style-type: none"><li>• Used aerobic bacterium <i>Lysinibacillus fusiformis</i> strain DB-1 to determine its capability to debrominate BDE-209 in sediments of the Lianjiang River, China; DB-1 is an indigenous bacterium in PBDE-contaminated sediments.</li><li>• DB-1 efficiently transformed BDE-209 to lower brominated BDEs using lactate, pyruvate, and acetate as carbon sources, and this debromination was an aerobic (oxygen-consuming) process.</li></ul>
He et al. (2006)	<ul style="list-style-type: none"><li>• Studied degradation of BDE-209 in various microbial cultures.</li><li>• Debromination of BDE-209 was observed with anaerobic bacteria including <i>Sulfurospirillum multivorans</i> and <i>Dehalococcoides</i> species.</li></ul>
Huang et al. (2010)	<ul style="list-style-type: none"><li>• Studied behavior of BDE-209 in soil-plant system; transportation of BDE-209 within plants was examined using 6 plant species.</li><li>• OH-metabolized and debrominated products of BDE-209 were measured in plants and soil; higher proportions of penta- through diBDE congeners in plant tissues than in the soil suggest either further debromination of PBDEs within plants or lower PBDEs are more readily taken up by plants; significant negative correlation between residual BDE-209 concentration and soil microbial biomass, suggesting microbial metabolism and degradation of BDE-209.</li></ul>

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Table D-1, cont. Relevant studies of transformation (debromination) of BDE-209.

Citation	Relevant Study Information <sup>1</sup>
<b>Biotic Debromination</b>	
Tokarz et al. (2008)	<ul style="list-style-type: none"> <li>Studied reductive debromination in an anaerobic sediment microcosm experiment.</li> <li>BDE-209 debrominated slowly; its half-life ranged from 6 to 50 yr, and averaged about 14 yr; formation of nona-, octa-, hepta-, and hexaBDEs and 9 new congeners, including lower brominated congeners that are greater environmental concern (more bioavailable); experiments suggested anaerobic reductive debromination of BDE-209; authors noted competing influences of hydrophobicity and reactivity that can significantly retard rate of debromination.</li> </ul>
Wang et al. (2011)	<ul style="list-style-type: none"> <li>Examined microbial degradation of BDE-209 in the rhizosphere of ryegrass using arbuscular mycorrhizae.</li> <li>12 lower brominated congeners were detected in soil samples and 24 were detected in plant samples; there was evidence of debromination in soil and within plants based on higher proportion of di- through hepta-BDEs.</li> </ul>
<b>Abiotic Debromination (Photolysis)</b>	
Ahn et al. (2006)	<ul style="list-style-type: none"> <li>Characterized photodegradation of BDE-209 adsorbed on clay, metal oxides, and sediment using sunlight and artificial UV light.</li> <li>Photodegradation rates were likely dependent on the chemical and physical properties of the sorbent; however, degradation product distribution was not believed to be dependent on sorbent type.</li> <li>Enhanced photolytic transformation rates observed when BDE-209 was adsorbed to clay minerals; no significant BDE-209 degradation observed on metal oxides; very slow degradation rates of BDE-209 sorbed to carbon-rich sediment; results indicated stepwise (sequential) debromination.</li> <li>Suggested that organic matter has inhibitory effect on photodegradation possibly by shielding BDE-209 from the light or by satisfying excited states of the BDE-209 before they can form products.</li> </ul>
An et al. (2008)	<ul style="list-style-type: none"> <li>Characterized photolytic activity on BDE-209 degradation using a TiO<sub>2</sub> photocatalyst.</li> <li>TiO<sub>2</sub> was an effective photocatalyst for degrading BDE-209; results suggested sequential debromination occurred in the formation of products during BDE-209 transformation; products were hexa-, penta, and tetraBDEs.</li> </ul>
Bezares-Cruz (2004)	<ul style="list-style-type: none"> <li>Examined BDE-209 photochemical transformation using a hexane solvent and solar light.</li> <li>Reaction rate of photolysis was dependent on solar intensity and what the BDE-209 was adsorbed to; 43 PBDEs were detected, including BDE-47.</li> </ul>
Christiansson et al. (2009)	<ul style="list-style-type: none"> <li>Examined BDE-209 photochemical transformation in the laboratory using various solvents and UV irradiation.</li> <li>BDE-202 was identified as a marker of BDE-209 photolysis; PBDEs accounted for about 90% of products formed (primarily heptaBDEs to nonaBDEs); Poly brominated dibenzofurans (PBDFs) accounted for approximately 10% of products formed; authors noted the formation of BDE-183 and BDE-153 as important environmental congeners.</li> </ul>
Hua et al. (2003)	<ul style="list-style-type: none"> <li>Measured photochemical reactions of BDE-209 on artificial surfaces—quartz glass, silica particles, humic acid-coated silica particles—using UV light and natural sunlight.</li> <li>Transformation occurred more slowly using sunlight irradiation; presence of humic acid slowed transformation; tetraBDE and pentaBDE not found at detectable levels.</li> </ul>



Table D-1, cont. Relevant studies of transformation (debromination) of BDE-209.

Citation	Relevant Study Information <sup>a</sup>
<b>Abiotic Debromination (Photolysis)</b>	
Raff and Hites (2007)	<ul style="list-style-type: none"> <li>Examined the role of photolysis in the atmospheric removal of BDE-209.</li> <li>Determined that photolysis is minor removal process; removal of particle-bound BDE-209 more likely due to wet (primarily) and dry deposition.</li> </ul>
Schenker et al. (2008)	<ul style="list-style-type: none"> <li>Used multimedia model that incorporated photolysis to predict fate of BDE-209 in environmental compartments.</li> <li>Model estimated that about 13% of pentaBDE and 2% of tetraBDE in the environment occurs from degradation of BDE-209; model-predicted degradation in the atmosphere (e.g., by photolysis) represents 45% of BDE-209 loss; loss to deposition estimated at 30%.</li> </ul>
Shih and Wang (2009)	<ul style="list-style-type: none"> <li>Examined solar and UV-lamp degradation of BDE-209.</li> <li>Observed that photodegradation of BDE-209 was not affected by initial BDE-209 concentrations; photodegradation rate increases with increasing light intensity; photodegradation of higher brominated congeners faster than for lower brominated congeners; photodegradation of BDE-209 is a sequential dehalogenation mechanism with stepwise bromine losses.</li> </ul>
Söderstrom et al. (2004)	<ul style="list-style-type: none"> <li>Studied photodegradation of BDE-209 in toluene, on silica gel, and in sand, soil, sediment using artificial UV light and natural outdoor sunlight.</li> <li>Debromination rates were strongly dependent on matrix type; half-lives were shorter using artificial matrices (&lt;15 min); longer half-lives observed on more complex natural matrices (40–200 hr); no matrix-related or light intensity-related differences in the debromination pattern of the BDE congeners formed; formation of nona-hexa BDEs occurred, including BDE-154 and BDE-183; PBDFs were also formed.</li> </ul>
Stapleton and Dodder (2008)	<ul style="list-style-type: none"> <li>Studied photodegradation of BDE-209 in house dust exposed to natural sunlight.</li> <li>Initial BDE-209 concentration decreased by about 38%, 35% of which believed to be due to debromination.</li> </ul>

<sup>1</sup>Additional information obtained from USEPA (2010).

Table D-2. Relevant studies of MWCNTs in aqueous media.

Citation	Relevant Study Information
Chae et al. (2011)	<ul style="list-style-type: none"> <li>Studied photochemical reactivity of CNT aggregates and compared with other fullerene nanoparticles.</li> <li>After photosensitization from ultraviolet irradiation, the primary mode of oxidation of chemical compounds by CNTs is singlet oxygen production; this reactivity appeared to be correlated with the surface area of colloidal aggregates in solution.</li> </ul>
Chappell et al. (2009)	<ul style="list-style-type: none"> <li>Examined the mechanism by which humic substances stabilize MWCNT dispersions in aqueous media.</li> <li>Adding humic substances to MWCNTs in solution enhanced stability, decreased particle diameter, and decreased polydispersity; presence of surfactive domains in the structure of the humic substances directly impacts CNT dispersal in solution.</li> </ul>
Christian et al. (2008)	<ul style="list-style-type: none"> <li>Studied aggregation of nanoparticles and effects of humic acid and cations on CNT stability.</li> <li>Cations, in particular divalent cations (e.g., Ca<sup>2+</sup> and Mg<sup>2+</sup>), were found to reduce the stability of CNT with or without NOM surface coating.</li> </ul>
Desai et al. (2012)	<ul style="list-style-type: none"> <li>Investigated antisolvent precipitation of functionalized MWCNTs and aggregation behavior in the aqueous media.</li> <li>Organic-soluble MWCNTs functionalized to be hydrophobic by addition of octadecylamine were shown to form stable dispersions in water/solvent systems even after antisolvent precipitation via aggregation; stability was shown to be long term, and particle aggregation increased with the addition of electrolytes.</li> </ul>
Han et al. (2008b)	<ul style="list-style-type: none"> <li>Investigated the influence of clay minerals on the stability of surfactant-facilitated MWCNTs.</li> <li>Solutions of MWCNTs facilitated by three surfactants reacted differently to addition of two minerals—kaolinite and montmorillonite; stability of the solutions after mineral addition depended on the surfactant and the mineral; two mechanisms by which minerals were shown to affect the stability of MWCNT solution were by mineral adsorption to surfactants and bridging between mineral and MWCNTs by surfactant.</li> </ul>
He et al. (2012)	<ul style="list-style-type: none"> <li>Studied the behavior of stabilized MWCNTs in a ferric chloride coagulation system and the structure characteristics of the produced flocs.</li> <li>MWCNTs stabilized by humic acid were effectively removed from solution by coagulation after application of relatively large amounts of ferric chloride.</li> </ul>
Holbrook et al. (2010)	<ul style="list-style-type: none"> <li>Examined surface water constituents that affect MWCNT coagulation.</li> <li>Higher influent concentrations of kaolin and alginate increased MWCNT removal by coagulation; higher concentrations of NOM reduced MWCNT removal by coagulation.</li> </ul>
Hyung et al. (2007)	<ul style="list-style-type: none"> <li>Studied the aqueous stability of MWCNTs in the presence of NOM.</li> <li>For the same initial MWCNT concentrations, suspended MWCNT concentrations were considerably higher in solutions of synthetic modeled Suwannee River NOM and actual river water than in solutions of sodium dodecyl sulfate, a common surfactant; the mechanism for CNT-NOM interactions are dependent on the characteristics of the MWCNTs and the NOM.</li> </ul>

Table D-2, cont. Relevant studies of MWCNTs in aqueous media.

Citation	Relevant Study Information
Hyung and Kim (2008)	<ul style="list-style-type: none"> <li>Investigated the effect of NOM characteristics and water quality parameters on NOM adsorption to MWCNTs.</li> <li>Adsorption capacity was directly proportional to NOM aromatic carbon content and the ionic strength of the solution; adsorption capacity was indirectly proportional to pH; adsorption strength was indirectly proportional to ionic strength and not significantly changed by pH.</li> </ul>
Kennedy et al. (2008)	<ul style="list-style-type: none"> <li>Investigated factors that influence the partitioning of CNTs (raw versus functionalized [either engineered or natural]) in the aquatic environment.</li> <li>Pure CNTs had limited potential for aqueous transport; instead, aggregation and adsorption to sediment particles; no ionic strength influences on aggregate size; hydrophobicity of CNTs likely increased affinity for particles and enhanced aggregation; aqueous destabilization by van der Waals attractions and rapid sedimentation; sedimentation rate might accelerate with increased concentration; dispersion was enhanced by surface modifications (engineered or NOM)—increased residency time in surface water, aggregate size/structure changes.</li> </ul>
Kennedy et al. (2009)	<ul style="list-style-type: none"> <li>Examined influence of surface modifications and various dispersal methods on MWCNT fate and toxicity.</li> <li>Dissolved organic matter, humic acid, and fulvic acid were shown to be dispersing agents of MWCNTs; humic acid was a more effective dispersant than fulvic acid; sonication treatment of MWCNTs was shown to increase fragmentation of the particles relative to magnetic stirring; functionalization and laboratory methods of dispersal of MWCNTs affect their behavior in aqueous solutions in the presence of NOM.</li> </ul>
Kummerer et al. (2011)	<ul style="list-style-type: none"> <li>Investigated biodegradability of functionalized and nonfunctionalized MWCNTs in aqueous media.</li> <li>MWCNTs were not biodegradable under the conditions tested. Surface modification resulted in better solubility, but not better biodegradability.</li> </ul>
Lin et al. (2009b)	<ul style="list-style-type: none"> <li>Studied the influence of solution pH and ionic strength on the interaction between tannic acid-facilitated MWCNTs of various diameters.</li> <li>Suspension of MWCNTs in tannic acid solution greatly improved with tannic acid concentration until a plateau concentration was reached; suspension was greatest for particles of 40 nm diameter, followed by 60 nm, 20 nm, 100 nm, and 10 nm, respectively; MWCNTs stabilized in tannic acid were stable at pH &gt; 5, and precipitated at pH &lt; 5; presence of ions Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and La<sup>3+</sup> caused tannic acid-stabilized MWCNTs to aggregate, in a manner exponentially correlated to ionic valence.</li> </ul>
Lin et al. (2010)	<ul style="list-style-type: none"> <li>Described stabilities of MWCNTs in forms of particulate aggregates and surfactant-facilitated suspensions in various fresh surface waters.</li> <li>Nonfunctionalized MWCNTs could not stabilize in eight samples of natural surface waters by shaking, but stabilized in one sample with high dissolved organic content after sonication; nonfunctionalized MWCNTs did not stabilize in one surface water sample that also had a high NOM content, suggesting that other characteristics of the sample affected MWCNT stabilization; MWCNTs stabilized with CTAB surfactant were destabilized in all surface water samples, TX100- and SDBS- facilitated MWCNT suspensions remained stable in all eight surface water samples; addition of cations to solutions were shown to destabilize surfactant-facilitated MWCNT suspensions.</li> </ul>

Table D-2, cont. Relevant studies of MWCNTs in aqueous media.

Citation	Relevant Study Information
Liu et al. (2009)	<ul style="list-style-type: none"> <li>Examined the mobility of MWCNTs in porous media using column experiments.</li> <li>At low flow rates similar to those found in natural subsurface aqueous environments, OH- and COOH-functionalized MWCNTs were retained in porous media to a significant extent; at high flow rates, OH- and COOH-functionalized MWCNTs were very mobile; a medium with a large number of small pores was shown to retain the functionalized MWCNTs better than media with fewer wider pores.</li> </ul>
Petersen et al. (2008)	<ul style="list-style-type: none"> <li>Studied ecological uptake in sediment spiked with MWCNTs by sediment-burrowing <i>Lumbriculus variegatus</i>.</li> <li>Study showed that CNTs did not readily absorb into organism tissues; sizes of MWCNTs could have been a factor in the lack of absorption by organisms.</li> </ul>
Saleh et al. (2008)	<ul style="list-style-type: none"> <li>Examined aggregation kinetics of MWCNTs in aquatic media with varying solution pH and salt concentrations and presence of organic matter.</li> <li>Increasing monovalent and divalent salt concentration in aqueous solution and increasing solution pH from acidic to basic in aqueous solution reduced aggregation of sonicated MWCNTs; addition of humic acid to solution also reduced aggregation rate and enhanced sonicated MWCNT stability; these results show that sonicated MWCNTs are relatively stable in solution chemistries with electrolyte and pH levels typical of natural aquatic environments.</li> </ul>
Wang et al. (2009)	<ul style="list-style-type: none"> <li>Investigated sorption of humic acid and aromatic compounds by MWCNTs.</li> <li>With increasing concentration of humic acid in solution, MWCNTs increasingly sorbed humic acid until a plateau was reached; maximum humic acid sorption capacity of MWCNTs depended on <math>\pi</math>-<math>\pi</math> interactions, surface area of MWCNTs, and dispersion of MWCNTs; sorption of hydrophobic organic compounds decreased with increasing humic acid concentrations, suggesting that sorption of hydrophobic organic compounds would be suppressed in the presence of NOM.</li> </ul>
Zhang et al. (2010)	<ul style="list-style-type: none"> <li>Investigated NOM, pH, and ionic strength effects on adsorption of SOCs by MWCNTs in natural waters.</li> <li>NOM showed a more significant effect on sorption of SOCs by MWCNTs than pH or ionic strength of solution, which had negligible impacts on SOC sorption; surface functionalization of MWCNTs with hydroxyl and carboxyl groups slightly suppressed the effects of NOM on SOC sorption by MWCNTs, and this suppression decreased with increasing hydrophobicity of the SOC.</li> </ul>
Zhang et al. (2011)	<ul style="list-style-type: none"> <li>Examined interactions (phase distribution) between MWCNTs and aqueous systems containing peat under various conditions (ionic strength and pH).</li> <li>Presence of DOM greatly increased the stability of MWCNTs in aqueous solution in a way similar to surfactant stabilization; solid peat did not adsorb MWCNTs except with the increasing concentration of sodium cations.</li> </ul>

CNT = carbon nanotube; MWCNT = multiwalled carbon nanotube; CTAB = cetyl trimethyl ammonium bromide; NOM = natural organic matter, DOM = dissolved organic matter; SDBS = sodium dodecyl benzene sulfonate; SOC = synthetic organic chemicals

Table D-3. Relevant studies of BDE-209 in soils and plants.

Citation	Relevant Study Information
<b>Soils</b>	
Li et al. (2010)	<ul style="list-style-type: none"> <li>Collected wet and dry particle deposition samples at the urban sites of Guangzhou and Hong Kong, South China.</li> <li>Depositional fluxes of BDE-209 ranged from 273 to 6000 (mean 2220) ng/m<sup>2</sup>/day in Guangzhou and from 29.1 to 1100 (mean 259) ng/m<sup>2</sup>/day in Hong Kong.</li> <li>BDE-209 was most abundant PBDE congener; distinct seasonal patterns were observed—higher depositional fluxes during winter; lower fluxes during the summer; seasonal variation associated with local usage and meteorological factors.</li> </ul>
Liu et al. (2011)	<ul style="list-style-type: none"> <li>Studied the effects of BDE-209 on soil microbial activities and function using soil enzymatic activity analysis.</li> <li>Bacterial counts were suppressed as BDE-209 concentration increased; BDE-209 inhibited microbial diversity and altered soil microbial community structure.</li> </ul>
Yu et al. (2010)	<ul style="list-style-type: none"> <li>Studied the effects of humic acids (HA) and microorganisms on the migration of BDE-209 in soils using soil enzymatic activity analysis.</li> <li>Distribution of BDE-209 in the colloidal fraction related to the HA and microorganism concentration; HA acted as surface modifier and microorganisms acted as biosurfactants; BDE-209 transported by soil colloids along with water currents especially in the presence of HA and microorganisms.</li> </ul>
Zhu et al. (2010)	<ul style="list-style-type: none"> <li>Studied the response of bacterial communities in soils spiked with BDE-209; soil microbial activities and composition were affected by BDE-209.</li> <li>BDE-209, although expected to be of low bioavailability, had an adverse impact on the structure and function of the soil microbial community and microbial processes; high doses of BDE-209 were toxic, inhibiting growth for some microorganisms.</li> </ul>
Zou et al. (2007)	<ul style="list-style-type: none"> <li>Investigated the distribution and fate of BDE-209 in soils, Pearl River Delta, China.</li> <li>Concentrations of BDE-209 generally decreased with increasing soil depth; BDE-209 in soil was significantly correlated with total organic carbon levels; sorption of BDE-209 on organic matter influences its distribution, transportation, and fate in the environment.</li> </ul>

Table D-3, cont. Relevant studies of BDE-209 in soils and plants.

Citation	Relevant Study Information
<b>Plants</b>	
Huang et al. (2010)	<ul style="list-style-type: none"> <li>• Described the uptake, translocation, and metabolism of BDE-209 in six plant species—ryegrass, alfalfa, pumpkin, summer squash, maize, and radish.</li> <li>• Accumulation of BDE-209 occurred in the roots and shoots of all plants.</li> <li>• Root lipid content was positively correlated with BDE-209 uptake.</li> <li>• Translocation factor (<math>\text{Concentration}_{\text{shoot}}/\text{Concentration}_{\text{root}}</math>) of BDE-209 was inversely related to BDE-209 concentration in the roots, suggesting root lipids restrict translocation of BDE-209 from roots to shoots because of its partitioning to root lipids.</li> </ul>
Salamova and Hites (2010)	<ul style="list-style-type: none"> <li>• Evaluated air samples and tree bark for levels of PBDEs.</li> <li>• BDE-209 concentration in tree bark was strongly correlated with concentrations of these compounds in the air and precipitation; highest air and tree bark concentrations occurred at urban sites.</li> </ul>
Vrkoslavova et al. (2010)	<ul style="list-style-type: none"> <li>• Studied the ability of plants (tobacco and nightshade) to accumulate and translocate PBDEs from contaminated sewage sludge.</li> <li>• BDE-209 was accumulated via roots into tobacco tissue at 116.8 ng/g dwt; BDE-209 was not detected in nightshade; PBDEs detected in aboveground plant biomass provided evidence of translocation by plants.</li> </ul>

Table D-4. Relevant studies of carbon nanotubes (CNTs) in soils.

Citation	Relevant Study Information
Jaisi and Elimelech (2009)	<ul style="list-style-type: none"> <li>• Investigated the transport behavior of functionalized single-walled CNTs in columns of natural soil.</li> <li>• Single-walled CNT mobility in soils is likely limited because of its irregular shape, large aspect ratio, and bundled (aggregated) state—these properties would promote soil retention.</li> <li>• Natural soil environments that are more heterogeneous and contain “open soil structures” could promote CNT mobility in soil. Dissolved organic molecules in soil porewater could also enhance the colloidal stability of CNTs and increase their mobility.</li> </ul>
Petersen et al. (2011)	<ul style="list-style-type: none"> <li>• Studied the effects of modifying <math>^{14}\text{C}</math>-labeled MWCNTs with polyethyleneimine surface coatings—making them more stable in solution and modifying surface charges. Tested MWCNT sorption by soils and uptake and elimination behaviors by earthworms.</li> <li>• Nearly linear sorption isotherms for regular MWCNTs and nonlinear isotherms for modified MWCNTs, indicating that the PEI coatings influenced MWCNT interactions with soils; little difference in sorption results among the different soils tested; soil type might not be as important as the MWCNT characteristics in predicting soil sorption behaviors.</li> </ul>

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# Appendix E: Environmental Contaminant Concentrations

# Appendix E. Environmental Contaminant Concentrations

1 Appendix E provides information available from the literature regarding reported environmental  
2 concentrations of decaBDE (BDE-209) and multiwalled carbon nanotubes (MWNCTs) in environmental  
3 media (dust, indoor and outdoor air, aquatic systems, sewage, and soil) (Section E.1), and biota (Section  
4 E.2). Literature was identified primarily using review articles published in the past two years. Targeted  
5 literature searches were carried out as needed.

## E.1. Concentrations in Environmental Media

6 The following tables provide details from studies that measured BDE-209 in dust, air, water,  
7 sediment, soil, and sewage effluent/sludge. No data were identified on MWCNT concentrations in  
8 environmental media.

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Table E-1. BDE-209 concentrations in building dust.

Citation	Relevant study info	BDE-209 levels (ng/g)
<b>United States</b>		
Stapleton et al. (2005)	<ul style="list-style-type: none"><li>• Washington, DC</li><li>• Dust samples from 16 homes</li></ul>	Mean (dwt): 2090
Sharp and Lunder (2004) as cited in U.S. EPA (2010)	<ul style="list-style-type: none"><li>• Throughout United States</li><li>• 10 homes</li></ul>	Mean (dwt): 2394
Sjodin et al. (2008)	<ul style="list-style-type: none"><li>• Atlanta, GA</li><li>• Dust in vacuum cleaner bags analyzed from 10 homes</li><li>• BDE-209 was the dominant congener in dust samples</li></ul>	Median (range): 2000 (120–21,000)
Charles et al. (2005)	<ul style="list-style-type: none"><li>• Computer labs, CA</li><li>• 2 carpet dust samples</li><li>• BDE-209 was the dominant congener in carpet dust</li></ul>	Mean: 5180
Schechter et al. (2005)	<ul style="list-style-type: none"><li>• Dallas, TX</li><li>• 9 vacuum samples</li><li>• BDE-209 was the dominant congener in 7 samples</li></ul>	Mean (Median) (dwt): 8567 (665)

Table E-1, cont. BDE-209 concentrations in building dust.

Citation	Relevant study info	BDE-209 levels
<b>United States</b>		
Allen et al. (2008)	<ul style="list-style-type: none"> <li>• Boston, MA</li> <li>• 20 homes; 3 locations/home: living room, bedroom, vacuum</li> <li>• One sample contained highest concentration of BDE-209 in house dust reported to date (527,000 ng/g)</li> </ul>	Geometric means: 4502 (main living area); 1703 (bedroom); 1811 (vacuum)
Wu et al. (2007) [levels reported by U.S. EPA (2010)]	<ul style="list-style-type: none"> <li>• Boston, MA area</li> <li>• 46 women; 11 samples above detection limits</li> </ul>	Median: ND; 9020
Harrad et al. (2008b)	<ul style="list-style-type: none"> <li>• Amarillo, Austin, TX carpet dust from 17 homes</li> </ul>	Mean (geometric mean): 1600 (1300)
Johnson-Restrepo and Kannan (2009)	<ul style="list-style-type: none"> <li>• Albany, NY</li> <li>• Vacuum dust from 12 homes</li> </ul>	Mean (median) (dwt): 2810 (903)
Batterman et al. (2010)	<ul style="list-style-type: none"> <li>• Southeast Michigan (Ann Arbor area)</li> <li>• Vacuum dust from 10 office buildings</li> </ul>	Mean: 6930
Watkins et al. (2011)	<ul style="list-style-type: none"> <li>• Boston, MA area</li> <li>• Vacuum dust from 8 office buildings</li> </ul>	Geometric Mean: 4204
<b>International</b>		
Muenhor et al. (2010)	<ul style="list-style-type: none"> <li>• Thailand: 5 electronic/ electrical waste storage facilities</li> <li>• Dust, 25 samples</li> </ul>	Mean: 33,000
Harrad et al. (2008b)	<ul style="list-style-type: none"> <li>• Canada: carpet dust from 7 homes</li> <li>• U.K.: carpet dust from 16 homes</li> <li>• Concentrations of BDE-209 in 2 UK samples were highest recorded to date in a domestic (or office) indoor dust sample (520,000 &amp; 100,000 ng/g)</li> </ul>	Mean (geometric mean): 670 (590) (Canada); 45,000 (3800) (U.K.)
Harrad et al. (2008a)	<ul style="list-style-type: none"> <li>• Birmingham, UK</li> <li>• 30 homes, 18 offices, 20 cars</li> <li>• BDE-209 concentrations (ng/g) in three samples were highest to date at 2,600,000 (car), 2,200,000 (home), 1,400,000 (home)</li> </ul>	Mean (median): 260,000 (8,100) (homes); 30,000 (6,200) (offices); 410,000 (100,000) (cars)
Ma et al. (2009)	<ul style="list-style-type: none"> <li>• Taizhou, China</li> <li>• 5 dust samples from electronic waste recycling workshop floor</li> <li>• BDE-209 accounted for major proportion of total PBDEs in dust</li> </ul>	Mean (range) (dwt): 29,800 (5560–80,600)
Sjodin et al. (2008)	<ul style="list-style-type: none"> <li>• Household dust in vacuum cleaner bags from 10 homes each in Germany, Australia, and Great Britain (n=30)</li> <li>• BDE-209 dominant congener</li> </ul>	Median (range): 63 (<6–410) (Germany); 730 (23–13,000) (Australia); 10,000 (910–54,000) (Great Britain)

Note: Additional information obtained from U.S. EPA (2010)

dwt = Dry weight; ND = Not detected

Table E-2. BDE-209 air concentrations in outdoor and indoor air.

Citation	Relevant study info	BDE-209 levels
<b>United States</b>		
Hoh and Hites (2005) as cited in U.S. EPA (2010)	<ul style="list-style-type: none"> <li>Outdoor sampling at 5 locations; sampling every 12 days (August 2003–January 2004)</li> <li>Chicago (urban), remote locations in Michigan and Louisiana, agricultural site in Arkansas, and small college town of Bloomington, Indiana</li> <li>BDE-209 dominant congener at all sites</li> </ul>	Means (pg/m <sup>3</sup> ) 60.1 (Chicago) 1.4 (Michigan) 2.6 (Louisiana) 9.0 (Arkansas) 2.2 (Indiana)
Hoh et al. (2005)	<ul style="list-style-type: none"> <li>Outdoor sampling at 5 locations; sampling every 12 days (September 2002–December 2003 or throughout 2003 [Chicago only])</li> <li>Chicago (urban), remote locations in Michigan and Louisiana, agricultural site in Arkansas, and small college town of Bloomington, Indiana</li> </ul>	Values at different sampling dates (pg/m <sup>3</sup> ) 15, 16, 17, 65 (Chicago) 9.7, 12 (Louisiana) 20, 22 (Arkansas) 0.2, 7.3 (Indiana)
Strandberg et al. (2001)	<ul style="list-style-type: none"> <li>Outdoor sampling at 4 locations; 4 samples/year at each location, May–October (1997–1999)</li> <li>1 urban (Chicago), 1 remote (Michigan), 2 rural (Michigan, New York)</li> </ul>	Means (pg/m <sup>3</sup> ) 0.3 (Chicago) ND (rural/remote sites)
Charles et al. (2005)	<ul style="list-style-type: none"> <li>Indoor and outdoor sampling at industrial and office sites, outdoors at UC Davis (2004)</li> <li>Control – outdoors at UC Davis</li> <li>Indoors at computer facility measured concentrations with computers on and off. Concentrations higher when computers turned on compared to when computers turned off.</li> </ul>	Mean (range) (pg/m <sup>3</sup> ) 10.6 (4.44–17.8) (control) 58 (50.2–65.3) (indoors, computer facility) 140–11,400 (range for outdoors surrounding electronics recycling facility) 79,700–833,000 (range for indoors at electronics recycling facility) 45.5–1940 (range for outdoors at auto shredder facility)
CADAMP (2006) as cited in U.S. EPA (2010)	<ul style="list-style-type: none"> <li>7 outdoor sampling sites in California, 4 Bay Area sites, 3 South Coast sites (2003–2004)</li> <li>6 monthly samples in 2003; 12 monthly samples in 2004</li> </ul>	25 pg/m <sup>3</sup>
Allen et al. (2007)	<ul style="list-style-type: none"> <li>Indoor air at 20 urban residences, Boston, MA area (January–March 2006)</li> <li>Personal air (within 30 cm of breathing zone), bedroom, and main living area</li> <li>Total personal air concentrations for BDE-209 was significantly higher than bedroom and main living room concentrations</li> <li>Inhalation may account for up to 22% of the total BDE-209 exposure in U.S. adults.</li> </ul>	Geometric means (pg/m <sup>3</sup> ) 173.6 (personal air) 94.8 (bedroom) 94.2 (living room)

Table E-2, cont. BDE-209 concentrations in outdoor and indoor air.

Citation	Relevant study info	BDE-209 levels
<b>United States</b>		
Johnson-Restrepo and Kannan (2009)	<ul style="list-style-type: none"> <li>Indoor air in 12 homes, Albany, NY (December 2007–January 2008)</li> </ul>	ND (ng/m <sup>3</sup> )
Salamova and Hites (2011)	<ul style="list-style-type: none"> <li>Vapor, particle, and precipitation samples collected at 2 urban sites, 1 rural site, 2 remote sites ) around the Great Lakes (2005–2009; part of the Integrated Atmospheric Deposition Network)</li> <li>Statistical analysis indicated that levels of BDE-209 have not changed between 2005 and 2009</li> </ul>	Means (pg/m <sup>3</sup> ) Vapor: 3.4, 1.8 (urban); 0.7 (rural); 0.5, 0.8 (remote) Particle: 13, 56 (urban); 1.9 (rural); 1.3, 2.5 (remote) Precipitation (ng/L): 2.1, 4.1 (urban); 0.6 (rural); 0.4, 0.5 (remote)
Batterman et al. (2010)	<ul style="list-style-type: none"> <li>Airborne particulate matter and vapor samples collected at 10 office buildings in southeast Michigan (Ann Arbor area)</li> </ul>	Means and medians were all below the limit of detection
<b>International</b>		
Su et al. (2007)	<ul style="list-style-type: none"> <li>Air samples collected in the Canadian High Arctic (Alert, Nunavut); PBDEs quantified in 104 samples (2002–2004)</li> <li>Lack of seasonality effects for BDE-209; BDE-209 likely particle-bound and experiences LRT</li> </ul>	Mean (range) (pg/m <sup>3</sup> ) 1.6 (0.091–9.8)
Chang et al. (2009)	<ul style="list-style-type: none"> <li>Characterized airborne exposure of students to BDE-209 and other PBDEs inside and outside a computer classroom with 61 computers, southern Taiwan college</li> <li>BDE-209 was 1 of the 5 highest indoor concentrations</li> <li>Mean BDE-209 concentration outdoors significantly higher than the mean in indoor air</li> </ul>	Means (pg/m <sup>3</sup> ) 23.0 (inside classroom) 53.3 (outside, open space in front of teacher building)
Agrell et al. (2004)	<ul style="list-style-type: none"> <li>Atmospheric concentrations (gaseous and particulate) of BDE-209 measured at solid waste incineration plant in Sweden</li> <li>Particulate concentrations at MSW significantly higher</li> </ul>	Medians (pg/m <sup>3</sup> ) 10.4 (MSW) 6.5 (reference site)
Gouin et al. (2006)	<ul style="list-style-type: none"> <li>Examined particle bound air transport of BDE-209, Southern Ontario, Canada (2002)</li> <li>Nearly all BDE-209 sorbed to aerosol particles</li> <li>LRT of BDE-209 might be controlled by transport characteristics of aerosols to which they sorb</li> </ul>	Mean (range) (pg/m <sup>3</sup> ) 19 (ND–105)

Note: Additional information obtained from U.S. EPA (2010)

LRT = Long range transport; MSW = Municipal solid waste; ND = Not detected



Table E-3. BDE-209 concentrations in aquatic systems.

Citation	Relevant study info	BDE-209 levels
<b>United States</b>		
Oros et al. (2005)	<ul style="list-style-type: none"> <li>San Francisco estuary (2002)</li> <li>48 sediment samples; 33 water samples</li> </ul>	Range (pg/L) ND–191 (surface water) ND (sediment)
Hun Yun et al. (2008)	<ul style="list-style-type: none"> <li>Saginaw River Watershed, Michigan (2004)</li> <li>53 surficial sediment samples</li> <li>BDE-209 was the predominant congener (79% and 90% of the total PBDE in the Shiawassee and Saginaw Rivers, respectively)</li> </ul>	Means (ng/g dwt) 2.28 (Shiawassee River) 4.76 (Saginaw River) 1.98 (Saginaw Bay)
Song et al. (2005b; 2005a; 2004)	<ul style="list-style-type: none"> <li>Great Lakes</li> <li>16 total sediment sampling stations</li> </ul>	Range (ng/g): 4.3–242 (surficial sediment)
Raff and Hites (2004)	<ul style="list-style-type: none"> <li>Mississippi and tributaries</li> <li>Suspended sediment samples from 31 sites (2002–2003)</li> <li>BDE-209 was the dominant congener (96.8% of total concentration)</li> </ul>	Range of 15 PBDEs (ng/g dwt): 29–1548
Ashley et al. (2006)	<ul style="list-style-type: none"> <li>Delaware River</li> <li>4 sediment samples</li> <li>BDE-209 was the dominant congener (49% of total concentration)</li> </ul>	Range (ng/g dwt): 0.16–14.79
Dodder et al. (2002)	<ul style="list-style-type: none"> <li>Lake Hadley, Indiana</li> <li>4 surficial sediment samples</li> <li>BDE-209 was the dominant congener</li> </ul>	Range (ng/g dwt): 19–36
La Guardia et al. (2007)	<ul style="list-style-type: none"> <li>Downstream of WWTP of plastics manufacturer, North Carolina</li> <li>8 sediment sample locations downstream of outfall (2002 and 2005); 2 sludge samples, 1 for each yr</li> <li>BDE-209 was the dominant congener in sediment (&gt;89% of total concentration)</li> </ul>	Range 2002 SD: 300–3150 ng/g 2005 SD: 181–2390 ng/g
<b>International</b>		
Toms et al. (2006) as cited in U.S. EPA (2010)	<ul style="list-style-type: none"> <li>Estuarine, freshwater, marine sediments, Australia</li> <li>90 sediment samples from remote and industrial areas (2002–2003 and 2005)</li> <li>BDE-209 was the dominant congener in 86% of samples</li> </ul>	Mean (range) (ng/g dwt) 4.7(ND–60.9) (all PBDEs)
Christensen and Platz (2001)	<ul style="list-style-type: none"> <li>Danish marine coastal areas, freshwater lakes, river (2000)</li> <li>BDE-209 was the dominant congener in marine and freshwater sediments</li> <li>Highest BDEs detected in urban sediments</li> </ul>	Range (ng/g dwt) <0.9–3.9 (marine) <1.3–8.1 (freshwater)

Table E-3, cont. BDE-209 concentrations in aquatic systems.

Citation	Relevant study info	BDE-209 levels
<b>International</b>		
Eljarrat et al. (2005)	<ul style="list-style-type: none"> <li>Coastal areas, Spain</li> <li>13 marine sediment samples</li> <li>BDE-209 was the dominant congener (50–99% of total concentration)</li> </ul>	Range (ng/g dwt) 2.46–132.10
Eljarrat et al. (2007)	<ul style="list-style-type: none"> <li>Spanish River Vero, samples collected up- and downstream from an industrial park (2004, 2005)</li> <li>6 sediment and 3 effluent samples</li> <li>Maximum BDE-209 in sediment downstream of industrial park (that includes textile industry)</li> </ul>	Maximum (ng/g dwt) 5395 (2004) 12,459 (2005) (collected 5 m downstream of textile industry effluent discharge)
Qiu et al. (2007)	<ul style="list-style-type: none"> <li>Lake Ontario</li> <li>Sediment core study</li> </ul>	Mean (ng/g dwt): 14 (surficial)
Zhu and Hites (2005)	<ul style="list-style-type: none"> <li>Lake Michigan and Lake Erie</li> <li>Sediment core study</li> <li>BDE-209 was the dominant congener in both sediment cores (95–99% of total concentration)</li> </ul>	Surface concentrations (ng/g) 315 (Lake Michigan) 39 (Lake Erie)
De Boer et al. (2003)	<ul style="list-style-type: none"> <li>Various locations, The Netherlands</li> <li>Collected 44 SPM samples at 18 locations</li> <li>Collected 22 sediment samples at 17 locations</li> <li>SPM identified as an important carrier for BDE-209 in aquatic environment. Maximum of 4,600 mg/kg dwt likely related to spills from textile industries; maximum of 510 mg/kg dwt in sediment at same location of maximum SPM</li> </ul>	Median (Range) (µg/kg dwt) 71 (<9–4600) (SPM) 22 (<4–510) (sediment)
Eljarrat et al. (2004) [also reported in Law et al. (2006b) review article]	<ul style="list-style-type: none"> <li>BDE-209 determined in 5 riverine and 8 marine sediments, Spain</li> </ul>	Range (ng/kg dwt) 2.06–39.89 (river) 2.95–132.11 (marine)
Sawal et al. (2004) [also reported in Law et al. (2006b) review article]	<ul style="list-style-type: none"> <li>BDE-209 determined in 29 surface sediment from River Elbe, Germany and Czech Republic</li> <li>BDE-209 represented 80% of total BDEs</li> </ul>	Range (µg/kg dwt): 0.5–17.4
From Law et al. (2006b) review article	<ul style="list-style-type: none"> <li>BDE-209 determined in sediments from Lake Mjosa, Norway (Schlabach et al., 2004)</li> <li>In some parts of the lake, BDE-209 represented 50–90% of total BDEs</li> </ul>	Range total BDE (µg/kg dwt): 0.6 – 27
Voorspoels et al. (2004) [also reported in Law et al. (2006b) review article]	<ul style="list-style-type: none"> <li>Analyzed sediments from Belgian North Sea, Western Scheldt Estuary</li> <li>BDE-209 was detected in 83% of samples from the Belgian North Sea and in 100% of samples from the Scheldt Estuary</li> </ul>	Maximum (ng/kg dwt): 1200 (at estuary)

Table E-3, cont. BDE-209 concentrations in aquatic systems.

Citation	Relevant study info	BDE-209 levels
<b>International</b>		
Ricklund et al. (2010)	<ul style="list-style-type: none"> <li>Measured levels of BDE-209 in 11 lake sediment samples and 7 marine sediment samples in Sweden</li> <li>No known point sources of BDE-209 exist; presence in sediments was presumed to be evidence of long-range atmospheric transport and deposition</li> </ul>	Range (ng/g dwt) 0.48–11 (lake) 1.0–88 (marine)
Mai et al. (2005)	<ul style="list-style-type: none"> <li>Examined 66 surface sediment samples from the Pearl River Delta and South China Sea, China</li> <li>Sources of PBDEs in the area: waste discharges from urban centers; regional growth of electronic manufacturing</li> <li>BDE-209 dominated congener compositions in sediments; PBDE composition analysis provided possible evidence of debromination of BDE-209</li> </ul>	Range (ng/g dwt): 0.4–7340
Chen et al. (2007b)	<ul style="list-style-type: none"> <li>Examined 3 sediment cores from the Pearl River Estuary, South China</li> <li>Increased BDE-209 flux in the upper sediment cores attributed to rapid regional growth of electronics and other industry</li> </ul>	Range (ng/g):13.5–30.3
Guzzella et al. (2008)	<ul style="list-style-type: none"> <li>PBDEs measured in sediment cores (2005) from Lake Maggiore and tributary grab samples, Italy and Switzerland</li> <li>BDE-209 was the dominate congener (&gt;95% of total PBDEs)</li> <li>Increase in BDE-209 attributed to textile industries</li> </ul>	Range (ng/g dwt): 1.6–15.3
Zhao et al. (2011)	<ul style="list-style-type: none"> <li>Measured concentrations of PBDEs in sediments of the Daliao River Estuary, China</li> <li>BDE209 was the dominating congener in all samples</li> <li>Intrusion of sea waters accelerated deposition of the colloid-associated PBDEs; significantly negative correlations observed between PBDE concentration and both pH and salinity in bottom waters; higher river flow in the flood season (summer) accelerated transport of PBDEs to the ocean; TOC and PBDE distributions indicated that TOC controlled distributions of PBDEs in sediments of the estuary</li> </ul>	Range of all PBDEs (ng/g dwt): 0.13–1.98 (BDE-209 levels stated to be about 1 order of magnitude higher)

Note: Additional information obtained from U.S. EPA (2010)

dwt = Dry weight; ND = Not detected; SPM = Suspended particulate matter; TOC = Total organic carbon; WWTP = Waste water treatment plant

Table E-4. BDE-209 concentrations in sewage effluent and sludge.

Citation	Relevant study info	BDE-209 levels	
		STP effluent	Sewage sludge
<b>United States</b>			
Hale et al. (2001)	<ul style="list-style-type: none"> <li>• Mid-Atlantic biosolids</li> <li>• Northeast biosolids</li> <li>• Gulf biosolids</li> <li>• West biosolids</li> </ul>	–	Ranges (µg/kg dwt) 84.8–1460 1940–4890 368 (single site) 340–450
Hale et al. (2003)	<ul style="list-style-type: none"> <li>• Lake Superior watershed communities</li> <li>• Lake Michigan watershed communities</li> </ul>	–	Mean (µg/g dwt) 510 Mean (µg/g dwt) 466
North (2004)	<ul style="list-style-type: none"> <li>• Samples analyzed for 41 BDE congeners in CA</li> <li>• STP discharges effluent into San Francisco estuary</li> <li>• In sludge, BDE-209 was 35% of total BDEs</li> <li>• Estimated that 96% of PBDEs that enter the STP adsorb to sludge; 4% in effluent</li> </ul>	1730 (pg/L)	Mean (µg/kg dwt) 1183
La Guardia (2007)	<ul style="list-style-type: none"> <li>• Downstream of WWTP of plastics manufacturer, North Carolina</li> <li>• 2 sludge samples, one taken in 2002 and the other in 2005</li> <li>• BDE-209 was the dominant congener in sludge</li> </ul>		58,800 µg/g dwt (2002 measurement) 37,400 µg/g dwt (2005 measurement)
U.S. EPA (2009)	<ul style="list-style-type: none"> <li>• National Sewage Sludge Survey</li> <li>• Evaluated 74 STPs in 35 states (2006-2007)</li> <li>• Nationally, BDE-209 was the dominant congener</li> </ul>	–	Mean (µg/kg dwt) 2181
<b>International</b>			
De Boer et al. (2003)	<ul style="list-style-type: none"> <li>• Various locations, The Netherlands</li> <li>• Collected 13 sewage treatment plant (STP) influent/effluent samples at 9 locations (measured filtering out particulate matter); 3 sludge samples</li> </ul>	Median (range) (µg/kg dwt) 24 (<0.5–330) (influent) 350 (310–920) (effluent)	<180, 190, 8.6 (µg/kg dwt)
Knoth et al. (2007)	<ul style="list-style-type: none"> <li>• Sewage sludge from 11 STPs in Germany (2002-2003)</li> <li>• BDE-209 was the dominant congener in sludges; no PBDEs with &lt;7 bromines observed</li> <li>• Estimated 350 kg/acre BDE-209 applied to land in Germany in 2001</li> </ul>	–	Mean (ng/g dwt) 429

Table E-4, cont. BDE-209 concentrations in sewage effluent and sludge.

Citation	Relevant study info	BDE-209 levels	
		STP effluent	Sewage sludge
<b>International</b>			
Wang et al. (2007)	<ul style="list-style-type: none"> <li>• Sewage sludge from 31 STPs in 26 cities in China</li> <li>• BDE-209 was dominant congener in most samples</li> </ul>	–	Mean (ng/g dwt) 68.5
Clarke et al. (2008)	<ul style="list-style-type: none"> <li>• Australian sewage sludge survey; 16 WWTPs (2006)</li> <li>• Presented urban mean, rural mean, and overall mean of BDE-209 in sludge samples</li> </ul>	–	Mean (µg/kg dwt) 880 (urban); 490 (rural) 720 (overall)
Kupper et al. (2008)	<ul style="list-style-type: none"> <li>• Switzerland, monitoring network</li> <li>• 16 WWTPs</li> </ul>	–	Mean (µg/kg dwt) 310
Eljarrat et al. (2007)	<ul style="list-style-type: none"> <li>• Spanish River Vero, samples collected up- and downstream from an industrial park (2004, 2005)</li> <li>• 6 sediment and 3 effluent samples</li> </ul>	1170 ng/L (2005 effluent maximum)	–
Ricklund et al. (2009)	<ul style="list-style-type: none"> <li>• Stockholm, Sweden</li> <li>• WWTP (2006, 2007)</li> </ul>	–	800 Mean (ng/g dwt)

Note: Additional information obtained from U.S. EPA (2010)

dwt = Dry weight; STP = sewage treatment plant; WWTP = Waste water treatment plant

Table E-5. BDE-209 concentration data in soil.

Citation	Relevant study info	BDE-209 levels
<b>United States</b>		
Offenberg et al. (2006) as cited in U.S. EPA (2010)	<ul style="list-style-type: none"> <li>• 33 surface soil samples, 15 states</li> <li>• BDE-209 detected in 24/33 samples</li> </ul>	Mean (ng/g dwt): 15.3
Hun Yun et al. (2008)	<ul style="list-style-type: none"> <li>• Saginaw River Watershed, Michigan</li> <li>• 26 floodplain surface soil samples (2004)</li> </ul>	Mean (ng/g dwt) 10.8 (Shiawassee River) 2.77 (Saginaw River) 0.6 (Saginaw Bay)

Table E-5, cont. BDE-209 concentration data in soil.

Citation	Relevant study info	BDE-209 levels
<b>International</b>		
Sellström et al. (2005)	<ul style="list-style-type: none"> <li>• 5 sites in Sweden</li> <li>• Evaluated sewage sludge amended soils and earthworms</li> </ul>	Range (ng/g dwt) 0.028–2220
Luo et al. (2009)	<ul style="list-style-type: none"> <li>• Southern China</li> <li>• Analyzed road and farmland soils from e-waste recycling region</li> <li>• BDE-209 contributions averaged 84% in samples from the e-waste region higher than 97% in samples from the industrial and reference sites</li> </ul>	Mean (range) (ng/g dwt) 19.7 (rural farmland soil) 59.8 (farmland soil near industrial) <u>E-waste region</u> 1539.3 (69.1–6319.6) (road soil) 32.2 (farmland soil near dismantling workshop) 29.9 (farmland soil near open burning site)
Zou et al. (2007)	<ul style="list-style-type: none"> <li>• Pearl River, China</li> <li>• 33 surface soil samples; 3 point source samples</li> </ul>	Mean (range) (ng/g dwt) 13.8 (2.38–66.6) (SS) 70.5 (25.7–102)(PS contaminated)

Note: Additional information obtained from U.S. EPA (2010)

dwt = Dry weight; SS = Surface soil; PS = Point source

Table E-6. Proxy data for estimating MWCNT concentrations in occupational air.

Citation	Relevant study info	Proxy data and CNT counts
<b>United States</b>		
Bello et al. (2008)	<ul style="list-style-type: none"> <li>• Personal breathing zone and area air sampling and real-time monitoring in an CNT research laboratory synthesizing and handling CNTs</li> <li>• Fast mobility particle sizer measured number concentration for particles sized 5.6–560 nm. Personal breathing zone and area air samples near the emission source were collected and analyzed for respirable dust and respirable fiber concentrations, and electron microscopy characterized particles and fibers on filters.</li> </ul>	<p>No increase in total particle number concentration or in particle number in any size range compared to background</p> <p>No individual or bundled CNTs detected</p>
Bello et al. (2009)	<ul style="list-style-type: none"> <li>• Personal breathing zone and area air sampling and real-time monitoring during machining of carbon, alumina, CNT-carbon, and CNT-alumina composites at a research laboratory</li> <li>• Fast mobility particle sizer and aerodynamic particle sizer measured number concentrations of particles sized 5.6–560 nm and 0.5–20 μm, respectively, and condensation particle counter counted all particles 10 nm–1 μm. Total dust mass was measured in real time using TSI Dust Trak™. Personal breathing zone and area air samples near the emission source were collected and analyzed for respirable dust and respirable fiber concentrations, and electron microscopy characterized particles and fibers on filters</li> <li>• No engineering controls were employed</li> <li>• Dry cutting of all composites produced significant numbers of nanoscale particles, and particle sizes were similar for all composites.</li> <li>• The thinnest CNT-alumina composite released fewer nanoscale particle than the other composites during dry cutting</li> <li>• No discernible difference between the number of respirable particles and fibers produced during dry cutting of CNT-composites versus base composites</li> </ul>	<p>No individual CNT structures or bundles were observed in the samples</p> <p>No CNT structures or bundles were observed in the composite particle dust</p>

Table E–6, cont. Proxy data for estimating MWCNT concentrations in occupational air.

Citation	Relevant study info	Proxy data and CNT counts
<b>United States</b>		
Dahm et al. (2011)	<ul style="list-style-type: none"> <li>• Task based area air, full-shift personal breathing zone (PBZ), and outdoor background sampling at 6 CNT/CNF primary and secondary manufacturing facilities</li> <li>• PBZ samples collected for inhalable fraction and area air samples collected for inhalable and respirable fractions of elemental carbon mass. Electron microscopy characterized CNT structures (both single CNTs and bundles) on filters</li> <li>• PBZ samples collected during dry powder handling tasks at two secondary MWCNT facilities exceeded the National Institute of Occupational Safety and Health recommended exposure limit (7 <math>\mu\text{g}/\text{m}^3</math> elemental carbon) in the presence of controls</li> <li>• CNT/CNF structure were identified on filters at all sites and correlation between filter mass and CNT structure count was statistically significant (<math>p = 0.01</math>) after exclusion of single outlier value</li> </ul>	<p><u>Elemental carbon mass (<math>\mu\text{g}/\text{m}^3</math>) and CNT structure count at primary MWCNT facilities</u></p> <p>Outdoor background: not detected  MWCNT production and harvesting: 1.6–2.74 (PBZ), 0.49–4.62 (area: inhalable), not detected to 0.78 (area: respirable), 0.090–0.399 CNTs/cm<sup>3</sup> (PBZ), 0.026–0.134 CNTs/cm<sup>3</sup> (area: inhalable)  MWCNT sonication, sieving, and spray coating: 1.13 (PBZ), not detected (area: inhalable), not detected to 0.7 (area: respirable), 0.010 CNTs/cm<sup>3</sup> (PBZ), 0.002 CNTs/cm<sup>3</sup> (area: inhalable)</p> <p><u>Elemental carbon mass (<math>\mu\text{g}/\text{m}^3</math>) and CNT structure count at secondary MWCNT facilities</u></p> <p>Outdoor background: not detected  Office work and waste collection: 0.8–1.06 (PBZ), 0.001–0.214 CNTs/cm<sup>3</sup> (PBZ)  Weighing, mixing, sonication, extruding, transferring MWCNTs: not detected to 7.86 (PBZ), not detected to 1.01 (area: inhalable), not detected to 2.76 (area: respirable), not detected to 0.242 CNTs/cm<sup>3</sup> (PBZ), not detected to 0.008 CNTs/cm<sup>3</sup> (area: inhalable)  Milling MWCNT composite: not detected</p>



Table E–6, cont. Proxy data for estimating MWCNT concentrations in occupational air.

Citation	Relevant study info	Proxy data and CNT counts
<b>United States</b>		
Johnson et al. (2010)	<ul style="list-style-type: none"> <li>• Area air sampling and real-time monitoring of MWCNT and hydroxylated MWCNT (MWCNT-OH) emissions during weighing, transferring, and sonicating with water and natural organic matter</li> <li>• HHPC-6 particle counter measured particle number per liter air for 6 size cuts: 300, 500, 1000, 3000, 5000, and 10,000 nm. Condensation particle counter measured total particle numbers 10–1000 nm. Electron microscopy characterized MWCNT structures on filters.</li> <li>• Area air sample collected prior to tasks was used as background concentration and subtracted from samples taken during performance of tasks</li> </ul>	<p><u>Adjusted number concentration (particles/L)</u></p> <p>Raw MWCNT weighing, transferring, and mixing without ventilation: 123,403 (300 nm: above limit of quantitation), 34,446 (500 nm), 4338 (1000 nm), 50 (3000 nm), 0 (5000 and 10,000 nm).</p> <p>MWCNT-OH weighing, transferring, and mixing without ventilation: 0 (300 and 10,000 nm), 3065 (500 nm), 1699 (1000 nm), 280 (3000 nm), 4 (5000 nm).</p> <p>Raw MWCNT sonication: 42,796 (300 nm), 23,777 (500 nm), 2184 (1000 nm), 86 (3000 nm), 0 (5000 and 10,000 nm).</p> <p>MWCNT-OH sonication: 144,623 (300 nm: above limit of quantitation), 65,402 (500 nm), 6205 (1000 nm), 0 (3000, 5000, and 10,000 nm).</p> <p><u>Total adjusted number concentration 10–1000 nm (particles/cm<sup>3</sup>)</u></p> <p>Raw MWCNT weighing, transferring, and mixing without ventilation: 1576</p> <p>MWCNT-OH weighing, transferring, and mixing without ventilation: 676</p> <p>Raw MWCNT sonication: 2776</p> <p>MWCNT-OH sonication: 726</p>

Table E–6, cont. Proxy data for estimating MWCNT concentrations in occupational air.

Citation	Relevant study info	Proxy data and CNT counts
<b>United States</b>		
Methner et al. (2010)	<ul style="list-style-type: none"> <li>• Area air sampling and real-time monitoring of 2 MWCNT research and development laboratories during specific handling tasks</li> <li>• Condensation particle counters (CPC) counted particles sized 10–1000 nm and optical particle counters (OPC) counted particle sized 300–500 nm and 500–1000 nm. Electron microscopy characterized MWCNT structures on filters and energy-dispersive X-ray analysis confirmed chemical identity.</li> <li>• MWCNT structures on microscopy grids were not quantified, but were detected in samples taken during weighing and sonication of both raw and functionalized MWCNTs. No MWCNT structures were observed on filters sampling background. Filters were not analyzed by electron microscopy for samples taken during opening of the growth chamber.</li> <li>• Measured particle number concentrations are background adjusted</li> </ul>	<p><u>CPC particle number concentrations (particles/cm<sup>3</sup>); 10–1000 nm fraction</u>            Opening MWCNT growth chamber: 300 (with exhaust), 42,400 (without exhaust)            Handling raw MWCNTs: 1480–1580 (weighing); 2200–2800 (sonicating)            Handling functionalized MWCNTs: 680 (weighing); 730 (sonicating)</p> <p><u>OPC particle number concentrations (particles/L); 300–500 nm fraction; 500–1000 nm fraction</u>            Opening MWCNT growth chamber: 0; 0 (with exhaust), 350; 400 (without exhaust)            Handling raw MWCNTs: 53,1000–123,400 (above limit of quantitation); 3900–34,400 (weighing); 23,900–42,800; 6500–23,800 (sonicating)            Handling functionalized MWCNTs: 0; 3100 (weighing); 144,600 (above limit of quantitation); 65,400 (sonicating)</p>
<b>International</b>		
Han et al. (2008a)	<ul style="list-style-type: none"> <li>• Personal and area air sampling and real-time aerosol monitoring conducted at MWCNT research facility</li> <li>• Scanning mobility particle sizer with ultrafine condensation particle counter and aerodynamic particle sizer monitored particle size distribution 14–630 nm and 0.5–20 μm, respectively, and aethalometer characterized mass exposure to carbon black. Electron microscopy characterized MWCNT structures on filters and energy-dispersive X-ray analysis confirmed chemical identity.</li> <li>• Exposure controls included installation of a fan, cleaning, and equipment rearrangement (i.e., isolation)</li> <li>• No values exceeded ACGIH TLVs or Korean Ministry of Labor OELs for carbon black or particles not otherwise specified, but fiber counts exceeded limits for asbestos and other fiber or tube-like materials</li> </ul>	<p><u>Total dust concentration (μg/m<sup>3</sup>)</u>            No control measures: 210–430            With control measures: not detected</p> <p><u>MWCNT counts (MWCNTs/cm<sup>3</sup>)</u>            No control measures: 172.9–193.6            With control measures: 0.018–0.05</p>

Table E–6, cont. Proxy data for estimating MWCNT concentrations in occupational air.

Citation	Relevant study info	Proxy data and CNT counts
<b>International</b>		
Lee et al. (2010)	<ul style="list-style-type: none"> <li>• Personal air sampling, area sampling, and real-time aerosol monitoring conducted at 7 MWCNT handling facilities (3 manufacturing plants, 4 research laboratories)</li> <li>• Scanning mobility particle sizer, dust monitor, and aetholometer characterized particle number, size distribution, and mass exposures. Electron microscopy characterized MWCNT structures on filters.</li> <li>• No values exceeded American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs) or Korean Ministry of Labor occupational exposure levels (OELs) for carbon black, particles not otherwise specified, or asbestos.</li> <li>• Nanoscale particles most often released during opening of chemical vapor deposition (CVD) reactor and catalyst preparation.</li> <li>• Nanoscale particles assumed to be primarily metal catalysts, not MWCNTs</li> </ul>	<p>One filter sample detected MWCNTs at 0.00312 tubes/cm<sup>3</sup>; all others were non-detects</p> <p><u>Total suspended particulate matter</u>            Personal air: 7.8 – 320 µg/m<sup>3</sup>            Area air: 12.6–187 µg/m<sup>3</sup></p> <p><u>Particle number count for mode particle sizes (particles/ cm<sup>3</sup>) – by task</u>            Catalyst preparation (mode diameter 20–30nm): 18,600–75,000            CVD opening (mode diameter 20 or 50 nm): 6974–16,857            Other operations (no mode diameters reported): 5276–6399</p>
Takaya et al. (2010) (English translation available only for abstract)	<ul style="list-style-type: none"> <li>• Real-time aerosol monitoring and personal air sampling in two MWCNT packing facilities (automated packing versus manual packing)</li> <li>• Nanoscale and submicron-/micron-scale particles measured using scanning mobility particle sizer and optical particle counter, respectively</li> <li>• Submicron scale particles (not nanoparticles) released during bagging</li> </ul>	<p>Airborne dust (both facilities): 240 µg/m<sup>3</sup>            Personal air at manual facility: 2390 µg/m<sup>3</sup> (total dust); 390 µg/m<sup>3</sup> (respirable dust)            Personal air at automated facility: 290 µg/m<sup>3</sup> (total dust); 80 µg/m<sup>3</sup> (respirable dust)</p>

## E.2. Concentrations in Biota

1 The following tables provide details from studies that measured BDE-209 in various biota. No  
 2 data were identified on MWCNT concentrations in biota.

Table E-7. Measured concentrations of PBDEs in biota.

Species	Location	Year	Tissue	PBDE burden (ng/g) <sup>a</sup>	Common congener(s)	Source	
<b>Terrestrial birds</b>							
Peregrine falcon	Chesapeake Bay	1993-2002	Eggs	Median: 201 <sup>b</sup>	BDE-153: 26%	Potter et al. (2009)	
	CT, MA, ME, NH, VT	1996, 1999-2006		Median: 440 <sup>b</sup>	BDE-153, BDE-99	Chen et al. (2008)	
Common blackbird	Switzerland	2003-2005	Brain	BDL	NA	Naert et al. (2007) as cited in U.S. EPA (2010)	
			Adipose	BDL	NA		
			TB	0.82	BDE-47: 100%		
Sparrow hawk	Switzerland	2003-2005	Brain	14	NR	Naert et al. (2007) as cited in U.S. EPA (2010)	
			Adipose	709	NR		
			TB	790.2	BDE-99: 40%		
	Belgium	NR	Liver	Mean: 4900 Median: 1300	Top 3: BDE-99, BDE-47, BDE-153	Voorspoels et al. (2006b)	
				Brain	Mean: 1200 Median: 360	NR	Voorspoels et al. (2006b)
				Adipose	Mean: 1900	NR	Voorspoels et al. (2006b)
	NR	NR	Liver	Mean: 9500	Top 4: BDE-99, BDE-47, BDE-100, BDE-153	Voorspoels et al. (2007) as cited in U.S. EPA (2010)	
	Common buzzard	Switzerland	2003-2005	TB	34.55	BDE-153: 29% BDE-99: 23% BDE-47: 22%	Naert et al. (2007) as cited in U.S. EPA (2010)
		Belgium	NR	Liver	Mean: 480 Median: 70	Top 3: BDE-153, BDE-47, BDE-99	Voorspoels et al. (2006b)
Beijing, China		NR	Liver	148	BDE-209: ~43%	Chen et al. (2007a)	

Table E-7, cont. Measured concentrations of PBDEs in biota.

Species	Location	Year	Tissue	PBDE burden (ng/g) <sup>a</sup>	Common congener(s)	Source
<b>Terrestrial birds</b>						
Common buzzard	NR	NR	Liver	Mean: 720	NR	Voorspoels et al. (2007) as cited in U.S. EPA (2010)
Cormorant	Switzerland	2003-2005	TB	98.76	BDE-47: 42%	Naert et al. (2007) as cited in U.S. EPA (2010)
Owls	Belgium	NR	NR	250	Top 3: BDE-153, BDE-99, BDE-47	Voorspoels et al. (2006b)
Common kestrel	Beijing, China	NR	Muscle	Mean: 12,300	NR	Chen et al. (2007a)
			Liver	Mean: 12,200	NR	
			Kidney	Mean: 5340	NR	
Passerines	NR	NR	Adipose	160	NR	Voorspoels et al. (2007) as cited in U.S. EPA (2010)
			Eggs	220	NR	
<b>Marine birds</b>						
Herring gull	Great Lakes	1981-2000	Eggs	9.4-1544	NR	Norstrom et al. (2002)
Fulmar	Northern Canada	1975-1998	Eggs	0.212-2.37	NR	Wakeford et al. (2002) as cited in U.S. EPA (2010)
Murre	Northern Canada	1975-1998	Eggs	0.442-2.93	NR	Wakeford et al. (2002) as cited in U.S. EPA (2010)
Heron	British Columbia	1983-2000	Eggs	1308-288	NR	Wakeford et al. (2002) as cited in U.S. EPA (2010)
<b>Mammals</b>						
Red fox	Belgium	NR	Adipose, liver, muscle	Median range: 2.2-3.4	Liver- BDE-209: 70%	Voorspoels et al. (2006a)
Ringed seals, female	Canadian Arctic	NR	Blubber	Mean: 25.8	Tetra, pentaBDE	Alaee et al. (1999)
Ringed seals, male	Canadian Arctic	NR	Blubber	Mean: 50.0	Tetra, pentaBDE	Alaee et al. (1999)
	Arctic	1981		0.6	Tetra, pentaBDE	Ikonomou et al. (2002)
	Arctic	2000		6.0	Tetra, pentaBDE	Ikonomou et al. (2002)

Table E-7, cont. Measured concentrations of PBDEs in biota.

Species	Location	Year	Tissue	PBDE burden (ng/g) <sup>a</sup>	Common congener(s)	Source
<b>Mammals</b>						
Beluga whales, female	Canadian Arctic	NR	Blubber	Mean: 81.2	Tetra, pentaBDE	Alaee et al. (1999)
	St. Lawrence estuary	NR		665	NR	Lebeuf et al. (2001) as cited in U.S. EPA (2010)
Beluga whales, male	Canadian Arctic	NR	Blubber	Mean: 160	Tetra, pentaBDE	Alaee et al. (1999)
	St. Lawrence estuary	NR		466	NR	Lebeuf et al. (2001) as cited in U.S. EPA (2010)
	Baffin Island	1982	Blubber	2	Tri to hexaBDE	Stern and Ikonomou (2000)
	1997	15		Tri to hexaBDE		
Harbor seals	San Francisco Bay	1989-1998	Blubber	Range: 88-8325	Tetra, penta, hexaBDE	She et al. (2002)
Harbor porpoise	Vancouver	NR	Blubber	2269	TetraBDE: >50%	Ikonomou et al. (2000)
<b>Fish</b>						
Lake trout	Lake Ontario	1997	NR	434	NR	Luross et al. (2002)
	Lake Erie			117		
	Lake Superior			392		
	Lake Huron			251		
Rainbow trout	Spokane River, WA	1999	NR	297 <sup>d</sup>	NR	Johnson and Olson (2001)
Mountain whitefish	Spokane River, WA	1999	NR	1250 <sup>d</sup>	NR	Johnson and Olson (2001)
	Columbia River, British Columbia	1992-2000	Muscle	Mean range 4.5-19.1	NR	Rayne et al. (2003)
Largescale sucker	Spokane River, WA	1999	NR	105 <sup>d</sup>	NR	Johnson and Olson (2001)
Carp	Virginia	1998-1999	NR	1140 <sup>d</sup>	NR	Johnson and Olson (2001)

Table E-7, cont. Measured concentrations of PBDEs in biota.

Species	Location	Year	Tissue	PBDE burden (ng/g) <sup>a</sup>	Common congener(s)	Source
<b>Lower trophic levels</b>						
Caddisflies	Pyrenees Mountains, Spain	NR	Larva TB	Mean range: 0.65-13.00 <sup>c</sup>	NR	Bartrons et al. (2007)
			Pupa TB	Mean range 9.32- 27 <sup>c</sup>		
Midges	Pyrenees Mountains, Spain	NR	Larva TB	Mean range: 0-13.07	NR	Bartrons et al. (2007)
			Pupa TB	Mean range 3.9-5.2 <sup>c</sup>		

<sup>a</sup> ng/g lipid weight, unless otherwise specified.

<sup>b</sup> Units = ng/g wet weight

<sup>c</sup> Units = ng/g dry weight

<sup>d</sup> Measurement for a single fish only

BDE-47: tetraBDE; BDE-99: pentaBDE; BDE-153: hexaBDE; BDE-209: decaBDE; BDL = Below detection level; TB = Total body; NR = Not reported; NA = Not applicable

Table E-8. Mean concentration of PBDEs in media/biota in an aquatic ecosystem.

Media	Total PBDEs	BDE-47	BDE-99	BDE-100	BDE-153	BDE-209
Water (pg/L)	47.01	16.98	9.01	1.89	1.02	<MDL
Sediment (ng/g dwt)	1.31	0.12	0.15	0.03	0.06	0.63
<b>Biota level 1 (mg/g lipid wt)</b>						
Mussels	127.32	21.11	26.41	5.7	8.13	50.84
<b>Biota level 2 (mg/g lipid wt)</b>						
Zooplankton	61.57	11.71	17.79	4.89	5.81	1.21
White fish	11.1	1.82	1.48	0.6	0.43	3.61
<b>Biota level 3 (mg/g lipid wt)</b>						
Emerald shiner	151.07	60.78	2.15	10.65	7.25	40.33
Goldeye	381.26	83.84	116.15	24	31.98	41.64
White sucker	150.03	71.4	1.22	16.49	12.55	12.03

Table E-8, cont. Mean concentration of PBDEs in media/biota in an aquatic ecosystem.

Media	Total PBDEs	BDE-47	BDE-99	BDE-100	BDE-153	BDE-209
<b>Biota level 4 (mg/g lipid wt)</b>						
Walleye	54.39	16.21	2.56	2.34	1.98	24.72
Burbot	240.32	44.37	20.48	10.49	12.12	98.68

<MDL = Concentration less than minimal detection limit, approximately half

Source: Law et al. ([2006a](#))



## Appendix E References

1

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# Appendix F. Toxicological and Ecological Effects



# Appendix F. Toxicological and Ecological Effects

1 Appendix F comprises tables summarizing the material characteristics, study design, and results  
2 of select toxicokinetic and toxicological studies for BDE-209 and MWCNTs. Much of the relevant  
3 toxicological data for BDE-209 has been summarized in reviews, and many of the toxicological endpoints  
4 of concern have been identified and used by regulatory agencies to establish reference values for the  
5 protection of human health and the environment (see Chapter 5). Because the BDE-209 studies have been  
6 described in detail in many previous reviews, a relatively small subset of the BDE-209 studies discussed  
7 in Chapter 5 of this document are summarized in the tables of this appendix. Select BDE-209 study  
8 summary tables are generally provided only for general comparison to MWCNT study summary tables or  
9 for the primary exposure route of concern (oral).

10 By comparison, the toxicokinetics and toxicological effects of MWCNTs are not well understood  
11 and only one draft reference value has been established for the protection of human health (see Chapter  
12 5). Moreover, as emphasized throughout this document, variations in certain physicochemical  
13 characteristics of MWCNTs are likely to affect their behavior in biological systems and impacts to  
14 humans and biota. Appendix F therefore provides summary tables for most of the MWCNT toxicokinetic  
15 and toxicological studies referenced in Chapter 5 of this case study. These tables supply more detailed  
16 information on material characteristics, study design, and observed effects than was presented in the text.

17 Appendix F provides information on the absorption, distribution, metabolism, and elimination of  
18 BDE-209 and MWCNTs from identified toxicokinetic studies (Section F.1.1). In addition, summary  
19 tables present information from select in vivo studies reporting effects other than carcinogenicity using  
20 the dermal, ocular, inhalation, and oral routes of exposure (Section F.1.2); in vitro studies including those  
21 investigating genotoxicity and mutagenicity (Section F.1.3); and carcinogenicity studies (Section F.1.4)  
22 for BDE-209 and MWCNTs.

23 Appendix F also provides summary tables of data from studies that investigated effects of BDE-  
24 209, other PBDEs, and MWCNTs on various biota. Data from studies in aquatic ecosystems are  
25 summarized in Sections F.2.1 and F.2.2; data from terrestrial ecosystems are summarized in Sections F.2.3  
26 and F.2.4.

27 Literature was identified primarily using review articles published in the past two years. Targeted  
28 literature searches were carried out as needed.

## F.1. Toxicological Effects

### F.1.1. Toxicokinetic Studies

Table F-1. Select toxicokinetic studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
Oral (diet)	Unlabeled decaBDE (92% pure) and [U- <sup>14</sup> C] decaBDE (98.9% pure)	Fischer 344 rat (male)	12 days (sacrificed 24, 48, 72 hours after exposure to [U- <sup>14</sup> C] on day 8)	0.0277%, 4.80 % diet	Excretion results: urine 0.004–0.012%, feces 82.5–86.4% (recovery not related to dose); tissue recovery: 0.109% in liver, 0.248% in muscle, 0.136% in skin (other smaller quantities reported); for all tissues the maximum % in organs and tissues was reported in the low-dose group; for both doses % of dose remaining in the gut contents and gut tissues decreased with time after exposure	el Dareer et al. (1987)
i.v.	[U- <sup>14</sup> C] decaBDE (98.9% pure)	Fischer 344 rat (male)	72 hours	1.07 mg/kg	Excretion results: urine 0.129%, feces 70.0%; tissue recovery: 4.27% in liver, 5.063% in GI, 12.9% in muscle, 7.25% in skin, 2.99% in fat (other smaller quantities reported)	el Dareer et al. (1987)
Oral (diet)	Unlabeled decaBDE (92% pure) and [U- <sup>14</sup> C] decaBDE (98.9% pure)	Fischer 344 rat (male)	12 days (sacrificed 72 hours after exposure to [U- <sup>14</sup> C] on day 8)	0.025, 0.0509, 0.250, 0.487, 2.49, 4.99 % diet	Recovery of radiolabeled decaBDE in feces ranged from 91.3–101% of the amount ingested; recovery was not related to dose; liver weights of rats increased as dose increased	el Dareer et al. (1987)

Table F-1, cont. Select toxicokinetic studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
Oral (diet)	[U- <sup>14</sup> C] decaBDE (97.9–99.2% pure) diluted with unlabeled decaBDE	Rat	>8 days (7 days unlabeled, 1 day labeled, then returned to unlabeled diet for remainder of holding period)	250–50,000 ppm	Excretion results: feces 61%, urine 0.1%	NTP (1986)
Oral (diet)	[U- <sup>14</sup> C] decaBDE (97.9–99.2% pure) diluted with unlabeled decaBDE	Rat	>8 days (7 days unlabeled, 1 day labeled, then returned to unlabeled diet for remainder of holding period)	250–50,000 ppm	Excretion results: urine 0.01%, feces >99% in 72 hours	NTP (1986)
Oral	[U- <sup>14</sup> C] decaBDE (assumed to be 77.4% pure based on reference description)	Sprague-Dawley rat (male and female)	16 days	1 mg/kg	Excretion results: urine <1.0%, feces 90.6% (day 1), >8.4% (day 2), >99% (at 48 hours); tissue recovery: limited absorption to GI at 1, 3, and 16 days; 0.06% in spleen, 0.01% in adrenals (no others reported) at 16 days	Norris et al. (1975)
Oral (diet)	>99.8% pure	Pregnant Wistar rat (female)	96 hours (gestation days 16–19)	2.61 mg/kg-day	>19% recovered in tissues; efficient absorption reported; highest residue concentrations in endocrine glands and the liver; most of recovered product was unchanged decaBDE with 9–27% biotransformation products (nona- and octaBDEs) in tissues and 14% in fetuses; main metabolic pathways are debromination and oxidation	Riu et al. (2008)

Table F-1, cont. Select toxicokinetic studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
Oral	77.4% decaBDE, 21.8% nonaBDE, and 0.8% octaBDE	Rat	NR	NR	Slight accumulation occurring very slowly over time in adipose tissue	Great Lakes (1976) and IRDC (1976, 1977) as cited in NRC (2000)
Oral (diet)	77.4% pure	Rat	2 years	0, 0.01, 0.1, 1 mg/kg-day	No increase in the kidney, muscle, or serum	Dow (1994) as cited in NRC (2000)
Oral (gavage)	>98% pure, specific activity 17.5 Ci/mol	Sprague-Dawley rat (male)	3, 7 days	3 µmol/kg, 15 Ci/mol, 1 mL/kg volume	>10% absorbed; 90% excreted in feces (65% metabolites); 10% excretion in bile (mostly metabolites)	Mork et al. (2003)
Oral (diet)	98.5% pure	Sprague-Dawley rat (male)	21 days followed by 21-day withdrawal period	0.3 µg/g of diet	After 21 days 5% of decaBDE was measured as BDE-209 (<4% in feces); nona- and octaBDEs were also present; BDE-209 was highest in the liver, followed by the GI track; several lower congeners were present at higher concentrations than could be attributed directly to dose impurities as the result of debromination	Huwe and Smith (2007)
Oral (diet)	NR	Lactating cow (female)	3 months	Naturally contaminated diet (not measured)	BDE-209 was dominant congener in all tissue samples except milk (milk concentrations were generally low); dominant output route was feces; congener profiles in adipose tissue and feed differed; BDE-207, BDE-196, BDE-197, and BDE-182 accumulated to a greater extent in the fat compared to their isomers suggesting metabolic debromination of BDE-209; indicates that meat may be a more important human exposure route to higher brominated BDEs than dairy products	Kierkegaard et al. (2007)
Oral	NR	Sprague-Dawley rat (male)	90 days	100 mg/kg bw-day	Preferential accumulation of BDE-209 in the liver; BDE-209 induced hepatotoxicity (indicated by serum clinical chemistry data for AST, ALP, T-CHO, HDL-C, Cr, and TBA); significantly increased CYP2B1 expression in mRNA; metabolites of BDE-183, 196, 197, 202, 203, 206, 207, and 208 were all found in kidney and liver tissues (207 most prominent)	Wang et al. (2010)

Table F-1, cont. Select toxicokinetic studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
In vitro (incubation)	98 ± 1% pure	Human hepatocytes; 2 cryopreserved (1 male, 1 female), 1 fresh (male)	48-hour exposure for cryopreserved cell cultures; 1 dose per 24 hours for three days for fresh hepatocyte cultures	10 nmol/well	No hydroxylated or debrominated metabolites observed; Up-regulation of genes encoding for cytochrome P450 monooxygenase (CYP) 1A2, CYP3A4, deiodinase type 1, and glutathione S-transferase M1	Stapleton et al. (2009)
Oral	98% pure	Sprague-Dawley rat (female)	Gestation day 7 to postpartum day 4	5 µmol/kg	Increased accumulation with time in maternal blood, placenta, fetuses, and neonates; more BDE-209 found in neonate whole-body samples obtained during lactation than fetal whole-body samples during pregnancy; increased nonaBDE in maternal blood and placenta over time; slight changes observed for octaBDEs in maternal blood and placenta; significant decrease observed in the fetuses or neonates for BDE-196 and 198/203	Cai et al. (2011)
Gavage or i.v.	Unlabeled BDE-209 (>98% pure)	Sprague-Dawley rat (male)	1, 3, 6, 24, 48, 72, 96, 120, or 144 hours	2 µmol/mL	Bioavailability calculated to be >26%; 13 metabolites were identified in the plasma (octa- nona-, and hexaBDEs) at concentrations 4 times higher than the parent compound on days 3 and 7; BDE-209 was rapidly distributed to well perfused tissues (e.g., liver)	Sandholm et al. (2003)
Liver microsomal depletion	BDE-209	Harbor seal ( <i>Phoca vitulina</i> ) and sperm whale ( <i>Physeter catodon</i> )	NR	31 µg/mL	No detectable depletion of parent BDE-209; lack of microsomal depletion consistent with persistent and accumulative nature of BDE-209	de Boer et al. (1998, 2000) as cited in Hakk and Letcher (2003)

Table F-1, cont. Select toxicokinetic studies for decaBDE.

Oral	DecaBDE (BDE-209)	Sprague-Dawley rat (male)	72 hours	3 mg/kg	Excretion results: urine <0.05%, feces: >90%, bile: 9.5%; tissue recovery: 0.9 in liver, 3.5 in GI, 0.7 in muscle (other smaller quantities reported); rats metabolized BDE-209 to fecal metabolites (including debrominated mono-OH- and ortho-MeO-OH-BDEs )via oxidative debromination	Morck and Klasson-Wehler (2001) as cited in Hakk and Letcher ( <a href="#">2003</a> )
Oral (diet)	BDE-209 with detectable amounts of nona- and octaBDEs	Rainbow trout ( <i>Oncorhynchus mykiss</i> ) (male and female)	16, 49, 120 days	1.7–10 mg/kg-day	Low uptake efficiency; elevated levels in liver and muscle (20–40 times greater in liver, 560 ± 210 ng/g fresh wt to 870 ± 220 ng/g fresh wt from day 16 to day 120 for liver and 10 ± 3.2 ng/g fresh wt to 38 ± 14 ng/g fresh wt from day 16 to day 120 for muscle), decreased upon depuration; metabolites detected in liver and muscle tissues, not all metabolites decreased with depuration	Kierkegaard et al. ( <a href="#">1999</a> )

GI = Gastrointestinal tract; NR = Not reported

Table F-2. Select toxicokinetic studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Absorption</b>									
Intratracheal instillation; i.v.; and gavage	10–20	0.01–0.6	NR	>95%	Kunming mouse (male)	Single exposure; 28-day observation	10 µg	20% of administered dose remained within the lung at 28 days (intratracheal instillation); 80% accumulate in the liver and remain at 28 days (i.v.); only levels measured in stomach, large and small intestines, 74% directly excreted (gavage)	Deng et al. (2007)
Inhalation (intratracheal instillation)	20–50	0.5–2	NR	(% w/w): 0.53 Ni, 0.08 S, <0.02 Mg, <0.01 Na, <0.01 V	Sprague-Dawley rat (male)	Single exposure; 1-, 7-, 30-, 90-, and 180-day observations and 6-month MWCNT elimination observation	1, 10, 100 µg/rat	MWCNTs did not significantly cross the pulmonary barrier; MWCNTs were evident within the lungs at 6 months	Elgrabli et al. (2008b)
Inhalation (aspiration)	Mean: 49 ± 13.4	Median: 3.86	NR	0.78%; 0.41% sodium, 0.32% iron	C57BL/6 mouse (male)	Single exposure; 1-, 7-, 28- and 56-day observations	10, 20, 40, 80 µg	MWCNTs reached the pleura and induced pleural inflammation at 56 days	Porter et al. (2010)
Oral (gavage)	10–20	0.01–0.6	NR	>95%	Kunming mouse (male)	Single exposure; 12-hour observation	10 µg	Majority of MWCNTs evident in feces, stomach, and small and large intestines; no detectable transport into the blood; MWCNTs remained unchanged suggesting biopersistence if not excreted	Deng et al. (2007)

Table F-2, cont. Select toxicokinetic studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Distribution</b>									
Inhalation	10–50	<0.1–10	NR	NR	C57BL6 mouse (male)	Single 6-hour exposure; 14-week observation	1, 30 mg/m <sup>3</sup>	MWCNTs reached the subpleura; nanotubes were embedded in subpleural wall and within subpleural macrophages	Ryman-Rasmussen et al. (2009a)
Inhalation (intratracheal instillation)	NR	0.9–0.15	197	NR	Wistar albino rat (male)	Single exposure; 24 hour, 1 week, 1- and 3-month observations	0.2, 1, 5 mg/kg	MWCNTs translocated from the lung to liver and kidney (not to the heart) at 1 month	Reddy et al. (2010)
<b>Elimination</b>									
Inhalation (intratracheal instillation)	20–50	0.5–2	NR	(% w/w): 0.53 Ni, 0.08 S, <0.02 Mg, <0.01 Na, <0.01 V	Sprague-Dawley rat (male)	Single exposure; 1-, 7-, 30-, 90-, and 180-day observations and 6-month MWCNT elimination observation	1, 10, 100 µg/rat	Following phagocytosis of the MWCNTs, the macrophages underwent apoptosis, with no inflammatory response or other physiological and histological pathology	Elgrabli et al. (2008a)

NR = Not reported



## F.1.2. In Vivo Studies (Excluding Carcinogenicity Studies)

Table F-3. Select dermal and ocular studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Irritation</b>						
Dermal	Dry solid	New Zealand albino rabbit	24 hours, 3 days, 2 weeks	500 mg, reported by NRC (2000)	No dermal response in intact skin; no indication of bromacne	Norris et al. (1975) [also reported in NTP (1986); Norris et al. (1973); Dow (1972) and IRDC (1974) as cited in NRC (2000)]
Dermal	NR	Rabbit	Single administration 24 hours; 14 days observation	200, 2000 mg/kg	Slight erythematous and edematous response in abraded skin	IRDC (1974) and Great Lakes (1977) as cited in NRC (2000); Norris et al. (1975)
<b>Sensitization</b>						
Dermal	Homogenous 5% suspension in petrolatum; 77.4% decaBDE, 21.8% nonaBDE, 0.8% octaBDE	Human	3 times per week for 3 weeks	NR	No skin sensitization response	Norris et al. (1975) [also reported in NTP (1986); Norris et al. (1973); Dow (1972) as cited in NRC (2000)]
<b>Systemic effects</b>						
Dermal	NR	Rabbit	Single administration 24 hours observation	200, 2000 mg/kg	No treatment-related effects in body weight gain or survival	IRDC (1974) and Great Lakes (1977) as cited in NRC (2000)

Table F-3. cont., Select dermal and ocular studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Ocular</b>						
Ocular	Saytex 102	Rabbit	Single application	100 mg	No primary eye irritation	Pharmakon (1981) as cited in NRC (2000)
Ocular	Dry solid	New Zealand albino rabbit	Single application	100 mg per eye	Transient irritation of conjunctival membranes in washed and unwashed eyes (not sustained past 24 hours)	Norris et al. (1975) [also reported in NTP (1986); Norris et al. (1973); IRDC (1974) Dow (1972) as cited in NRC (2000)]

NR = Not reported

Table F-4. Select dermal and ocular studies for MWCNTs.

Test substance	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Skin irritation</b>									
1% Nikkiso-MWCNTs	44	NR	69	176 ppm Ga, 80 ppm Al, 53 ppm Fe, 16 ppm Cd, 0.5 ppm Li	Kbl:New Zealand white rabbit (male)	4-hour exposure; 1-, 24-, 48-, and 72-hour observation	0.5 g	Exposure resulted in a primary irritation index of 0.6	Ema et al. (2011) (OECD 404 compliant; not GLP compliant)
2% Mitsui product of MWCNTs	60	NR	23	3600 ppm Fe, 14 ppm Cr, 6 ppm Bi, 4 ppm Ni	Kbl:New Zealand white rabbit (male)	4-hour exposure; 1-, 24-, 48-, and 72-hour observation	0.5 g	No erythema or edema was observed	Ema et al. (2011) (OECD 404 compliant; not GLP compliant)
MWCNTs	Inner: 3–8, outer: 140 ± 30	5–9	10–15	NR	New Zealand white rabbit (female)	4-hour under semi-occlusive conditions; 96-hour observation	0.5 g	No erythema or edema at 72 hours	Kishore et al. (2009) (OECD 404 compliant)
MWCNTs	Inner: 2–6, outer: 10–15	0.1–10	30–45	NR	New Zealand white rabbit (female)	4-hour under semi-occlusive conditions; 96-hour observation	0.5 g	No erythema or edema at 72 hours	Kishore et al. (2009) (OECD 404 compliant)

Table F-4, cont. Select dermal and ocular studies for MWCNTs

Test substance	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Skin sensitization</b>									
1% Nikkiso-MWCNTs	44	NR	69	176 ppm Ga, 80 ppm Al, 53 ppm Fe, 16 ppm Cd, 0.5 ppm Li	Slc:Hartley guinea pig (male)	3 doses; 6-hour challenge was conducted on day 28	0.4 g paste	No sensitization observed	Ema et al. (2011) (OECD 406 compliant; Buehler method)
2% Mitsui product of MWCNTs	60	NR	23	3600 ppm Fe, 14 ppm Cr, 6 ppm Bi, 4 ppm Ni	Slc:Hartley guinea pig (male)	3 doses; 6-hour challenge was conducted on day 28	0.4 g paste	No sensitization observed	Ema et al. (2011) (OECD 406 compliant; Buehler method)
<b>Ocular irritation</b>									
1% Nikkiso-MWCNTs	44	NR	69	176 ppm Ga, 80 ppm Al, 53 ppm Fe, 16 ppm Cd, 0.5 ppm Li	Kbl:New Zealand white rabbit (male)	Single exposure to left eye; right eye served as control	0.1%, 0.25% (0.1 mL)	Conjunctival redness and blood vessel hyperemia at 1 hour, not at 24 hours	Ema et al. (2011) (OECD 405 compliant)
2% Mitsui product of MWCNTs	60	NR	23	3600 ppm Fe, 14 ppm Cr, 6 ppm Bi, 4 ppm Ni	Kbl:New Zealand white rabbit (male)	Single exposure to left eye; right eye served as control	1% (0.1 mL)	No eye irritation observed	Ema et al. (2011) (OECD 405 compliant)

NR = Not reported

Table F-5. Select inhalation studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
Inhalation (Intratracheal injection)	77.4 % purity decabromodiphenyl oxide (DBDPO) dust, respirable size	Sprague-Dawley rat (male)	3, 10, 30, 91, 365, 416, 556 days	20 mg/mL rat serum	Slightly enlarged thoracic lymph nodes in 3/10 rats on Days 10 and 30; scattered focal aggregates of alveolar macrophages on Days 10 and 556	Dow Chemical Co. ( <a href="#">1990</a> )
Inhalation	DE-83, 97% purity aerosolized dust	Spartan rat (male and female)	1 hr (observed for 14 days)	2 or 48.2 mg/L air	1 instance of marked to slight respiratory difficulty, 1 instance of ocular porphyrin discharge at 2 mg/L dose level before Day 13; eye squint, changes in motor activity (first decreased, then increased), respiratory difficulty, ocular porphyrin discharge at 48.2 mg/L dose level before Day 13. All rats normal on Days 13 and 14.	Great Lakes Chemical Corporation ( <a href="#">1994</a> ) and IRDC ( <a href="#">1974</a> )

Table F-6. Select inhalation studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Acute or subacute</b>									
Inhalation (nose only)	1900–2900	~≤1	253	98.6% (bulk) and 99.1% (micronized)	Wistar rat (male)	Single exposure for 6 hours; 7-,28-, 90-day observation	11, 241 mg/m <sup>3</sup>	Deregulation of genes (inflammation, oxidative stress, and fibroses) at 241 mg/m <sup>3</sup> ; mild reversible inflammation and no fibroses at 11 mg/m <sup>3</sup> (LOAEC)	Ellinger-Ziegelbauer and Pauluhn (2009) (OECD 403 compliant)
Inhalation (intratracheal instillation)	50	10	280	>95%	Kunming mouse (female)	Single exposure; 8-, 16-, 24-day observation	1.7 mg/kg	Inflammation of lining of bronchi at 24 days; severe destruction of alveolar netted structure around CNT clumps	Li et al. (2007)
Inhalation	50	10	280	>95%	Kunming mouse (female)	6 hours/day; 5, 10, 15 days	32.61 mg/m <sup>3</sup>	Thickening of alveolar wall, but alveolar structure remained	Li et al. (2007)
Inhalation (whole body)	10–20	5–15	100	0.5% Ni and Fe	C57BL/6 mouse (male)	6 h/day; 7, 14 days	0.3, 1, 5.3 mg/m <sup>3</sup>	No local pulmonary effects; non-monotonic systemic immune suppression	Mitchell et al. (2007)
Inhalation (whole body)	10–20	5–15	100	0.5% Ni and Fe	C57BL/6 mouse (male)	6 h/day; 14 days	0.3, 1 mg/m <sup>3</sup>	Systemic immune suppression, not due to systemic uptake of MWCNTs, but release of immune suppressing signals from lung	Mitchell et al. (2009)

Table F-6, cont. Select inhalation studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Acute or subacute</b>									
Inhalation (intratracheal instillation)	NR	NR	NR	NR	SD rat (female)	Single exposure; 3-, 15-, 28-, 60-day observation	2.2, 8.9, 22.2 mg/kg	Inflammation and fibrosis; granulomas with ground MWCNTs	Muller et al. (2005)
Inhalation (intratracheal instillation)	11.3	0.7	NR	98%; traces of Co and Fe catalysts	Wistar rat (female)	Single exposure; 3-day observation	0.5, 2, 5 mg/rat	Significant dose-dependent increase in micronucleated pneumocytes	Muller et al. (2008a)
Inhalation (intratracheal instillation)	NR	NR	NR	NR	Wistar rat (female)	Single exposure; 3- and 60-day observation	2 mg/rat	Toxicity of CNT mediated by defective sites in carbon framework; significant differences between ground MWCNTs not heated, heated to 600°C, and to 2400°C for both short and long-term response	Muller et al. (2008b)
Intranasal injection	15.04 ± 0.47	0.5–200 (reported by supplier)	139.7	>90% carbon (as reported by supplier)	BALB/cAnNCr 1 mouse (female)	3 days	200, 400 µg/mouse (with 10 µg OVA per injection and 10 µg OVA booster given at 21, 22, and 23 days)	Increased IgE in serum and inflammatory cells in BALF	Nygaard et al. (2009)
Inhalation (intratracheal instillation)	11–170	5–9	12.83	>90% carbon	ICR mouse (male)	Single exposure; 1-, 3-, 7-, 14-day observation	5, 20, 50 mg/kg	Increase in immune cells and granulomas; increase in inflammatory cytokines (IL-1, TNF-α, IL-6, IL-4, IL-5, IL-10, IL-12, IFN-γ) and IgE; distribution of B cells in spleen	Park et al. (2009)

Table F–6, cont. Select inhalation studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
Inhalation (nose-only)	30–50	0.3–50	109.29	>94%	C57BL/6 mouse (male)	Single exposure; 6 hours; 1-, 14-day observation	~10 mg/kg; concentration in air was 103.6±8.34 mg/m <sup>3</sup> (both with and without 20 µg OVA injection given 14 and 7 d before exposure)	OVA sensitized group: significant airway fibrosis at 14 days, Elevated PDGF-AA and TGF- β1 at day 1 but not day 14; increased IL-5 mRNA levels  not sensitized group: elevated PDGF-AA, but not increased levels of TGF- β 1 and IL-13	Ryman-Rasmussen et al. (2009b)
Inhalation	10–15	~20	NR	95%	Sprague-Dawley rat (male)	6 hours/day; 5 days; 1 month observation	0.1, 0.34, 0.94 mg/m <sup>3</sup>	pulmonary DNA damage initiated; a Comet assay performed on lung cells showed a significant increase in DNA damage for high dose compared to controls immediately and 1 month following the last exposure	Kim et al. (In Press)
<b>Subchronic</b>									
Inhalation	50	10	280	>95%	Kunming mouse (female)	6 hours/day; 30, 60 days;	32.61 mg/m <sup>3</sup>	No obvious toxicity at 30 days; severe pulmonary toxicity at 60 days	Li et al. (2009)
Inhalation (head-nose)	5–15, 500–1300, 1300–2000/900–1500, 700–800	0.1–1	250–300	90%	Wistar rat (male and female)	6 hours/day; 13 weeks	0.1, 0.4, 2.5 mg/m <sup>3</sup>	Minimal granulomatous inflammation in lung at 0.1 mg/m <sup>3</sup> (LOEC); significant granulomatous inflammation <0.5 mg/m <sup>3</sup> ; no systemic toxicity; no pulmonary fibrosis	Ma-Hock et al. (2009) (OECD 413 compliant)



Table F-6, cont. Select inhalation studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Subchronic</b>									
Inhalation (intratracheal instillation)	67	3–30	26	99.79%	ICR mouse (male)		25, 50 µg/week/mouse (both with and without 1 µg OVA/2 wk)	Increased total cells in BALF, infiltration of inflammatory leukocytes in airways, induction of goblet cell hyperplasia in both groups, enhanced response in sensitized group	Inoue et al. (2009)
Inhalation (nose only)	1900–2900	~≤1	253	98.6% (bulk) and 99.1% (micronized)	Wistar rat (male and female)	6 hours/day; 5 days/week; 13 weeks	0.1, 0.4, 1.5, 6 mg/m <sup>3</sup>	Sustained pulmonary inflammation at ≥1.5 mg/m <sup>3</sup> ; granulomas and alveolar hyperplasia at ≥6 mg/m <sup>3</sup> ; no systemic toxicity; 0.1 mg/m <sup>3</sup> was NOAEC	Pauluhn (2010) (OECD 413 compliant)

NR = Not reported

Table F-7. Select oral and intragastric studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Acute</b>						
Oral (gavage)	NR	Rat	Single dose	5000 mg/kg	No clinical signs, toxicity, or death	Nissimov (1984); Great Lakes (1984); IRDC (1974) as cited in NRC (2000)
Intragastric intubation	77.4% decaBDE, 21.8% nonaBDE, 0.8% octaBDE	Sprague-Dawley rat (female)	Single dose (acute)	126, 252, 500, 1000, 2000 mg/kg (10% corn oil suspension)	No indications of toxicity; no detectable pathological changes	Norris et al. (1975) [also in Norris et al. (1973)]
<b>Subchronic</b>						
NR	97–99% pure	Rat (male and female)	28 days	0, 7.4, 75 mg/kg-day	No histology in liver or thyroid (NOAEL 74 mg/kg-day)	Great Lakes (1976); IRDC (1976) as cited in NRC (2000)
Intragastric	>98% pure	Wistar rat (female)	7–28 days	0, 10, 100, 1000 mg/kg-day	2-fold induction of CYP1A and CYP2B at 10–1000 mg/kg-day (not dose-dependent)	Bruchajzer et al. (2010)
Oral (diet)	94–98% pure	F344/N rat (male and female)	14 days	0, 5000, 10,000, 20,000, 50,000, 10,0000 ppm	No treatment-related clinical signs or gross pathologic effects	NTP (1986)
Oral (diet)	94–98% pure	B6C3F <sub>1</sub> mouse (male and female)	14 days	0, 5000, 10,000, 20,000, 50,000, 10,0000 ppm	No treatment-related clinical signs or gross pathologic effects	NTP (1986)

Table F-7, cont. Select oral and intragastric studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Subchronic</b>						
Oral (gavage)	97% pure	Wistar rat (male)	28 days	0, 1.9, 3.8, 7.5, 15, 30, 60 mg/kg	Increased weight of seminal vesicle/coagulation gland (BMDL 0.2 mg/kg-day); increased expression of hepatic CYP1A and CYP2B (BMDL 0.5–0.7 mg/kg-day)	Van der Ven et al. (2008)
Oral (gavage)	97% pure	Wistar rat (female)	28 days	0, 1.9, 3.8, 7.5, 15, 30, 60 mg/kg	Decreased activity of P450c17 (BMDL 0.18 mg/kg-day)	Van der Ven et al. (2008)
Oral (diet)	77.4% decaBDE, 21.8% nonaBDE, 0.8% octaBDE	Sprague-Dawley rat (male)	30 days	0, 8, 80, 800 mg/kg-day	Decrease in packed cell volume and total red blood cell count in highest dose group; enlarged livers in mid- and high-dose groups; liver and kidney lesions at 800 mg/kg-day; thyroid hyperplasia at 80 mg/kg-day	Norris et al. (1975)
Oral (diet)	94–98% pure	F344/N rat (male and female)	13 weeks	0, 3100, 6200, 12,500, 25,000, 50,000 ppm	No treatment-related clinical signs or gross or microscopic pathologic effects	NTP (1986)
Oral (diet)	94–98% pure	B6C3F <sub>1</sub> mouse (male and female)	13 weeks	0, 3100, 6200, 12,500, 25,000, 50,000 ppm	No treatment-related clinical signs or gross or microscopic pathologic effects	NTP (1986)
<b>Chronic</b>						
Oral (diet)	77.4% decaBDE, 21.8% nonaBDE, 0.8% octaBDE	Sprague-Dawley rat (male and female)	2 years	0, 0.01, 0.1, 1.0 mg	No differences observed in hematology or urinalysis at 1 year; no other results reported (report published before completion of study)	Norris et al. (1975)
Oral (diet)	94–98% pure	F344/N rat (male)	2 years	0, 2500, 50,000 ppm	Increased incidence of neoplastic lesions (nodules in the liver; acinar cell adenomas, sarcoma of the spleen, hepatocellular adenomas and carcinomas, thyroid gland follicular cell adenomas or carcinomas) and nonneoplastic lesions (thrombosis and degeneration of the liver; fibrosis of the spleen, lymphoid hyperplasia)	NTP (1986)

Table F-7, cont. Select oral and intragastric studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Chronic</b>						
Oral (diet)	94–98% pure	F344/N rat (female)	2 years	0, 2500, 50,000 ppm	Increased incidence of neoplastic lesions (nodules in the liver of high-dose group) and nonneoplastic lesions; degeneration of the eye in low dose group	NTP (1986)
Oral (diet)	94–98% pure	B6C3F <sub>1</sub> mouse (male)	2 years	0, 2500, 50,000 ppm	Dose-dependent increase in thyroid follicular cell hyperplasia; centrilobular hypertrophy (indicated by enlarged hepatocytes with frothy vacuolated cytoplasm)	NTP (1986)
Oral (diet)	94–98% pure	B6C3F <sub>1</sub> mouse (female)	2 years	0, 2500, 50,000 ppm	Increased incidence of nonneoplastic lesions	NTP (1986)
Oral (diet)	94–98% pure	F344/N rat (male)	2 years	1120, 2240 mg/kg (adjusted)	Increased incidences of thrombosis and degeneration of the liver in high-dose group; enzyme induction; significant increases in hepatic CYP1A mRNA, CYP2B mRNA, CYP1A1 protein, and 7-pentoxoresorufin <i>O</i> -dealkylase activity; increased 7-ethoxyresorufin <i>O</i> -deethylase activity	NTP (1986)
Oral (diet)	94–98% pure	F344/N rat (female)	2 years	1200, 2550 mg/kg (adjusted)	Increased 7-ethoxyresorufin <i>O</i> -deethylase activity	NTP (1986)
Oral (diet)	77.4% pure	Sprague-Dawley rat (male and female)	2 years	0, 0.01, 0.1, 1 mg/kg/d	No histology; NOAEL 1 mg/kg-day	Norris (1973); Dow (1994) and Kociba et al. (1975) as cited in NRC (2000)
Oral (metal gastric tube)	>99%	NMRI mice (male)	single dose given at age 3, 10, or 19 days	2.22, 20.1 mg/kg-d for 3 and 19 day old mice; 0, 1.34, 13.4, or 20.1 mg/kg-d for 10 day old mice	Statistically significant changes in spontaneous behavior variables (increased activity for locomotion, rearing, total activity) at 2, 4, and 6 months at highest dose when exposed on PND 3 (developmental effects), but not PND 10 or 19	Viberg et al. (2003)

Table F-8. Select intubation and injection studies for MWNCTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Acute/Subacute</b>									
intra-peritoneal injection	15-30	15-20		>95%; functionalized (2-7% COOH)	Swiss-Webster mice	daily, 5 days	0.25, 0.5, 0.75 mg/kg-d	Dose-related increase in ROS level in liver homogenate at all doses; increase in LHPs in liver homogenate and ALT in serum at medium and high dose; increase in serum ALP at high dose; non-statistically significant, dose-dependent increase in AST/GOT at all doses.	Patlolla et al. (2011)
<b>Developmental Studies</b>									
Oral (gavage)	10-15	~20	NR	~95%	Sprague-Dawley rat (pregnant dams)	Single dose on GD 6-19	of 0, 40, 200, and 1000 mg/kg/d	Dose-dependent decrease in absolute and relative thymus weight and increase in malondialdehyde concentration (maternal effects); no other treatment-related maternal or fetal (developmental) effects were reported; 1000 mg/kg/d was the embryo-fetal NOEL	Lim et al. (2011)

Table F-8, cont. Select intubation and injection studies for MWCNTs.

Route of exposure	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
<b>Developmental Studies</b>									
Intraperitoneal	Width distribution from 70-170 nm with the greatest frequency occurring at 90-110 nm, length distribution between 1 - 19 µm with the greatest frequency occurring between 1 - 5 µm [reported to be identical to those described by Takagi et al. (2008) and Sakamoto et al. (2009)]				ICR mice (pregnant dams)	Single dose on GD 9; fetuses examined on GD 18	0, 2, 3, 4, or 5 mg/kg-bw	Dose-dependent decreased maternal body weight; increased number of resorptions, decreased number of live fetuses per litter in the two highest dose groups; external and skeletal malformations (e.g., cleft palate, limb deformities, hypo/hyperphalangia) observed more frequently (ratio of litter with malformed fetuses and % incidence at all dose levels)	Fujitani et al. (2012)
Intratracheal injection	Width distribution from 70-170 nm with the greatest frequency occurring at 90-110 nm, length distribution between 1 - 19 µm with the greatest frequency occurring between 1 - 5 µm [reported to be identical to those described by Takagi et al. (2008) and Sakamoto et al. (2009)]				ICR mice (pregnant dams)	Single dose on GD 9; fetuses examined on GD 18	0, 3, 4, or 5 mg/kg-bw	Decreased final body weight of dams and decreased body weight of live fetuses in 5mg/kg group; external and skeletal malformations (e.g., limb deformities, fused ribs) observed more frequently (ratio of litter with malformed fetuses and % incidence) in two highest dose groups	Fujitani et al. (2012)

### F.1.3. Genotoxicity, Mutagenicity, and Other In Vitro Studies

Table F-9. Select genotoxicity, mutagenicity, and other in vitro studies for MWCNTs.

Assay	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Doses tested	Effects observed	Citation
<b>Cytotoxicity</b>								
Trypan blue test	110–170	5–9	22	>98%; <0.1% Fe; ~1.5% Ni; other metal catalysts	Murine macrophage cell line RAW 264.7	0.01, 0.1, 1, 10, 100 µg/mL	Significant cytotoxic effect at 10 and 100 µg/mL	Migliore et al. (2010)
<b>Bacterial mutation</b>								
Ames assay	110–170	5–9	130	>90%; <0.1% Fe; residual amorphous carbon; other metal contaminants	<i>Salmonella typhimurium</i> strains TA 98, TA 100; <i>Escherichia coli</i> strain WP2uvrA	0.01, 0.05, 0.13, 0.23, 0.46, 1.26, 2.30, 4.60, 9.0 µg/plate, ±S9	No significant increase in number of revertant colony with or without metabolic activation	Di Sotto et al. (2009)
Ames assay	100 to >150 (bimodal distribution)	0.2–1	NR	>95%; no free amorphous carbon	Salmonella strains TA1535, TA100, TA1537, TA98, TA102	50, 158, 500, 1581, 5000 µg/plate, ±S9	Not mutagenic and bacteriotoxic up to 5000 µg/plate with or without metabolic activation	Wirnitzer et al. (2009) (OECD 471)

Table F-9, cont. Select genotoxicity, mutagenicity, and other in vitro studies for MWCNTs.

Assay	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Doses tested	Effects observed	Citation
<b>DNA damage and unscheduled DNA synthesis</b>								
Chromosome aberration	88 ± 5	5 ± 4.5	NR	NR	Chinese hamster lung cells	0.078, 0.31, 1.4, 5.0, 20, 80 µg/mL, –S9	Formation of polyploidy with no structural chromosome aberration at ≥5.0 µg/mL for 24-hour test and ≥1.3 µg/mL for 48-hour test	Asakura et al. (2010)
Comet assay	110–170	5–9	22	>98%; <0.1% Fe; ~1.5% Ni; other metal catalysts	Murine macrophage cell line RAW 264.7	0.01, 0.1, 1, 10, 100 µg/mL	Significantly higher % DNA in comet tails for doses ≥1 µg/mL; significant dose-related effect overall	Migliore et al. (2010)
Comet assay	20–40	0.5–200	NR	93.37%	human lung epithelial A549 cells	5, 10, 40, 100 µg/mL	Significantly higher % DNA in comet tails concentration-dependent for 10, 40 µg/mL at 2 h post exposure and 5, 10, 100 µg/mL 4 h post exposure; corresponds with reduced cell viability	Cavallo et al. (2012)
Comet assay	15–30	15–20	NR	> 95%	normal human dermal fibroblast cells (NHDF)	40, 200, 400 µg/mL	statistically significant, dose-dependent increase in % DNA in comet tails	Patlolla et al. (2010b; 2010a).
Sister chromatid exchange; micronucleus assay	10–30	1–2	NR	95–98%	Human lymphocyte cells	1 mg/mL, –S9	No significant cytotoxic effects	Szendi and Varga (2008)
Chromosome aberration	100 to >150 (bimodal distribution)	0.2–1	NR	>95%; no free amorphous carbon	V79 cells	2.5, 5, 10 µg/mL, ±S9	No cytotoxic or clastogenic effects detected with or without metabolic activation	Wirnitzer et al. (2009) (OECD 473)



Table F-9, cont. Select genotoxicity, mutagenicity, and other in vitro studies for MWCNTs.

Assay	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Doses tested	Effects observed	Citation
<b>DNA damage and unscheduled DNA synthesis</b>								
Sister chromatid exchange	>80% of particles 70–110, Gaussian peak at 90	>70% of particles 1–4, peak: 2	NR	3500, 470, and 20 ppm iron, sulfur, and chlorine contaminants	Chinese hamster ovary AA8 cells	0.1, 1.0, 2.0 µg/mL	Significant increase in sister chromatid exchange frequency at all doses; approximately 3-fold increase over controls at 1.0 µg/mL	Kato et al. ( <a href="#">In Press</a> ); CNT characteristics in Sakamoto et al ( <a href="#">2009</a> )
Comet assay (in vivo intra-tracheal instillation; 3 hours)	>80% of particles 70–110, Gaussian peak at 90	>70% of particles 1–4, peak: 2	NR	3500, 470, and 20 ppm iron, sulfur, and chlorine contaminants	Male ICR mice (6 weeks old); lung cells	Single doses of 0.05 or 0.2 mg/animal	Significant, dose-dependent increase in DNA damage observed by significant increases in DNA tail moment and percentage of DNA in the tail compared to controls.	Kato et al. ( <a href="#">In Press</a> ); CNT characteristics in Sakamoto et al ( <a href="#">2009</a> )
DNA adduct assay (in vivo intra-tracheal instillation; 3, 24, 72, 168 hours)	>80% of particles 70–110, Gaussian peak at 90	>70% of particles 1–4, peak: 2	NR	3500, 470, and 20 ppm iron, sulfur, and chlorine contaminants	Male ICR mice (6 weeks old); lung DNA	Single dose of 0.2 mg/animal	Three (out of four analyzed) DNA adducts related to oxidative stress and lipid peroxidation significantly increased (relative to controls) in a time dependent manner up to 72 hours; a significant smaller significant increase relative to controls was observed at 168 hours.	Kato et al. ( <a href="#">In Press</a> ); CNT characteristics in Sakamoto et al ( <a href="#">2009</a> )
DNA damage via Western blot	NR	NR	NR	NR	Mouse embryonic stem cells	100 µg/mL	Increased expression of two isoforms of base excision repair protein 8-oxoguanine-DNA glycosylase 1 (OGG1), double strand break repair protein Rad 51; phosphorylation of H2AX histone at serine 139; SUMO modification of XRCC4	Zhu et al. ( <a href="#">2007</a> )

Table F-9, cont. Select genotoxicity, mutagenicity, and other in vitro studies for MWCNTs.

Assay	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Doses tested	Effects observed	Citation
<b>Mutation</b>								
Micronucleus assay	88 ± 5	5 ± 4.5	NR	NR	Chinese hamster lung cells	0.02, 0.078, 0.31, 1.3, 5.0 µg/mL, -S9	Increased bi- and multi-nucleated cells at ≥0.31 µg/mL; no micronucleus induction	Asakura et al. (2010)
Mutation at hgprt locus	88 ± 5	5 ± 4.5	NR	NR	Chinese hamster lung cells	6.3, 12.5, 25, 50, 100 µg/mL, -S9	Negative hgprt mutagenicity at all doses	Asakura et al. (2010)
Micronucleus assay	20–40	1–5	NR	>99% wt	Human blood cells	0.25–150 µL/5 mL total cell culture volume, -S9	MWCNTs acted as clastogen and aneugen agents simultaneously	Cveticanin et al. (2010)
Micronucleus assay	>80% of particles 70–110, Gaussian peak: 90	>70% of particles 1–4, peak: 2	NR	3500, 470, and 20 ppm iron, sulfur, and chlorine contaminants	Human lung carcinoma A549 cells	20, 100, 200 µg/mL	6 hour treatment at 20 µg/mL inhibited cell growth to around 70% of control levels. Significant, dose-dependent increase in frequency of micronucleated cells at all doses (up to 8.6% at 200 µg/mL)	Kato et al. (In Press); CNT characteristics in Sakamoto et al (2009)
Mutation assay (in vivo intra-tracheal instillation; 8 – 12 weeks)	>80% of particles 70–110, Gaussian peak at 90	>70% of particles 1–4, peak: 2	NR	3500, 470, and 20 ppm iron, sulfur, and chlorine contaminants	Male guanine phosphoribosyl-transferase ( <i>gpt</i> ) mice (9 weeks old)	One, two, or four single doses of 0.2 mg/animal given once, two weeks apart, and every week, respectively	No increase in <i>gpt</i> mutant frequencies following single or double dose, but significant increase (approx.. 2-fold over control) after 4 doses. No increases observed in SPI- (sensitive to P2 interference) mutation frequencies.	Kato et al. (In Press); CNT characteristics in Sakamoto et al (2009)
Micronucleus assay	110–170	5–9	22	>98%; <0.1% Fe; ~1.5% Ni; other metal catalysts	Murine macrophage cell line RAW 264.7	0.01, 0.1, 1, 10, 100 µg/mL, -S9	Significantly more micronucleated cells for doses ≥1 µg/mL	Migliore et al. (2010)

Table F-9, cont. Select genotoxicity, mutagenicity, and other in vitro studies for MWCNTs.

Assay	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Doses tested	Effects observed	Citation
<b>Mutation</b>								
Micronucleus assay	11.3	0.7	NR	98%; traces of Co and Fe	Rat lung epithelial cells	10, 25, 50, 100, 150 µg/mL, -S9	Significant increase in micronuclei	Muller et al. (2008a)
platelet aggregation (Aggro-Link data reduction system; Chronolog)	NR	NR	NR	NR	human platelet cells	0.2–300 µg/mL; platelets isolated and resuspended in Tyrode's solution; aggregation was studied for 8 min post-addition of MWCNTs	concentration-dependent increase in platelet aggregation; activation of GPIIb/IIIa	Radomski et al. (2005)
T-cell viability; Trypan Blue exclusion assay	20–40	1–5	NR	95%	Jurkat T lymphocyte (leukemia) cells from healthy human blood donors	1, 10 ng/cell (40, 400 µg/mL); Cell aliquots collected at 0, 24, 48, 72, 96, 120 h post-exposure; stained for 5 min with Trypan Blue to determine cell proliferation and percentage of apoptotic Jurkat or peripheral blood lymphocytes (PBL) determined using annexin V-FITC	time-dependent decrease in the viability of Jurkat T leukemia cells; increased number of cells staining with annexin V indicating increased apoptosis	Bottini et al. (2006)

NR = Not reported

## F.1.4. Carcinogenicity Studies

Table F-10. Select carcinogenicity studies for decaBDE.

Route of exposure	Description of decaBDE	Species	Exposure duration	Doses tested	Effects observed	Citation
Oral	94–98% pure	F344/N rat (male)	2 years	1120, 2240 mg/kg-day (adjusted)	Some evidence of carcinogenicity; increased incidences of neoplastic nodules of the liver (low dose 7/50, high dose 15/49, control 1/50)	NTP (1986)
Oral	94–98% pure	F344/N rat (female)	2 years	1120, 2550 mg/kg-day (adjusted)	Some evidence of carcinogenicity; increased incidences of neoplastic nodules of the liver (low dose 3/49, high dose 9/50, control 1/50)	NTP (1986)
Oral	94–98% pure	B6C3F <sub>1</sub> mouse (male)	2 years	25,000, 50,000 ppm	Equivocal evidence of carcinogenicity; increased incidences of hepatocellular adenomas or carcinomas (combined) in both dose groups	NTP (1986)
Oral	94–98% pure	B6C3F <sub>1</sub> mouse (female)	2 years	25,000, 50,000 ppm	No evidence of carcinogenicity	NTP (1986)
Oral	77.4% decaBDE, 21.8% nonaBDE, 0.8% octaBDE	Sprague-Dawley rat (male and female)	2 years	0, 0.01, 0.1, 1.0 mg/kg-day	No alterations in appearance, behavior, bodyweight, feed consumption, hematologic analyses, urinalysis, clinical chemistry, organ weights, survival, or tumor incidence	Kociba et al. (1975) as reported in NTP (1986) and NRC (2000)

Table F-11. Select carcinogenicity studies for MWCNT.

Test substance	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
MWCNTs with structural defects	11.3 ± 3.9	~0.7	299	1.97% Al, 0.49% Fe, 0.48% Co	Wistar rat (male)	Single injection, 24-month observation	2, 20 mg/rat	2 mesotheliomas at low dose (1 at 20 months and 1 at terminal sacrifice); 1 other peritoneal tumor at low dose at 16.6 months; no mesotheliomas at high dose; 3 other peritoneal tumors (1 lipoma at 13.8 months, 1 angiosarcoma and 1 liposarcoma at terminal sacrifice) at high dose; no significant difference in body weight or survival rates	Muller et al. (2009)
MWCNTs without structural defects	11.3 ± 3.9	~0.7	190	0.37% Al, <0.01% Fe, <0.01% Co	Wistar rat (male)	Single injection, 24-month observation	2, 20 mg/rat	No tumors observed at low dose; 3 mesotheliomas (at 10.7, 18.9, and 19.8 months) and 3 lipomas (at terminal sacrifice) at high dose; no significant difference in body weight or survival rates	Muller et al. (2009)
Short MWCNTs	14.84 ± 0.50	1–5	NR	7.9% Fe, 5.1% Cu, 9.7% Ni, 5.5% Zn, 3.7% Co	C57Bl/6 mouse (female)	Single injection, 24-hour, 7-day observations	100 µg/mL	No significant effects	Poland et al. (2008)
Short MWCNTs	10.40 ± 0.32	5–20	NR	(µg/g) 13.4 Fe, 1 Cu, 5 Ni, 7.5 Zn	C57Bl/6 mouse (female)	Single injection, 24-hour, 7-day observations	100 µg/mL	No significant effects	Poland et al. (2008)
Long MWCNTs	165.02 ± 4.68	Maximum 56	NR	(µg/g) 37.3 Fe, 1.2 Cu, 6.2 Ni, 3.4 Co	C57Bl/6 mouse (female)	Single injection, 24-hour, 7-day observations	100 µg/mL	Inflammatory responses; formation of granulomas on peritoneal surface of the diaphragm; foreign body giant cells comparable to long-fiber amosite asbestos	Poland et al. (2008)

Table F-11, cont. Select carcinogenicity studies for MWCNTs.

Test substance	Diameter (nm)	Length (µm)	Surface area (m <sup>2</sup> /g)	Purity	Species	Exposure duration	Doses tested	Effects observed	Citation
MWCNTs	70–110, peak at 90	72.5% within 1–4, peak at 2	NR	(ppm) 3500 Fe, 470 S, 20 Cl, <5 Br, <40 F	p53 (+/-) mouse (male)	Single injection, 25-week observation	3 mg/mL	100% mortality by week 25; mesothelioma incidence 14/16 (87.5%, 11 as cause of death, 3 incidental); moderate to severe fibrous peritoneal adhesion with slight ascites; fibrous peritoneal thickening with black-colored depositions; high incidence of macroscopic peritoneal tumors; peritoneal mesothelial lesions	Takagi et al. (2008)
MWCNTs	10–30	1–2	NR	95–98%	F344 rat	Single exposure; 12-month observation	10 mg/rat	Granulomatous reactions of foreign body type with multinucleated giant cells in liver; abdominal cavities dispersed carbon on the adjacent organs (omentum, peritoneum), resulting in partial expansion of the gastric wall and residual carbon in peritoneal envelope of liver; no signs of mesothelioma	Varga and Szendi (2010)
MWCNTs	>80% of particles 70–110, Gaussian peak at 90	>70% of particles 1–4, peak: 2	NR	3500, 470, and 20 ppm iron, sulfur, and chlorine contaminants	F344 rat (male)	single intrascrotal injection; observed at 52 weeks	1 mg/kg	85.7% mortality by 37-40 weeks; intraperitoneally disseminated hypertrophic mesothelioma (cause of death in 6/7 animals); nodular and papillary lesions of mesothelioma; mesotheliomas invasive to adjacent organs and metastasized into pleura	Sakamoto et al. (2009)

NR = Not reported

## F.2. Ecological Effects

### F.2.1. Effects of DecaBDE and Other PBDEs on Aquatic Receptors

Table F-12. Effects of exposure to PBDEs in aquatic invertebrates.

Life stage	Number/group	Test type / duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Algae<sup>a</sup></b>								
NR	NR	Semi-chronic/ 96 hours	Commercial decaBDE	NR	NR	EC50	>1 mg/L	Marine algae; review article, study-specific details were not provided
NR	NR	Semi-chronic/ 96 hours	Commercial pentaBDE	NR	NR	NOEC	>water solubility	Freshwater algae; review article, study-specific details were not provided
<b>Zebra mussels (<i>Dreissena polymorpha</i>)<sup>b</sup></b>								
Post-spawn	150	Comet assay/ 48, 96, 168 hours; micronucleus (MN) assay/ 48, 96 hours	Technical grade decaBDE, 98% pure	Water	0.1, 2, 10 µg/L	Mortality, hemocyte viability DNA damage, chromosomal aberrations	NOE All tested doses	None Increasing trend over time @ 0.1, 2 µg/L; damage increased until 96hr then decreased at 168 hr @10 µg/L
<b>Freshwater oligochaete (<i>Lumbriculus variegates</i>)<sup>c</sup></b>								
NR	NR	Chronic/28 days	Commercial decaBDE	Sediment	NR	EC50 NOEC	>5000 mg/kg ≥5000 mg/kg	Review article, endpoints not specified Review article, endpoints not specified

Table F-12, cont. Effects of exposure to PBDEs in aquatic invertebrates.

Life stage	Number/group	Test type/duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Freshwater oligochaete (<i>Lumbriculus variegates</i>)<sup>c</sup></b>								
NR	NR	Chronic/28 days	Commercial pentaBDE	Sediment	NR	EC50	>50 mg/kg	Review article, endpoints not specified
Adult	80	Chronic/28 days	55%pentaBDE, 36% tetraBDE, 8.5% hexaBDE	Sediment	0, 3.1, 6.3, 13, 25, 50 mg/kg	EC50, survival, reproduction	>50 mg/kg	Review article, study-specific details were not provided
						LOEC, survival, reproduction	6.3 mg/kg	Review article, study-specific details were not provided
Adult	80	Chronic/28 days	Mixture, 97% decaBDE	Sediment	0, 313, 625, 1250, 2500, 5000 mg/kg	NOEC, survival, reproduction	>5000 mg/kg (mean measured 3841 mg/kg)	Review article, doses listed are minimal measured conc.
<b>Water fleas (<i>Daphnia magna</i>)<sup>d</sup></b>								
24 hours old at test start	40	Acute/96 hours	55%pentaBDE, 34% tetraBDE, 12% hexaBDE	NR	0, 1.4, 2.6, 5.3, 9.8, 20 µg/L	EC50 mortality, immobility	17 µg/L	Review article, study-specific details were not provided
24 hours old at test start	40	Chronic/21 days	55%pentaBDE, 34% tetraBDE, 12% hexaBDE	Water	0, 1.4, 2.6, 5.3, 9.8, 20 µg/L	EC50 mortality, immobility	14 µg/L	Review article, study-specific details were not provided
						EC50 reproduction	14 µg/L	Review article, study-specific details were not provided
						LOEC mortality, immobility	20 µg/L	Review article, study-specific details were not provided
						LOEC growth	9.8 µg/L	Review article, study-specific details were not provided



Table F-12, cont. Effects of exposure to PBDEs in aquatic invertebrates.

Life stage	Number/group	Test type/duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Water fleas (<i>Daphnia magna</i>)<sup>d</sup></b>								
24 hours old at test start	20	Chronic/21 days	42% heptaBDE, 36% octaBDE, 14% nonaBDE, 6% hexaBDE, 2% decaBDE	Water	0, 0.13, 0.25, 0.54, 0.83, 1.7 µg/L	NOEC survival, reproduction, growth EC50, LOEC survival, reproduction, growth	>1.7 µg/L — >2.0 µg/L	Review article, study-specific details were not provided
NR	NR	Chronic/21 days	Commercial octaBDE	NR	NR	EC50, NOEC	>water solubility	Review article, study-specific details were not provided
NR	NR	Acute/48 hours	Commercial pentaBDE	NR	NR	EC50	14 µg/L	Review article, study-specific details were not provided
NR	NR	Chronic/21 days	Commercial pentaBDE	NR	NR	LOEC	9.8 µg/L	Review article, endpoints not specified

<sup>a</sup>Source: Hardy (2002)

<sup>b</sup>Source: Riva et al. (2007)

<sup>c</sup>Source: Rows 1–3: Hardy (2002); rows 4–6: Environment Canada (2006)

<sup>d</sup>Source: Rows 1–7: Environment Canada (2006); rows 8–10: Hardy (2002)

EC50 = Median effective dose; LOEC = Lowest observed effect concentration; NR: Not reported; NOE: No observed effects at tested doses; NOEC = Maximum no observed effect concentration

Table F-13. Effects of exposure to PBDEs in fish and frogs.

Duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Juvenile rainbow trout (<i>Oncorhynchus mykiss</i>)<sup>a</sup></b>						
16 days					NOE	None
49 days	Dow FR-300-BA <sup>b</sup>	Diet	7.5–10 mg/kg/day <sup>c</sup>	Increased liver weight, increased blood lactate concentrations, decreased lymphocyte count	NOE	Saw effects in group after 71 days of depuration (non-exposure). indicating potential delayed chronic effects
120 days					7.5 mg/kg/d	None
96 hours	Commercial pentaBDE	NR	NR	LC50	≥water solubility	Review article, study-specific details were not provided
NR	PentaBDE, tetraBDE mix	Injection	NR	Egg mortality	≥12 µg/egg	Review article, study-specific details were not provided
72 hours	Tetra-, penta-, and octaBDE	Cell culture	0–264 µg/l	Vitellogenin production	10–50 µg/l	In vitro hepatocyte assay; intensity of response increased with increasing number of bromine atoms
<b>Juvenile lake whitefish (<i>Coregonus clupeaformis</i>)<sup>d</sup></b>						
30 days	DecaBDE; 97.5–99.25% pure	Diet	0, 0.1, 1, 2 µg/g	Negative growth effects	2 µg/g	Otolith increment widths narrowed starting day 1

Table F-13, cont. Effects of exposure to PBDEs in fish and frogs.

Duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Juvenile lake trout (<i>Salvelinus namaycush</i>)<sup>e</sup></b>						
56 days	DecaBDE, >96% pure	Diet	0, 2.5, 25 ng/g	Mortality, whole body growth rate	NOE	No effects observed during exposure period and up to 112 days depuration
				Phase I EROD activity in liver microsomes	NOE	Measured on days 14, 56 of uptake and 14, 56 of depuration
				Liver somatic index changes (liver weight ÷ whole fish weight × 100)	NOE	No effects observed during exposure period and up to 112 days depuration
				Decreased free thyroxine (T4) concentrations	2.5, 25 ng/g	Level significantly decreased at both doses (greater decrease at 25 ng/g) at 56 days, no effects at earlier time points; levels remain decreased in high dose but not low dose after 112 days depuration
				Decreased free tri-iodothyronine (T3) concentrations	2.5 ng/g	Level significantly decreased at 2.5 ng/g at 56 days, no effects at earlier time points; no effects at 25 ng/g at any time; author states "no consistent differences related to PBDE exposure level were evident"
<b>Adult Chinese rare minnow (<i>Gobiocypris rarus</i>)<sup>f</sup></b>						
21 days	DecaBDE, ≥99% pure	Water	0.01, 0.1, 1, 10 µg/L	Mortality, malformations	NOE	None
				Decreased body length, gonadosomatic index (GSI) changes	10 µg/L	GSI = Gonad weight ÷ whole fish weight × 100
				Inhibition of spermatogenesis, reduction of spermatocytes	10 µg/L	Males only
				mRNA levels of thyroid hormone related genes	Variable at all doses	Upregulation of <i>nis</i> at all doses; <i>tr-a</i> in all male groups but not female; <i>ttr</i> in all female groups but not male; <i>dio2</i> in females at 0.01 µg/L, females + males at 0.1 µg/L.

Table F-13, cont. Effects of exposure to PBDEs in fish and frogs.

Duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Adult Chinese rare minnow (<i>Gobiocypris rarus</i>)<sup>f</sup></b>						
21 days	DecaBDE, ≥99% pure	Water	0.01, 0.1, 1, 10 µg/L	Liver degeneration, hepatocyte swelling	10 µg/L	Females only
<b>Unspecified/general fish<sup>g</sup></b>						
48 hours	Commercial decaBDE	NR	NR	LC50	>500 mg/L	Review article, study-specific details were not provided
48 hours	Commercial octaBDE	NR	NR	LC50	>500 mg/L	Review article, study-specific details were not provided
48 hours	Commercial pentaBDE	NR	NR	LC50	≥500 mg/L	Review article based value on data for <i>Oryzias latipes</i> , details were not provided
NR	Commercial pentaBDE	Diet	NR	Reproduction (spawning success)	NOE	Review article based value on data for <i>Gasterpsteis aculeatus</i> , details were not provided

Table F-13, cont. Effects of exposure to PBDEs in fish and frogs.

Duration	Test substance	Medium	Doses tested	Effect	Effect dose	Notes
<b>Tadpoles (<i>Xenopus laevis</i>)<sup>h</sup></b>						
				Physical malformation, abnormal behavior, increased mortality	NOE	None
				Delayed time to metamorphosis	1000 ng/L	Statistically significant at 1000 ng/L; concentration-dependent trend of metamorphic delay in all groups
51 days	DE-83R	Water	1, 10, 100, 1000 ng/L	Histological alterations in thyroid glands (epithelial cell height, follicle size, colloid depletion, colloid vacuolation)	All doses	Statistically significant increase in mean epithelial cell height at 100 and 1000 ng/L; multilayer follicular epithelial cells at all doses
				Decrease in TR-β-A mRNA expression (thyroid hormone) in tail tissue	All doses	None

<sup>a</sup>Source: Rows 1–3: Kierkegaard et al. (1999); row 4: Hardy (2002); row 5, Nakari and Pesala (2005); individuals per group not reported

<sup>b</sup>Commercial mixture contains 77.4% decaBDE, 21.8% nonaBDE, 0.8% octaBDE as reported in Hardy (2002)

<sup>c</sup>One dose administered, dose was minimum 7.5 mg/kg/day, maximum 10 mg/kg/day

<sup>d</sup>Source: Kuo et al. (2010); 75 individuals per test group

<sup>e</sup>Source: Tomy et al. (2004); 70 individuals per test group

<sup>f</sup>Source: Li et al. (2011); individuals per group not reported

<sup>g</sup>Source: Hardy (2002) (Review article)

<sup>h</sup>Source: Qin et al. (2010); free swimming larvae 5 days post-fertilization (stage 46/47) through forelimbs emergence (FLE, stage 57/58); n = 70 in rows 1–2; n = 10–12 in row 3, n = 8 in row 4

EROD = Ethoxyresorunfin-*O*-deethylase enzyme; LC50 = Median lethal concentration; LOEC = Lowest observed effect concentration; NOE: No observed effects at tested doses; NOEC = Maximum no observed effect concentration tested; NR: Not reported

## F.2.2. Effects of MWCNTs on Aquatic Receptors

Table F-14. Effects of exposure to MWCNTs in algae, macrophytes, and aquatic macroinvertebrates.

Organism	Test substance	Dimensions	Test duration	Medium	Doses tested	Effect	Effect dose	Notes
Unicellular green algae ( <i>Dunaliella tertiolecta</i> ) <sup>a</sup>	Carboxylated MWCNT	OD: 20–30 nm L: 50 µm	96 hours	Water	0.1, 0.5, 1, 2.5, 5, 10 mg/L	Inhibited growth	LOEL 1 mg/L, NOEL 0.5 mg/L	Growth lagged up to 23 days at 10 mg/L, 36% reduction in exponential growth rate
Aquatic macrophytes ( <i>Chara</i> , <i>Elodea nuttallii</i> , <i>Potamogeton obtusifolius</i> , <i>Glyceria</i> , <i>Alisma plantagoaquatica</i> ) <sup>b</sup>	Pure MWCNT	OD: 20–30 nm ID: 5–10 nm L: 10–30 µm	3 months	Stream bed sediment	0.002, 0.2, 2 g/kg	Changes in macrophyte density	LOEL 0.002 g/kg	Density increased compared to control at all levels; significant at 0.002 and 2 g/kg
Macroinvertebrates (Gastropoda, Crustacea, Oligochaeta, Hirundinea, Bivalvia, Arachnida, Diptera) <sup>b</sup>	Pure MWCNT	OD: 20–30 nm ID: 5–10 nm L: 10–30 µm	3 months	Stream bed sediment	0.002, 0.2, 2 g/kg	Recolonization rates	LOEL 0.002 g/kg	Dose-dependent increase in recolonization (# of taxa and individuals) compared to control
						Biodiversity	NOEL >2 g/kg	No observed effect
Amphipods ( <i>Leptocheirus plumulosus</i> ) <sup>c</sup>	Pure MWCNT	OD: 10–30 nm L: 10–30 µm	10 days	Sediment	4, 10, 33, 99, 300 g/kg	Death	LOEL 99 g/kg, LC50 68 g/kg	Mortality 30 ± 10% at 99 g/kg, 30 ± 0% at 300 g/kg
Amphipods ( <i>Hyalella azteca</i> ) <sup>c</sup>	Pure MWCNT	OD: 10–30 nm L: 10–30 µm	10 days	Sediment	3, 9, 29, 87, 264 g/kg	Death	LOEL 264 g/kg	Mortality 53 ± 25%

<sup>a</sup>Source: Wei et al. (2010); microwave assisted acid oxidation was used to carboxylate pristine nonfunctionalized MWCNT resulting in functionalized MWCNTs with 7.61% carboxylation, 1% residual cobalt by weight, elemental composition 948:51:1 carbon:oxygen:cobalt

<sup>b</sup>Source: Velzeboer et al. (2011); MWCNTs nonfunctionalized, purity 95% wt

<sup>c</sup>Source: Kennedy et al. (2008); authors note that mortality increased as particle size decreased

L = Length; LC50 = Median lethal concentration; ID = Inner diameter; LOEL = Lowest observed effect level; NOEL = Maximum no observed effect level; NR: Not reported; OD= Outer diameter

Table F-15. Effects of exposure to MWCNTs via water on *Ceriodaphnia dubia*.

Individuals per test group	Outer diameter (nm) <sup>c</sup>	Functionalization	Concentrations tested (mg/L)	Effect	Effect dose
<b>Acute (24 hours)<sup>a</sup></b>					
20	10–20	NF	1–200	LC50	17 mg/L
20	30–40	NF	1–200	LC50	8 mg/L
20	50–70	NF	1–200	LC50	20 mg/L
20	10–20	Ozone-treated	1–200	LC50	100 mg/L
20	30–40	Ozone-treated	1–200	LC50	100 mg/L
20	50–70	Ozone-treated	1–200	LC50	100 mg/L
20	10–20	Ultrasound-probe treated	1–200	LC50	8 mg/L
20	30–40	Ultrasound-probe treated	1–200	LC50	7 mg/L
20	50–70	Ultrasound-probe treated	1–200	LC50	2 mg/L
<b>Subchronic (48 hours)<sup>b</sup></b>					
NR	10–30	NF	25.1, 39.5, 59.6	EC50	50.9 mg/L
NR	20–30	MWNT-OH	120.2	mortality increase	No effects
NR	20–30	MWNT-COOH	88.9	mortality increase	No effects
>12	50–70	Ozone-treated	5, 10, 20, 50, 100	Body length decrease <sup>d</sup>	LOEC 5 mg/L; 73% of control at 100 mg/L
>12	50–70	Ultrasound-probe treated	1, 2, 3, 5, 10	Body length decrease <sup>d</sup>	NOEC 1 mg/L; LOEL 2 mg/L; 75% of control at 10 mg/L

Table F-15, cont. Effects of exposure to MWCNTs via water on *Ceriodaphnia dubia*.

Individuals per test group	Outer diameter (nm) <sup>c</sup>	Functionalization	Concentrations tested (mg/L)	Effect	Effect dose
<b>Chronic (8 days)<sup>a</sup></b>					
>8	50–70	Ozone-treated	5 concentrations, 0.5 to >30	EC50 decreased reproduction <sup>e</sup>	17 mg/L
>8	50–70	Ultrasound-probe treated	5 concentrations, 0.5 to >30	EC50 decreased reproduction <sup>e</sup>	4 mg/L

<sup>a</sup>Source: Li and Huang (2011)

<sup>b</sup>Source: Rows 1–3: Kennedy et al. (2008); rows 4–5: Li and Huang (2011)

<sup>c</sup>Other properties not reported in Li and Huang (2011), Kennedy et al. (2008) reported length 10–30 µm and purity 95%

<sup>d</sup>Dose-response growth assay

<sup>e</sup>Three generation reproductive test

EC50 = Median effect concentration; LC50 = Median lethal concentration; LOEC = Lowest observed effect concentration; NF= Not Functionalized; NOE: No observed effects at tested doses; NOEC = Maximum no observed effect concentration tested; NR = Not reported

Table F-16. Effects of exposure to MWCNTs on zebrafish (*Danio rerio*) embryos.

Number per group	Outer diameter (nm)	Test substance	Exposure medium	Doses tested	Effect	Effect dose	Notes
<b>Zebrafish, 72 hours post fertilization<sup>a</sup></b>							
75	30–40	MWCNT	Microinjection at 8-cell stage	2.5, 5, 10, 20, 30, 40, 50, 60, 70, 100, 200, 300 µg/mL	Heart rate decrease	NOEC 10 µg/mL, LOEC 20 µg/mL	Measured at 24, 48, 72 hpf; dose-dependent drop at 48 and 72 hpf
					Reduced blood circulation	NOEC 60 µg/mL, LOEC 70 µg/mL	Observed at 24, 48, and 72 hpf
60	30–40	MWCNT	Water	2.5, 5, 10, 20, 30, 40, 50, 60, 70, 100, 200, 300 µg/mL	Delayed hatching	NOEC 50 µg/mL <sup>c</sup> , LOEC 60 µg/mL	8% at 60 µg/mL, 60% at 100 µg/mL
					Increased mortality	NOEC 50 µg/mL, LOEC 60 µg/mL	10% at 60 µg/mL, 80% at 100 µg/mL, 97% at 200 µg/mL



Table F-16, cont. Effects of exposure to MWCNTs on zebrafish and medaka embryos.

Number per group	Outer diameter (nm)	Test substance	Exposure medium	Doses tested	Effect	Effect dose	Notes
<b>Zebrafish, 96 hours post injection<sup>b</sup></b>							
NR	19.9	BSA-MWCNT	Microinjection at 1-cell stage	2 ng/embryo	Developmental defects	NOE	Through adult stage
					Immune response	2 ng	Observed at 24 hpf
<b>Medaka, 96 hours continual exposure<sup>c</sup></b>							
12	NR	oxidized MWCNT	Water	500, 1000, 1500, 2000 µg/mL	Increased mortality	NOEC 1000 µg/mL, LOEC 1500 µg/mL	MWCNTs were functionalized by acid treatment
<b>Medaka, 10 days following 4 days of continual exposure<sup>c</sup></b>							
12	NR	oxidized MWCNT	Water	500, 1000, 1500, 2000 µg/mL	Increased malformations	NOEC 1000 µg/mL, LOEC 1500 µg/mL	MWCNTs were functionalized by acid treatment
12	NR	oxidized MWCNT	Water	500, 1000, 1500, 2000 µg/mL	Hatching delay	NOEC 1000 µg/mL, LOEC 1500 µg/mL	MWCNTs were functionalized by acid treatment
<b>Zebrafish, 56 days post injection<sup>b</sup></b>							
NR	19.9	BSA-MWCNT	Microinjection at 1-cell stage	2ng/embryo	Reduced survival of 2nd generation	2 ng	Measured at day 14 of 2nd generation lifecycle

<sup>a</sup>Source: Asharani et al. (2008)

<sup>b</sup>Source: Cheng et al. (2009)

<sup>c</sup>Source: Kim et al. (2012)

<sup>d</sup>Authors state NOEC of 40 µg/mL and LOEC of 60 µg/mL but do not provide the effect level at 50 µg/mL.

BSA = bovine serum albumin; hpf = hours post fertilization; LOEC = Lowest observed effect concentration; NOE: No observed effects at tested doses; NOEC = Maximum no observed effect concentration tested; NR: Not reported

Table F-17. Immune responses in rainbow trout (*Oncorhynchus mykiss*) head kidney cells following MWCNT exposure.

Endpoint	Measured as	Pure MWCNT <sup>a</sup>	Anionic MWCNT <sup>a</sup>
Antiviral response	IFN $\alpha$ expression observed after 6 hours incubation	NOE	NOE
Macrophage stimulation	IL-1 $\beta$ expression observed after 24 hours incubation	LOEL 5 $\mu$ g/mL	LOEL 0.1 $\mu$ g/mL (dose-dependent)
Cytotoxicity	Measured after 24 hours incubation	NOE	NOE

<sup>a</sup>Pure MWCNTs: >95% pure; Anionic MWCNTs: functionalized with sulfonate groups, centrifuged and ultrafiltrated to purify. Both had diameter 10–20nm, length 1–2  $\mu$ m

Note: Testing protocol: head kidney cells of adult fish were collect and incubated 5 days prior to experiment; doses tested: 0.1, 0.5, 1, 5, and 10  $\mu$ g/mL MWCNTs diluted in water solution; 8 replicates for antiviral response/ macrophage stimulation, duplicate for cytotoxicity

LOEL = Lowest observed effect level; NOE: No observed effects at tested

Source: Klaper et al. (2010)

### F.2.3. Effects of DecaBDE and Other PBDEs on Terrestrial Receptors

Table F-18. Effects of exposure to decaBDE in soil microbes, terrestrial invertebrates, and plants.

Test duration	Test substance	Doses tested (mg/kg dry weight soil)	Effect	Effect dose (mg/kg)	Notes
<b>Soil microbes<sup>a</sup></b>					
180 days	DecaBDE	1, 10, 100	Altered community structure	All doses	Control shows increase in Shannon-Weaver index at each checkpoint from 15 days to 180 days; index number decreased compared to control (continues to increase over time) at all doses beginning at ~90 days, indicating less diversity over time
			Cytotoxicity	100	Total bacteria count was ~50%; dose-dependent decrease observed at all doses; alpha, beta, gamma-proteobacteria groups were decreased to 74.7–84.7% at 100 mg/kg; decreases not observed at lower doses
180 days	DecaBDE	1, 10, 100	Changes in alkaline phosphatase (APA) enzyme activity	All doses	Increased activity from 60–120 days at 10, 100 mg/kg then decreased activity (inhibition) at 180 days; increased activity through full study at 1 mg/kg
			Changes in urease enzyme activity	All doses	Increased activity through 150 days at 1 mg/kg; activity increased at 10 mg/kg from 15 days to 120 days, and at 100 mg/kg at every checkpoint except 150 days
<b>Nitrifying bacteria<sup>b</sup></b>					
4 weeks	DecaBDE	15.1, 230, 2274	Change in behavior	NOE	Measured by change in nitrate/nitrite content
<b>Red clover (<i>Trifolium pratense</i>)<sup>c</sup></b>					
21 days	DecaBDE	15.1, 230, 2274	Early life growth	NOE	Measured by mean fresh weight of seedlings per soil plot for 15–17 days post seedling emergence

Table F-18, cont. Effects of exposure to decaBDE in soil microbes, terrestrial invertebrates, and plants.

Test duration	Test substance	Doses tested (mg/kg dry weight soil)	Effect	Effect dose (mg/kg)	Notes
<b>Corn (<i>Zea mays</i>)<sup>d</sup></b>					
21 days	55% pentaBDE,	62.5, 125, 250, 500, 1000	Germination	NOE	None
	36% tetraBDE,		LOEL reduced shoot height	250	None
	8.6% hexaBDE		LOEL reduced shoot height	62.5	None
<b>Soil invertebrate (<i>Enchytraeus crypticus</i>)<sup>e</sup></b>					
21 days	DecaBDE	15.1, 230, 2274	Reproductive effects	NOE	Measured as number of juveniles per soil plot
<b>Earthworms (<i>Eisenia fetida</i>)<sup>f</sup></b>					
7 days	DecaBDE	0.01, 0.1, 1, 5, 10, 50, 100	Hydroxyl free radical generation	All doses	Dose-dependent increase starting at lowest dose, reached level 2× control at highest dose
56 days	DecaBDE, 98% pure	320, 668, 1240, 2480, 4910	Reproductive effects	NOE	Also observed at 28 days (no effects seen)
56 days	Commercial octaBDE	84.9, 166, 361, 698, 1470	Mortality	NOE	None
			Reproductive effects	NOE	None

<sup>a</sup>Source: Liu et al. (2011); 3 replicates per group

<sup>b</sup>Source: Sverdrup et al. (2006); number of replicates per group not reported

<sup>c</sup>Source: Sverdrup et al. (2006); 20 seeds per test group

<sup>d</sup>Source: Environment Canada (2006); 40 seeds per test group

<sup>e</sup>Source: Sverdrup et al. (2006); 40 adult worms per test group

<sup>f</sup>Source: Row 1: Xie et al. (2011), 60 worms per test group; row 2–4: Environment Canada (2006), 80 worms per test group

NOE = No observed effects

## F.2.4. Effects of MWCNTs on Terrestrial Receptors

Table F-19. Effects of exposure to MWCNTs in bacteria.

Test substance	Properties	Test duration	Exposure protocol	Medium	Doses tested	Effect	Effect dose	Notes
<b>General soil microorganisms<sup>a</sup></b>								
MWCNT	OD: 15.1 nm, L: 10–20 µm, SA: 237.1 m <sup>2</sup> /g, V: 0.86 cm <sup>3</sup> /g, P: 96%	11 days	MWCNTs suspended in water, suspension applied to soil	Soil	50, 500, 5000 µg/g	LOEL decreased microbial activity	500 µg/g	Indicated by enzyme presence; nonsignificant tendency to be repressed at 500 µg/g; activity decreased by 34.2–60.5% at 5000 µg/g
		20 days	MWCNTs suspended in water, suspension applied to soil	Soil	50, 500, 5000 µg/g	LOEL decreased biomass	5000 µg/g	C decreased by 36.9–43.4%, N decreased n by 27.8–30.4%
<b>Gram negative <i>Escherichia coli</i><sup>b</sup></b>								
MWCNT	OD: 44.0 nm, L: 1.5 µm, SA: 42 m <sup>2</sup> /g, 0.08 %wt Fe	24 hours	Exposure to aqueous suspensions of MWCNT at room temp, gentle stirring; strain: MG1655	Water	10, 100 mg/mL	LOEL cytotoxicity	100 mg/mL	~ 50% loss in viability
MWCNT-Fe	OD: 44.0 nm, L: 1.5 µm, SA: 42 m <sup>2</sup> /g, 4.24 %wt Fe	24 hours	Exposure to aqueous suspensions of MWCNT at room temp, gentle stirring; strain: MG1655	Water	10, 100 mg/mL	LOEL cytotoxicity	100 mg/mL	~ 60% loss in viability
MWCNT	OD: 17.4 ± 6.1 nm, L: 77 ± 31 µm	1 hour	Incubation exposure to MWCNT-coated filter in 0.9% NaCl solution	Filter in culture	CNQ	cytotoxicity	Effect seen	~32% inactivated cells

Table F-19, cont. Effects of exposure to MWCNTs in bacteria.

Test substance	Properties	Test duration	Exposure protocol	Medium	Doses tested	Effect	Effect dose	Notes
<b>Gram negative <i>Escherichia coli</i><sup>b</sup></b>								
MWCNT	OD: 30 nm, L: 70 µm, 0.62 %wt metal catalysts	1 hour	5×10 <sup>7</sup> cells/mL incubated with MWCNTs in saline for 1 hour at 37 °C; strain: K12	Cell culture	5 µg/mL	Cytotoxicity	5 µg/mL	~3× reduction in viability compared to controls
			Incubation exposure to MWCNT-coated filter in 0.9% NaCl solution; strain: K12	Filter in culture	CNQ	Cytotoxicity	Effect seen	~3.8× reduction in viability compared to controls
						Reduced metabolic activity	Effect seen	30% metabolic activity compared to 74% in control
<b>Metallic-pollutant resistant <i>Cupriavidus metallidurans</i> CH34<sup>c</sup></b>								
MWCNT	OD: 44.0 nm, L: 1.5 µm, SA: 42 m <sup>2</sup> /g, 0.08 %wt Fe	24 hours	Exposure to aqueous suspensions of MWCNT at room temp, gentle stirring	Water	10, 100 mg/mL	NOEL cytotoxicity	NOE	NOE
MWCNT-Fe	OD: 44.0 nm, L: 1.5 µm, SA: 42 m <sup>2</sup> /g, 4.24 %wt Fe	24 hours	Exposure to aqueous suspensions of MWCNT at room temp, gentle stirring	Water	10, 100 mg/mL	NOEL cytotoxicity	NOE	NOE
<b>Gram negative <i>Pseudomonas aeruginosa</i><sup>d</sup></b>								
MWCNT	OD: 17.4 ± 6.1 nm, L: 77 ± 31 µm	1 hour	Incubation exposure to MWCNT-coated filter in 0.9% NaCl solution	Filter in culture	CNQ	Cytotoxicity	Effect seen	~25% inactivated cells

Table F-19, cont. Effects of exposure to MWCNTs in bacteria.

Test substance	Properties	Test duration	Exposure protocol	Medium	Doses tested	Effect	Effect dose	Notes
<b>Gram positive <i>Staphylococcus epidermidis</i><sup>d</sup></b>								
MWCNT	OD: 17.4 ± 6.1 nm, L: 77 ± 31 µm	1 hour	Incubation exposure to MWCNT-coated filter in 0.9% NaCl solution	Filter in culture	CNQ	Cytotoxicity	Effect seen	~50% inactivated cells
<b>Gram positive <i>Bacillus subtilis</i><sup>e</sup></b>								
MWCNT	OD: 17.4 ± 6.1 nm, L: 77 ± 31 µm	1 hour	Incubation in 0.9% NaCl solution	Filter in culture	CNQ	Cytotoxicity	NOE	None
OH-MWCNT	OD: 15–30 nm, L: 1–5 µm	1 hour	Cells suspended in 1 mL of solution	Water, culture	100 µg/mL	Delayed growth	CNQ	NOE in solutions of DI water, PBS, BHI, or 0.9% NaCl
COOH-MWCNT	OD: 15–30 nm, L: 1–5 µm	1 hour	Cells suspended in 1 mL of solution	Water, culture	100 µg/mL	Delayed growth	NOE	NOE in solutions of DI water, PBS, BHI, or 0.9% NaCl
NH <sub>2</sub> -MWCNT	OD: 15–30 nm, L: 1–5 µm	1 hour	Cells suspended in 1 mL of solution	Water, culture	100 µg/mL	Delayed growth	NOE	NOE in solutions of DI water, PBS, BHI, or 0.9% NaCl

Table F-19, cont. Effects of exposure to MWCNTs in bacteria.

Test substance	Properties	Test duration	Exposure protocol	Medium	Doses tested	Effect	Effect dose	Notes
<b>Gram negative <i>Salmonella typhimurium</i><sup>f</sup></b>								
OH-MWCNT	OD: 15–30 nm L: 1–5 µm	1 hour	Cells suspended in 1 mL of water	Water	100, 170, 290, 375, 500 µg/mL	Delayed growth	NOE	Nonsignificant reductions in viability at all doses
			Cells suspended in 1 mL of solution	Culture	100, 170, 290, 375, 500 µg/mL	Delayed growth	NOE	NOE up to 500 µg/L in BHI broth, PBS, or 0.9% NaCl
COOH-MWCNT	OD: 15–30 nm L: 1–5 µm	1 hour	Cells suspended in 1 mL of solution	Water, culture	100, 170, 290, 375, 500 µg/mL	Delayed growth	NOE	NOE up to 500 µg/L in DI water, BHI broth, PBS, or 0.9% NaCl
NH <sub>2</sub> -MWCNT	OD: 15–30 nm L: 1–5 µm	1 hour	Cells suspended in 1 mL of solution	water, culture	100, 170, 290, 375, 500 µg/mL	Delayed growth	NOE	NOE up to 500 µg/L in water, BHI broth, PBS, or 0.9% NaCl

<sup>a</sup>Source: Chung et al. (2011)

<sup>b</sup>Source: Rows 1–2 Simon-Deckers et al. (2009), created with aerosol-assisted catalytic chemical vapor deposition using Fe as catalyst, heat purified; row 3, Kang et al. (2009), purified with hydrochloric acid then dispersed in 0.1 µg/mL ethanol sonicated for 10 min in a bath sonicator; rows 4–6: Kang et al. (2008)

<sup>c</sup>Source: Simon-Deckers et al. (2009), details same as footnote b

<sup>d</sup>Source: Kang et al. (2009), details same as footnote b

<sup>e</sup>Source: Row 1: Kang et al. (2009), details same as footnote b; rows 2–4: Arias and Yang (2009), no details provided

<sup>f</sup>Source: Arias and Yang (2009), no details provided; OH-MWCNT: Functionalized with OH groups derived directly from the surface of CNTs

BHI = Brain heart infusion broth; COOH-MWCNT= Carboxylated, acid treated with COOH groups derived from the surface of CNTs by acid treatment; DI = deionized water; NH<sub>2</sub>-MWCNT=Functionalized with NH<sub>2</sub> groups by activation of carboxyl moieties with thionyl chloride and subsequent reaction with CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>CH<sub>2</sub>-NH<sub>2</sub>; CNQ= Could not quantify; L = Length; LOEL = Lowest observed effect level; NOE = No observed effect; NOEL = Maximum no observed effects level; ND = Not determined; OD = Outer diameter; P = Purity; PBS = Phosphate buffers saline; SA = Surface area; V = Volume



Table F-20. Effects of exposure to MWCNTs on plants.

MWCNT properties	Exposure protocol	Plant	Doses tested	Effect dose	Notes
<b>Decreased germination rates<sup>a</sup></b>					
SA: 126 m <sup>2</sup> /g, OD: 10–20 nm, L: 1–2 μm	30 seeds in water, 5 days	Rapeseed	2000 mg/L	NOE	Non-significant decrease
		Radish	2000 mg/L	NOE	Non-significant decrease
		Ryegrass	2000 mg/L	NOE	None
		Corn	2000 mg/L	NOE	Non-significant decrease
		Lettuce	2000 mg/L	NOE	No observed effect
		Cucumber	2000 mg/L	NOE	Non-significant decrease
SA: 73 m <sup>2</sup> /g, OD: 40–60 nm, L: NR	10 seeds in sewage sludge, 3 days	Garden cress	0.01, 0.1, 0.5% wt	LOEL 0.01%	50–70% inhibition (compared to 10% in control)
SA: 357 m <sup>2</sup> /g, OD: <10 nm, L: NR	10 seeds in sewage sludge, 3 days	Garden cress	0.01, 0.1, 0.5% wt	LOEL 0.1%	60% inhibition at 0.1%, 40% inhibition at 0.5% (compared to 10% in control)
SA: NR, OD: 110–170 nm, L: 5–9 μm	60 seeds in water, 4 days	Mustard	10, 20, 40 μg/mL	NOE	None
		Urad bean	10, 20, 40 μg/mL	NOE	None
<b>Changes in root growth<sup>a</sup></b>					
>95% pure, SA: 126 m <sup>2</sup> /g, OD: 10–20 nm, L: 1–2 μm	30 seeds in water, 5 days	Rapeseed	2000 mg/L	NOE	None
		Radish	2000 mg/L	NOE	None
		Ryegrass	2000 mg/L	NOE	Non-significant total root growth decrease; root length increase
		Corn	2000 mg/L	NOE	None
		Lettuce	2000 mg/L	NOE	None
		Cucumber	2000 mg/L	NOE	None

Table F-20, cont. Effects of exposure to MWCNTs on plants.

MWCNT properties	Exposure protocol	Plant	Doses tested	Effect dose	Notes
<b>Changes in root growth<sup>a</sup></b>					
SA: 357 m <sup>2</sup> /g, OD: <10 nm, L: NR	10 seeds in sewage sludge, 3 days	Garden cress	0.01, 0.1, 0.5% wt	LOEL 0.01%	Root length inhibition ~30% greater than control at all doses
SA: 73 m <sup>2</sup> /g, OD: 40–60 nm, L: NR	10 seeds in sewage sludge, 3 days	Garden cress	0.01, 0.1, 0.5% wt	NOE	None
SA: NR, OD: 110–170 nm, L: 5–9 µm	60 seeds in water, 4 days	Mustard	10, 20, 40 µg/mL	LOEL 10 µg/mL	138% increase in root length at 10 µg/mL, 202% increase at 20 µg/mL, 135% increase at 40 µg/mL
		Urad bean	10, 20, 40 µg/mL	NOE	None
<b>Cytotoxicity<sup>b</sup></b>					
SA: 250–300 m <sup>2</sup> /g, OD: 9.5 nm, L: 1.5 µm	T87 cells in suspension, 7 days (in exponential growth phase on day 3)	Thale cress	10 mg/L	LOEL 10 mg/L	Began on day 2; dose-dependent inhibition observed; poor linearity of curves; more severe with fine MWCNT agglomerates than loose MWCNT agglomerates

<sup>a</sup>Source: Rows 1–6: Lin and Xing (2007)- MWCNT purity >95%; rows 7–8: Oleszczuk et al. (2011)- MWCNT purity >95%; rows 9–10: Ghodake et al. (2010)- MWCNT purity 90%

<sup>b</sup>Source: Lin et al. (2009a), MWCNT carbon purity 90%; MWCNT properties reported for loose agglomerates, fine agglomerates had same average diameter but other dimensions not analyzed

L = Length; LOEL = Lowest observed effect level; NOE = No observed effect; NR = Not reported; OD = Outer diameter; SA = Surface area; V = Volume

## Appendix F References

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