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United States
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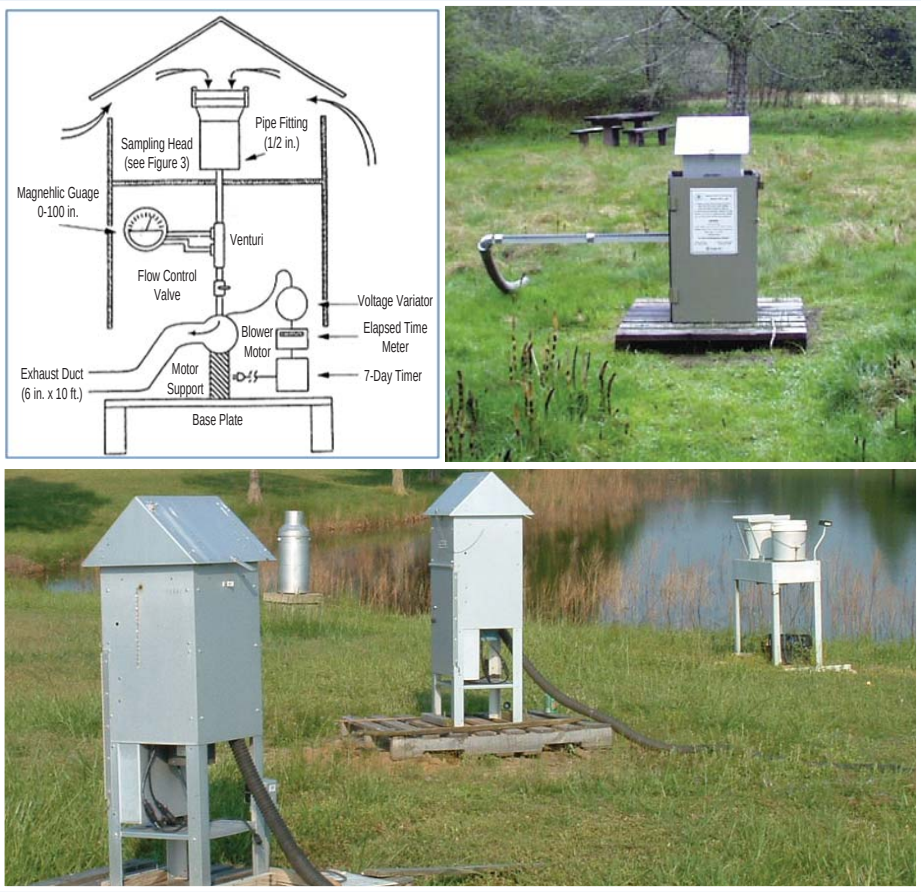
Agency

The National Dioxin Air Monitoring Network (NDAMN)



Report of the Results of Atmospheric Measurements of Polychlorinated Dibenzo-*p*-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), and Dioxin-Like Polychlorinated Biphenyls (PCBs) in Rural and Remote Areas of the United States from June 1998 through November 2004

National Center for Environmental Assessment
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U.S. Environmental Protection Agency
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ABBREVIATIONS AND ACRONYMS

CADAMP	California Ambient Dioxin Air Monitoring Program
CDEP	Connecticut Department of Environmental Protection
DL	detection limit
dl-PCBs	dioxin-like PCBs
EPA	Environmental Protection Agency
GFF	glass fiber filter
HpCDD	heptachlorodibenzo-*p*-dioxin
HpCDF	heptachlorodibenzofuran
HRGC	high-resolution gas chromatography
HRMS	high-resolution mass spectrometry
HxCDD	hexachlorodibenzo-*p*-dioxin
HxCDF	hexachlorodibenzofuran
IMPROVE	Interagency Monitoring of Protected Visual Environments
NA	data not available
NADP	National Atmospheric Deposition Program
ND	not detected
NDAMN	National Dioxin Air Monitoring Network
NTN	National Trends Network
OCDD	octochlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PeCB	pentachlorobiphenyl
PeCDD	pentachlorodibenzo-*p*-dioxin
PeCDF	pentachlorodibenzofuran
PUF	polyurethane foam
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
QFF	quartz fiber filter
RF	response factor
RPD	relative percent difference
RSD	relative standard deviation
S/N	signal-to-noise
TCB	tetrachlorobenzene
TCDD	tetrachlorodibenzo-*p*-dioxin
TCDF	tetrachlorodibenzofuran
TEF	toxicity equivalency factor
TEQ	toxic equivalent
WHO	World Health Organization

PREFACE

To help characterize the ubiquitous presence of dioxins in the environment, the U.S. Environmental Protection Agency (EPA) established the National Dioxin Air Monitoring Network (NDAMN) in 1998. The objective of NDAMN was to determine background air concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) in the United States. NDAMN began operation on June 16, 1998, with 10 NDAMN sampling stations. Stations were added over time and composed of 34 by the beginning of 2003. The last sample of NDAMN was taken in November 2004. The full database is composed of 685 samples, measured for 17 dioxin and furan congeners, 8 dioxin and furan homologue groups, and 12 dioxin-like polychlorinated biphenyl (PCB) congeners. The overall average total toxic equivalent (TEQ) concentration was 11.1 fg/m^3 with dioxin-like PCBs contributing only 0.8 fg/m^3 (7%) of this total. The purpose of this document is to provide information on the overall purpose, design, implementation, analytical chemistry, and results of NDAMN. This document also accompanies an NDAMN database made available now so that others can use the individual sample data for their own purposes.

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EXECUTIVE SUMMARY

To help characterize the ubiquitous presence of dioxins in the environment, the U.S. Environmental Protection Agency (EPA) established the NDAMN in 1998. The objective of NDAMN was to determine background air concentrations of PCDDs, PCDFs, and dioxin-like PCBs (dl-PCBs) in the United States. "Background" is defined as areas where there is no expected influence of nearby known dioxin sources. To meet this objective, sampling focused on rural and remote areas, although a few stations were added that are closer to urban areas.

NDAMN began operation on June 16, 1998, with 10 NDAMN sampling stations. NDAMN was expanded to 23 sampling stations by the last sample event in 1999. It was then expanded to 30 stations at the end of 2000, 32 stations at the end of 2001, 34 stations at the end of 2002, and finally, 35 at the end of 2003 when the last station was added for the first sampling event. Sampling concluded in September 2004. The count of 35 stations includes Quality Assurance/Quality Control (QA/QC) Station 2, which will not be considered as a sampling station; therefore, the full NDAMN data set is considered to be composed of 34 stations. Sampling occurred four times per year, roughly corresponding to the four seasons of the year. Each sampling event was termed a "sampling moment" in which all NDAMN samplers were in operation, and each event consisted of 20 to 24 days of active sampling over a 28-day period, on a weekly schedule of 5 or 6 days of continuous operation followed by 1 or 2 days of inactivity. Sampling was conducted with a Tisch Environmental® TE1000 polyurethane foam (PUF) (PS-1 sampler) in accordance with procedures described in EPA Method TO 9A, as revised in the Quality Assurance Project Plan for NDAMN. The PS-1 sampler is equipped with a quartz fiber filter (QFF) and a PUF adsorbent plug for collecting particulate matter and gaseous compounds, respectively. Each week, the QFF was harvested, and a new QFF was placed in the sampler, yielding four QFFs per sampling moment. This was done to prevent saturation and clogging of the filter media with collected particles. With this procedure, each sampling moment entailed a collection of air mostly in the range of 6,000 to 8,000 m^3 of volume.

The harvested samples (PUFs/QFFs) and their associated field blanks were shipped to EPA's Environmental Chemistry Laboratory in Mississippi for extraction, clean-up, and analysis by high-resolution gas chromatography coupled with high-resolution mass spectrometry in accordance with a modification of EPA Method 1613. Four sample sets were generated for each

sampling event at each NDAMN station: (1) one PUF filter from active sampling, (2) one PUF field blank, (3) one set of four QFFs from active sampling, and (4) one set of four QFF field blanks. Field blanks were used to determine contamination affecting the active samples (which are passively exposed only during setup and collection), so field blanks were only exposed to ambient air during sample setup and collection. Analytes measured include 17 dioxin and furan congeners, 8 dioxin and furan homologue groups, and 12 polychlorinated biphenyls (PCBs) that have dioxin-like toxicity. These PCBs are commonly referred to as dl-PCBs. All samples had seven PCBs, and PCBs 81, 114, 123, 167, and 189 were added in the summer sample of 2002. The analytical detection limits (DLs) ranged from 0.5 pg for tetra congeners to 20 pg for octa congeners, and from 1 pg (PCB 69) to 500 pg (PCB 118) for the individual PCBs. Sample-specific DLs expressed on a concentration basis can be calculated by dividing these masses by the actual volume for each sampling event.

If all 34 sampling stations operated for all moments following their initially collected moment, there would be a total of 736 samples. However, only 685 sampling events were completed. There were 51 sampling events that were not completed and these were characterized as data not available (NA). Causes for NAs include (1) station not operating (26 times), (2) QA failure at the lab, all analytes (eight times), (3) QA failure at the lab, PCDDs/PCDFs only, PCB analysis available but not included in survey results (seven times), (4) sample volume data lost (two times), and (5) low sample volume (less than 2,000 m^3) (eight times). The protocol to obtain four weeks of air volume guaranteed low DLs and a high detection frequency. The frequency of positive measurements was mostly above 95% and at 85% for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The lowest detection frequency was 74% for 1,2,3,7,8,9-hexachlorodibenzofuran (HxCDF). All results in this report have been generated assuming not detected (ND) = 0 (but a quick check on a few averages showed virtually no change when assuming ND = ½ DL).

The overall average TEQ concentration was 11.1 fg/m^3 with dioxin-like PCBs contributing only 0.8 fg/m^3 (7%) of this total (with PCB 126 explaining most of this PCB contribution, ~88%). The top six contributors explained 67% of the TEQ (1,2,3,7,8-PeCDD at 27.8%; 2,3,4,7,8-PeCDF at 11.4%; 1,2,3,4,6,7,8-HpCDD at 9.1%; 1,2,3,6,7,8-hexachloro-dibenzo-*p*-dioxin [HxCDD] at 6.5%; 1,2,3,7,8,9-HxCDD at 6.4%; and PCB 126 at 6.1%). The compound 2,3,7,8-TCDD contributed 5% to the TEQ. All dioxin-like PCBs, excluding PCB

126, contributed about 0.9% of the TEQ. The archetype dioxin and furan background air congener profile was seen in the survey averages and in most individual samples. This archetype profile is characterized by low and similar concentrations for tetra- through hexa dioxins and furan congeners, with elevations in 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF.

Average TEQ concentrations throughout most of the Eastern Seaboard and into the central part of the United States range between 5 and 20 fg/m^3. From the central part of the United States into the western portion, as well as Alaska, excluding California, the average TEQ concentration appears to be near or less than 5 fg/m^3. Two of the stations on the Western Seaboard, one in California and one in Oregon, showed average TEQ concentrations just above 20 fg/m^3. The other four stations on the Western Seaboard showed average TEQ concentrations less than 10 fg/m^3. Station 20, Fond du Lac Indian Reservation in Minnesota, showed the highest average TEQ concentration at 47 fg/m^3, but this was skewed by a single outlier at 847 fg TEQ/m^3. Without this concentration, the average for the station was 6.9 fg TEQ/m^3. Station 28, Rancho Seco (closed nuclear power plant), was also influenced by a single high concentration, although not as much. The station average concentration of 36 fg TEQ/m^3 was reduced to 21 fg TEQ/m^3 by removing the high concentration of 241 fg TEQ/m^3.

Stations were generally categorized as either urban (4 stations), rural (23 stations), or remote (7 stations). These characterizations were for purposes of this study and should not be considered representations of any of these three land-use categorizations, particularly for urban. The average TEQ concentrations over all stations and moments within these categories were (1) urban at 15.9 fg TEQ/m^3, (2) rural at 13.9 fg TEQ/m^3, and (3) remote at 1.2 fg TEQ/m^3. An examination of trends over time suggests that the rural stations, as a group, may show elevations during the fall or winter months as compared to the spring or summer months. Perhaps that could be said as well for urban stations, but the remote stations appear to show little variation over the course of a year. Concentrations of dioxin-like compounds appear to be constant between 1998 and 2004, with no evidence of either a decline or rise in concentrations.

An examination of the four highest measurements reveals some interesting trends. The locations of these high measurements and the TEQ concentrations are (1) Station 20, Fond du Lac Indian Reservation in Cloque, MN, at 847 fg TEQ/m^3; (2) Station 3, Clinton Crops Research Station in Clinton, NC, at 292 fg TEQ/m^3; (3) Station 28, Rancho Seco in Herald, CA, at 241 fg

TEQ/m^3; and (4) Station 29, Hyslop Farm, Oregon Agricultural Experiment Station in Albany, OR, at 132 fg TEQ/m^3. For Stations 3 and 20, the concentrations of all congeners and homologue groups in the anomalous reading are substantially higher (from 10 to over 100 times higher) than the station averages. The only pattern for these two stations is that everything appears elevated. For Stations 28 and 29, a very different picture emerges. The concentrations for only the dioxin congeners and dioxin homologue groups are 10 to more than 100 times higher than the station averages. For the furan congeners, furan homologues, and PCBs, the concentrations are only slightly elevated or less than the station averages. It is also noted that the station averages of dioxins (congeners and homologues) for Stations 28 and 29 are generally higher (by a factor of 2) than averages for Stations 3 and 20. Meanwhile, furan and PCB congener/homologue group averages are about the same for all four stations. These trends suggest a source near Stations 28 and 29 that might occasionally elevate dioxin concentrations leading to potentially very high levels. These sources do not appear to influence the general background of furans and PCBs. This pattern of exaggerated elevation in dioxins with essentially background levels of furans was also found in ball clay, which was discovered to be a contaminant in animal feed in the 1990s. Research on dioxins in ball clay from animal feeds showed TEQ concentrations above 1,500 ppt (for comparison, soil TEQ concentrations are typically 10 ppt or less), explained in full by elevated dioxins while furan concentrations were either absent or at least two orders of magnitude lower than dioxin concentrations. Investigations have not occurred to identify potential sources near Sites 28 and 29; certainly it is possible that combustion of a product high in PCDDs in comparison to PCDFs, such as clays, might explain the findings in these monitors. Thermal processes that preferentially emit dioxins over furans could also be the cause.

1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) represent a class of toxic semi-volatile aromatic compounds commonly referred to as being "dioxin-like." The dioxin-like classification combines these organic compounds into a single chemical class defined as having analogous chemical and physical properties, chlorine substitution patterns, a planar molecular orientation, a common mode of action of toxicity in mammals, and common endpoints or manifestations of toxicity. The compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is the prototype dioxin-like compound and serves as the reference compound to this class.

The PCDDs and PCDFs are aromatic hydrocarbons consisting of a triple-ring structure of two benzene rings interconnected by a third oxygenated ring. There are eight positions whereby a chlorine atom(s) can be attached. Theoretically, 75 PCDD and 135 PCDF congeners are possible, and their physical chemical properties are determined by the number of chlorine atoms and their respective positions on the molecular nucleus. The environmental effects and toxicology of PCDDs/PCDFs are largely mediated and controlled by the presence of chlorine atoms in the 2,3,7,8 positions. There are 7 PCDDs and 10 PCDFs with this substitution pattern.

Polychlorinated biphenyls (PCBs) are aromatic hydrocarbon compounds consisting of two benzene rings of carbon atoms interconnected by carbon to carbon bonds. The generalized molecular formula (chemical class) of PCBs is $C_{12}H_{10-n}Cl_n$, where *n* is the number of chlorine atoms (in a range of 1 to 10) substituting for hydrogen atoms on the biphenyl rings. Although there is the possibility for 209 PCB congeners, this report focuses on the dioxin-like PCBs. The dioxin-like PCBs are nonortho substituted compounds with chlorine atoms on the para and, minimally, two meta positions to the molecule. These are considered as having structural conformity to 2,3,7,8-TCDD. Other dioxin-like congeners include those PCBs having only one chlorine in the ortho position. There are 12 dioxin-like PCBs, and all were measured in this program.

In many situations, PCDDs, PCDFs, and dioxin-like PCBs appear as mixtures in environmental samples. The total toxic equivalent (TEQ) procedure is an accepted convention for converting the total concentration of toxic congeners within the mixture to an equivalent concentration of 2,3,7,8-TCDD (the most toxic member of the class). This procedure involves

assigning individual toxic equivalency factors (TEFs) to the 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin/polychlorinated dibenzofuran (PCDD/PCDF) congeners and dioxin-like PCBs, and then summing the product of each congener concentration multiplied by its respective TEF, as follows:

$$TEQ = \sum_{i-n} \left(congener_i \times TEF_i\right) + \left(congener_j \times TEF_j\right) + ...\left(congener_n \times TEF_n\right)$$

where:

TEQ = total toxic equivalent of the mixture of PCDDs, PCDFs, and dioxin-like PCBs to the reference compound 2,3,7,8-TCDD
TEF = toxic equivalency factors assumed for each PCDD, PCDF, and dioxin-like PCB congener

TEF values are equal to or less than 1.00, with values as low as 0.00001. TEF schemes have been published in 1994 (Van den Berg et al., 1994), 1998 (Van den Berg et al., 1998), and 2006 (Van den Berg et al., 2006). These publications represent World Health Organization (WHO) consensus opinions on the final values of the TEFs, and the schemes have been abbreviated as WHO 1994, 1998, and 2006. In 2010, EPA formally adopted the WHO 2006 TEF scheme (U.S. EPA, 2010). These TEFs for dioxin-like compounds are used in this report and are provided in Table 1-1.

Dioxin-like compounds are extremely persistent in soils and sediments, bind to organic carbon, and readily accumulate in fatty tissues of animals. Although there is evidence that dioxin-like chemicals can be formed in nature, the dominant sources to the environment are inherently anthropogenic. Combustion-related activities such as incineration of human-generated waste materials, secondary and primary metal smelting, the production of steel, backyard trash burning, forest fires, and the combustion of diesel fuel in cars and trucks are all viewed as sources to the atmosphere. Dioxins in organochlorine products such as the wood preservative pentachlorophenol can be emitted to air from use of the product. For dioxin-like PCBs, products still in use such as building caulk which contain PCBs are also thought to be a source of air emissions. The physical mechanism of atmospheric transport and deposition is understood to be the primary pathway for the ubiquitous distribution of PCDDs, PCDFs, and dl-PCBs in terrestrial and aquatic environments. Plants, animals, and ultimately humans

bioaccumulate these deposited dioxin-like compounds. The contamination of ecological and terrestrial food chains arises by atmospheric deposition into photosynthesizing plants and grasses that are eventually consumed by animals.

This paradigm points to the atmosphere as an essential transport media, ultimately causing environmental exposures to PCDDs, PCDFs, and dl-PCBs, albeit through secondary and indirect pathways.

To help characterize the ubiquitous presence of dioxins in the environment, the U.S. Environmental Protection Agency (EPA) established the National Dioxin Air Monitoring Network (NDAMN) in 1998. Preliminary results from this network have been presented at several of the annual International Symposia on Halogenated Persistent Organic Pollutants, commonly referred as the Dioxin Conference (Cleverly et al., 2000, 2002; Riggs et al., 2003; Byrne et al., 2002), and were published in the peer reviewed literature (Cleverly et al., 2007). An overview of final results from this network was presented at the Dioxin 2011 symposium (Lorber et al., 2011). In addition to providing the final NDAMN results, this report identifies trends associated with land-use type and season, discusses key findings from the QA program, and reports on anomalous findings from NDAMN. This report accompanies the electronic version of the data from NDAMN. Chapter 2 reviews the sampling procedures and describes the various NDAMN sampling stations. Chapter 3 describes the laboratory analytical procedures, and Chapter 4 provides an overview of the results from the network. Appendix A provides an overview of the Excel workbook that contains the NDAMN data. Appendix B includes copies of Quality Assurance Project Plans (QAPPs) for NDAMN that are associated with the field implementation and laboratory analysis of samples.

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Table 1-1. The toxic equivalency factors (TEFs) for the dioxin-like compounds using the WHO approach

Dioxin Congener	TEF	Furan Congener	TEF	Dioxin-Like PCB	TEF
2,3,7,8-TCDD	1.0	2,3,7,8-TCDF	0.1	PCB 77	0.0001
1,2,3,7,8-PeCDD	1.0	1,2,3,7,8-PeCDF	0.03	PCB 81	0.0003
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.3	PCB 126	0.1
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1	PCB 169	0.03
1,2,3,7,8,9-HxCDD	0.1	1,2,3,7,8,9-HxCDF	0.1	PCB 105	0.00003
1,2,3,4,6,7,8-HpCDD	0.01	2,3,4,6,7,8-HxCDF	0.1	PCB 114	0.00003
OCDD	0.0003	1,2,3,4,6,7,8-HpCDF	0.01	PCB 118	0.00003
		1,2,3,4,7,8,9-HpCDF	0.01	PCB 123	0.00003
		OCDF	0.0003	PCB 156	0.00003
				PCB 157	0.00003
				PCB 167	0.00003
				PCB 189	0.00003

Notes: TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl.

Source: Van den Berg et al. (2006).

2. AMBIENT AIR SAMPLING

2.1. SAMPLING OBJECTIVE

The objective of NDAMN was to determine background air concentrations of PCDDs, PCDFs, and dl-PCBs in rural and remote areas of the United States. "Background" is defined as areas where there are no expected influences of nearby known dioxin sources. To meet this objective, sampling focused on rural and remote areas, although a few stations closer to urban areas were added. The rural NDAMN stations were chosen in order to obtain air concentrations in areas where crops and livestock are grown. Remote stations were selected on the basis that they were relatively free of human habitation and greater than 100 km from likely dioxin sources (i.e., urban, suburban, industrial settings, etc.). The locations of sampling stations covered a wide range of climate conditions from tropical subhumid to subarctic. The idea behind the sampling configuration was to provide reasonable geographic coverage of "background areas" of the United States, limited only by budgetary constraints.

2.2. SAMPLING DESIGN

The locations of sampling stations did not entail a purely random sampling approach. In order to reduce the costs associated with maintaining air monitoring stations and to ensure access and security at the stations, most NDAMN stations were co-located on pre-existing nationally based air monitoring networks. These networks included the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), and the Interagency Monitoring of Protected Visual Environments (IMPROVE). These networks were designed to determine the spatial and temporal measurements of pollutants on a national scale, and to establish time trends of environmental impacts. The stochastic basis of the design, and other information of the NADP/NTN and IMPROVE, can be obtained online at http://nadp.sws.uiuc.edu/ and http://vista.cira.colostate.edu/improve, respectively.

Funding was sufficient for the establishment and maintenance of 35 NDAMN stations for a period of 6 years. Of the 35 stations, 22 were established at or near existing stations in the NADP/NTN; one (Station 34) was located at an IMPROVE site. Station 2 was designated as the QA co-located station. Its purpose was to provide a quality check for the nearby NDAMN station. For several of the initial moments, Station 2 was set up adjacent to Station 1 at Penn

Nursery, PA, and later, it was moved to be adjacent to Station 3 at Clinton Crops, NC. The geographic locations of the NDAMN monitoring stations are illustrated in Figure 2-1. Table 2-1 gives the names, cities, latitude/longitude coordinates, elevation measurements, and classifications (i.e., remote, rural, or urban) of the NDAMN stations. Table 2-2 lists the sampling moments, dates and years of sampling, and the season during the sampling moment.

2.3. AIR SAMPLING PROCEDURES

Long-term sampling for dioxin in air was pioneered by the Connecticut Department of Environmental Protection (CDEP) with their program in the 1990s (Hunt, 2008; Hunt and Lihzis, 2011). They began sampling for dioxin in air in 1987 using a more traditional 48-hour sampling strategy, but then switched to a 30-day sampling approach in 1993. They reported on the details of their method's performance at Dioxin '97, the annual international conference on dioxin and related compounds (Maisel and Hunt, 1997), and presented an overall evaluation of the method using data from measurements made in Connecticut in the 2000s (Hunt and Lihzis, 2011). EPA adopted their method for NDAMN and amended it with a strategy of 5 or 6 days of continuous sampling, followed by 1 or 2 days of down time while the quartz fiber filter (QFF) was harvested and replaced (see details below). California then adopted this 5 days on, 2 days off, approach to their 30-day monitoring of dioxins in their California Ambient Dioxin Air Monitoring Program (CADAMP; http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm). This section provides an overview of the sampling method. Further details on field implementation can be found in Appendix B.

2.3.1. Description of the Tisch Environmental® TE1000 PUF (PS-1 sampler)

Ambient air sampling was conducted with a Tisch Environmental® TE1000 PUF (PS-1 sampler) ambient air sampler in accordance with procedures described in EPA Method TO 9A (U.S. EPA, 1999), as revised in the QAPP for NDAMN (see Appendix B). The PS-1 sampler is equipped with a QFF and a polyurethane foam (PUF) adsorbent plug for collecting contaminants bound to total suspended particulates and contaminants in the gaseous phase, respectively. Initially, glass fiber filters (GFFs) were used to collect the particulate phase. After the November 1998 sampling moment was completed, QFFs were used instead of GFFs because of

their durability and low background dioxin levels. The use of QFFs is consistent with EPA Method TO 9A. Figure 2-2 is an illustration of the components of the PS-1 sampler.

The PS-1 sampler consists of a sampling head, a meter equipped with a magnehelic gauge to measure air flow, and a blower-type vacuum pump. Sample air flow of 240 liters per minute is controlled by adjusting the speed of the vacuum blower using a voltage variator. The sampler is turned on and off using a seven-day timer, and the number of hours that the sampler operates is recorded with an elapsed time meter. The sampling head assembly consisted of a 10.16 cm (internal diameter) QFF and a 5.85 cm (internal diameter) by 12.7 cm (length) glass sample cartridge containing a 5.08 cm (length) PUF absorbent plug.

A regulated air flow was drawn through the top of the sampling head assembly with a vacuum pump, and the particle-bound phase of the contaminants in the air stream was collected on the filter surface (porosity down to 0.1 μm), while the vapor phase was absorbed into the PUF. Approximately 6,000 to 8,000 m^3 of air passed through the sampling head assembly during a single sampling moment. Thirty-two percent of the final study samples were outside this range, but only 7% were lower than 5,000 or more than 9,000 m^3, with a low of 2,655 m^3 and a high of 13,035 m^3. The average volume of air was 6,827 m^3, with a standard deviation of 1,074 m^3. The purpose of sampling such a large volume of air was to achieve a target detection limit (DL) of 0.1 fg/m^3 for 2,3,7,8-TCDD. Each sampling event consisted of 20 to 24 days of active sampling over a 28-day period, on a weekly schedule of 5 or 6 days of continuous operation followed by 1 or 2 days of inactivity. The protocol required that sampling start on a Wednesday night at midnight, and run approximately 120 hours until midnight of the following Monday. Then on Tuesday, the QFF was harvested, packaged, and refrigerated until shipment to the laboratory, and then a new QFF was placed in the sampler. This cycle was to run four times for each 28-day sampling event, yielding four QFFs. Records were not available to confirm that all samples were obtained according to this schedule. The practice of harvesting QFFs was done to prevent saturation and clogging of the filter media with collected particles. Another benefit of changing the QFFs was the potential to reduce volatile loss of particle-bound dioxin. The PUF was collected once at the end of the sampling moment. Prior to sampling, the PUFs were commercially precleaned by heating at 100°C for 16 hours, and then analytically determined to be free of dioxin contamination. The QFFs were also precleaned to ensure they were free of dioxin contamination. Two compounds, ^{13}C-labeled 1,2,3,4- tetrachlorodibenzofuran (TCDF)

and PCB 81, were added to the PUF as a QA procedure. Both compounds were selected to represent the most volatile members of the class of analytes and were intended to gauge the possibility of any loss of sample during the sampling period.

Prior to the start of a sampling moment, the onsite field technician performed a multipoint calibration. In addition to initial and final multipoint calibrations, a single-point flow check was conducted each week during sampling to ensure the accuracy of flow rates for each sampling station. New motor brushes or a new motor in the PS-1 samplers were required at the onset of each sampling moment in order to assure the sampler would not fail in the field.

2.3.2. Preparation of PUF Sampling Cartridge

The QFF and PUF sampling media were precleaned prior to set-up in the PS-1 sampler to ensure that these components were free from contamination of PCDDs, PCDFs, and dl-PCBs. All QFFs were placed in an oven and baked at 400°C for 5 hours before use. This volatilized and destroyed any dioxin-like compounds that might have contaminated the filter medium. PUFs were purchased and certified precleaned from a supplier. The cleanup of new PUFs involves Soxhlet extraction with acetone for 16 hours at approximately four cycles per hour. When PUF cartridges are reused, diethyl ether/hexane (5 to 10% volume/volume) is typically used as the cleanup solvent. As a final step to assure the sample media were free of contamination, at least 10% of the batch of PUFs and QFFs that were deployed into the field for the sample moment were tested in the laboratory and certified to be dioxin-free. These steps were in conformance with the procedures set forth in EPA Method TO 9A (U.S. EPA, 1999).

2.3.3. Multipoint Calibration of the PS-1 sampler

The PS-1 sampler was calibrated prior to the start of the sampling moment using a calibration kit consisting of a calibration orifice and a water manometer. A post-sampling calibration was also conducted at the completion of the sampling moment. The sampling head contains an empty glass cartridge during the calibration process. If an empty glass cartridge is not available, then a glass cartridge containing the sample PUF for calibration is used. The NDAMN field operator calibrated the PS-1 sampler using the following procedures as stipulated in EPA Method TO 9A (U.S. EPA, 1999):

- Recorded ambient temperature and barometric pressure during calibration.
- Placed an empty glass cartridge in the sampling head. Installed the sampling head onto the sampler vacuum blower inlet.
- Installed the calibration orifice on the sampling head.
- Installed a manometer from the calibration kit on the front of the air sampler housing. Opened the shutoff valves on the top of the manometer.
- Adjusted the manometer so the "0" inch mark was on the scale.
- Connected the tubing from one of the manometer inlet ports to the side port on the calibration orifice.
- Adjusted the sampler airflow using the voltage variator until the sampler magnehelic gauge indicated a reading of 70 inches.
- Allowed the system to run for approximately 1 minute at this speed. Recorded the difference in the inches of water from the manometer on the NDAMN field calibration data form. This was achieved by reading the liquid level on each of the two sides of the manometer and documenting them on the NDAMN field calibration data forms.
- Readjusted the voltage variator counter-clockwise until the sampler magnehelic indicated a reading of 60 inches and then repeated the previous step documenting the manometer readings on the NDAMN field calibration data forms. This step was then repeated for magnehelic readings of 50, 40, 30, and 20 inches. The PS-1 sampler was turned off at the completion of the calibration.
- Using the recorded atmospheric temperature and pressure, the operator calculated the sampler set point using the provided electronic spreadsheet. The spreadsheet calculated the calibration slope, intercept, and correlation coefficient. All calculations were recorded at the bottom of the NDAMN field calibration data form. It was required that the resulting correlation coefficient, R, of this calibration was greater than or equal to 0.98. If R was less than 0.98 (R^2 less than 0.96), the calibration procedure was repeated. The resulting magnehelic set point corresponded to an airflow of 0.24 m^3/minute. This magnehelic set point was the setting at which the PS-1 sampler was operated.

2.3.4. Sample Collection

There were four sample "moments" per year corresponding to the four seasons of the year. Sampling occurred during a 4-week period during one of the seasons, and all NDAMN stations were operated at the same time. For example, the "fall" sample of 1998 occurred between November 24 and December 22, 1998, and all operating NDAMN monitors were sampling during this time. The PS-1 sampler motor automatically switched off at the completion of the timed sampling moment. At the end of each 4-week sampling moment, the onsite operator recorded the flow and elapsed time, collected the QFF and PUF from the PS-1 sampler, and

performed a multipoint calibration. The sampling head was disassembled, and the glass sample cartridge was removed, wrapped with aluminum foil, and placed into a sample jar. The caps on the PUF and filter sample jars were then replaced. All four QFF samples were wrapped in foil and labeled as "sample" or "field blank." Bubble wrap or a similar material was used to protect the jars from breakage during shipment. Samples were packed in a shipping container and kept at 4°C. Samples were shipped to the EPA Environmental Chemistry Laboratory in Mississippi for chemical analysis.

2.3.5. Field Quality Assurance (QA)/Quality Control (QC) Procedures

Four sample sets were generated for each sampling moment for each NDAMN station: (1) one PUF filter from active sampling; (2) one PUF field blank; (3) one set of four QFFs from active sampling; and (4) one set of four QFF field blanks for a total of 10 samples. Field blanks were used to determine contamination affecting the active samples (which are passively exposed only during setup and collection), so field blanks were only exposed to ambient air during sample setup and collection. The PUF field blank remained inside the sampler housing and, thus, underwent the same environmental conditions (e.g., temperature, pressure, etc.) as the field samples. The PUF field blank occupied available space, inside the sampler, in a closed jar, and was exposed to the environment only while the onsite operators were performing sampling activities. Based on the minimum background contamination detected in most field blanks, EPA decided that beginning with Moment 9 (November/December 1999), all field blanks did not need to be analyzed. Therefore, approximately only half of the field blanks collected after that date were analyzed.

Initially, trip blanks were also part of the protocol, but these were eliminated as a QC check because analysis of trip blanks collected in Moment 1 (June/July 1998) demonstrated very low contamination and because trip blanks are not required by EPA Method TO 9A.

At the start of the NDAMN program, two sampling stations were located at Penn Nursery, PA: Station 1 was the formal NDAMN sampler, and Station 2 was the duplicate sampler that was maintained for QA/QC purposes. The NDAMN sampler and the PS-1 duplicate sampler were located approximately 10 feet apart. This duplicate sampler operated at Penn Nursery until the spring 2002 sampling moment, after which time it was moved to the Clinton Crops, NC location. The presumption for a co-located sampler is that the results from it

should be similar to the results of the study sampler since they measure essentially the same mass of air. If the results are not the same, there may be more than one reason: the sampler possibly drew in different/contaminated air, somehow the sampler was contaminated (either the program or the co-located sampler), or the sampling matrices were contaminated (again either the program or the co-located sample matrices).

2.4. REFERENCES

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Table 2-1. Description of the NDAMN air monitoring stations

Station No.	Complete Station Name[a]	Nearest City	Latitude[b] (d/m/s)	Longitude[b] (d/m/s)	Elevation (m)	Classification
1	State of Pennsylvania Dept. of Conservation Tree Nursery (Penn Nursery)	Potters Mill, PA	40 46 30	77 37 17	466	Rural
2	State of Pennsylvania Dept. of Conservation Tree Nursery (Penn Nursery) (duplicate QA/QC sampler)[c]	Potters Mill, PA	40 46 30	77 37 17	466	Rural
3	Clinton Crops Research Station (NC35)	Clinton, NC	35 01 33	78 16 39	40	Rural
2	Clinton Crops Research Station (NC35) (duplicate QA/QC sampler)[c]	Clinton, NC	35 01 33	78 16 39	40	Rural
4	Everglades National Park (FL11)	Florida City, FL	25 23 24	80 40 48	2	Rural
5	Lake Dubay State Park) (WI28)	Dancy, WI	44 39 52	89 39 08	350	Rural
6	NW Illinois Agricultural Center (IL78)	Monmouth, IL	40 56 02	90 43 23	230	Rural
7	McNay Agricultural Research Farm, Chariton, IA (IA23)	Chariton, IA	40 57 47	93 23 30	320	Rural
8	Lake Scott State Park, KS (KS32)	Scott City, KS	38 40 19	100 55 05	863	Rural
9	Bixby Drinking Water Treatment Plant[d]	Bixby, OK	36 08 19	96 15 48	260	Rural
9	Lake Keystone State Park[d]	Sand Springs, OK	36 08 27	96 16 28	300	Rural
10	Caddo Valley, Arkadelphia (AR03)	Arkadelphia, AR	34 10 46	93 05 55	71	Rural
11	Bennington County Farm (VT01)	Bennington, VT	42 52 34	73 09 48	305	Rural
12	Jasper Farm (NY65)	Jasper, NY	42 06 23	77 32 09	634	Rural
13	USDA Agricultural Research Center	Beltsville, MD	39 01 00	76 56 45	46	Urban
14	Caldwell Farm (OH49)	Caldwell, OH	39 47 34	81 31 52	276	Rural
15	Oxford Farm (OH09)	Oxford, OH	39 31 53	84 43 27	284	Rural
16	Dixon Springs Agricultural Center (IL63)	Dixon Springs, IL	37 26 08	88 40 19	161	Rural
17	North Florida Research & Educational Center (FL14)	Quincy, FL	30 32 53	84 36 03	60	Rural
18	NASA Stennis Space Center	Bay St. Louis, MS	30 22 06	89 37 01	8	Rural

Table 2-1. Description of the NDAMN air monitoring stations (continued)

Station No.	Complete Station Name	Nearest City	Latitude[b] (d/m/s)	Longitude[b] (d/m/s)	Elevation (m)	Classification
19	Padre Island National Seashore	Corpus Christi, TX	27 25 37	97 17 55	8	Rural
20	Fond du Lac Indian Reservation (MN05)	Cloque, MN	46 42 47	92 30 39	390	Rural
21	North Platte Agricultural Research Center	North Platte, NE	41 03 33	100 44 47	919	Rural
22	Goodwell Agricultural Research Station (OK29)	Goodwell, OK	36 35 27	101 37 03	999	Rural
23	Big Bend National Park (TX04)	Alpine, TX	29 18 08	103 10 38	1,056	Remote
24	Grand Canyon National Park (AZ03)	Tuba City, AZ	36 03 35	112 11 01	2,152	Remote
25	Theodore Roosevelt National Park	Medora, ND	46 53 41	103 22 40	841	Remote
26	Craters of the Moon National Park (ID03)	Hailey, ID	43 27 41	113 33 17	1,807	Remote
27	Chiricahua National Monument (AZ98)	Willcox, AZ	32 00 35	109 23 20	1,570	Remote
28	Rancho Seco (closed nuclear power plant)	Herald, CA	38 20 36	121 06 27	64	Urban
29	Hyslop Farm, OR Agricultural Experiment Station[e] (OR97)	Albany, OR	44 38 05	123 11 24	69	Rural
29	Marval Ranch (cattle ranch)[e]	Corvallis, OR	44 37 11	123 33 36	190	Rural
30	Lake Ozette , Olympia National Park	Ozette, WA	48 05 45	124 37 48	69	Remote
31	Fort Cronkhite National Monument	San Francisco, CA	37 50 03	122 31 54	30	Urban
32	EPA Ecological Research Laboratory, Newport, OR	Newport, OR	44 37 18	124 02 35	30	Urban
33	Craig	Craig, AK	55 27 07	133 05 17	5	Rural
34	Denali National Park (IMPROVE)	Trapper Creek, AK	62 18 57	150 18 42	646	Remote
35	Yaquina Head State Park	Newport, OR	44 40 30	124 03 56	39	Rural

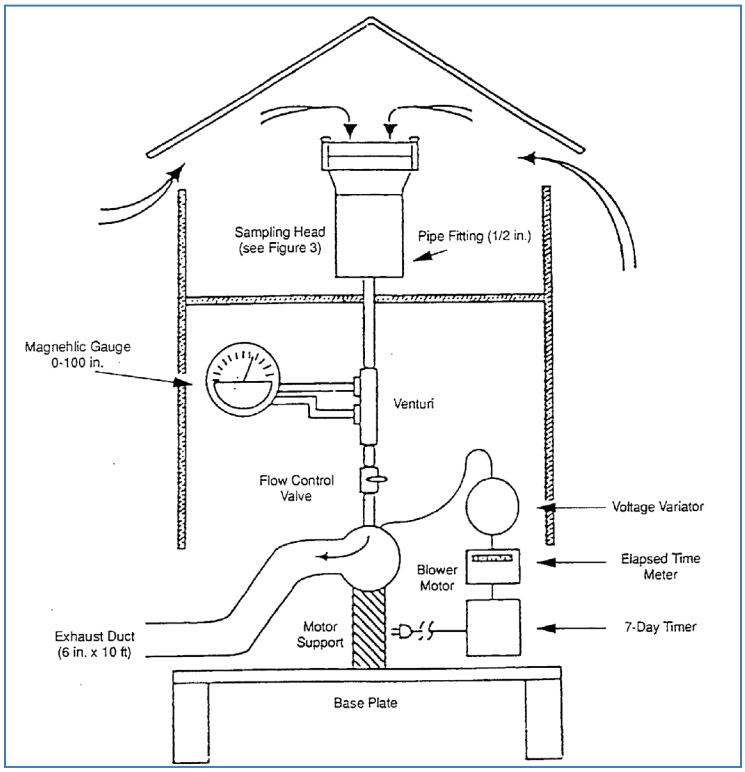
Table 2-1. Description of the NDAMN air monitoring stations (continued)

[a] Stations that are co-located at NADP/NTN monitoring sites have the NADP/NTN identification noted in parentheses.
[b]Latitude and longitude are reported as degrees, minutes, and seconds.
[c]Sampling Station 2 was designated as a QA station where a duplicate sampler was located . The duplicate sampler was run at Penn Nursery, PA, for sampling Moments 1−19. The duplicate sampler was then moved to the Clinton Crops, NC, location. The duplicate sampler operated at Clinton Crops, NC, for sampling Moments 20−29.
[d]Sampling Station 9at the Bixby Drinking Water Treatment Plant, Bixby, OK, was shut down after sampling Moment 17 due to technical difficulties. The sampling station was then set up and operated at Lake Keystone State Park, Sand Springs, OK, for sampling Moments 18−29. Taken together, Station 9 operated a total of 29 sampling moments.
[e]Sampling Station 29 at Hyslop Farm (dairy farm), Albany, OR, was shut down after sampling Moment 25 due to technical difficulties. The sampling station was then set up and operated at Marval Ranch, Benton County, OR, for sampling Moments 26−29. Taken together, Station 29 operated a total of 20 sampling moments.

Table 2-2. Dates and seasons of the 29 sampling moments of NDAMN

Sampling Moment	Dates	Year	Season	Sampling Moment	Dates	Year	Season
1	06/16−07/14	1998	Summer	16	08/02−08/27	2001	Summer
2	08/18−09/15	1998	Summer	17	11/01−11/26	2001	Fall
3	11/24−12/22	1998	Fall	18	02/07−03/04	2002	Winter
4	01/26−02/23	1999	Winter	19	05/02−05/27	2002	Spring
5	03/23−04/20	1999	Spring	20	08/01−08/26	2002	Summer
6	05/18−06/15	1999	Spring	21	10/31−11/25	2002	Fall
7	07/13−08/10	1999	Summer	22	02/13−03/10	2003	Winter
8	08/24−09/21	1999	Summer	23	05/01−05/26	2003	Spring
9	11/09−12/07	1999	Fall	24	07/31−08/25	2003	Summer
10	01/18−02/15	2000	Winter	25	11/06−12/01	2003	Fall
11	04/04−05/02	2000	Spring	26	02/26−03/16	2004	Winter
12	08/22−09/19	2000	Summer	27	05/25−06/21	2004	Spring
13	11/22−12/19	2000	Fall	28	08/04−08/31	2004	Summer
14	01/31−02/26	2001	Winter	29	11/02−11/30	2004	Fall
15	05/03−05/28	2001	Spring				

Figure 2-1. Geographic locations of the NDAMN monitoring stations.



Source: U.S. EPA (1999).

Figure 2-2. Illustration of the components of the Tisch Environmental® TE-1000 PUF (PS-1 sampler).

3. ANALYSIS OF NDAMN SAMPLES

This chapter briefly describes the analytical procedures used to analyze the NDAMN samples retrieved from each sampling moment. Further details are provided in the laboratory QAPP for this sampling program (U.S. EPA, 1999).

3.1. OVERVIEW OF THE ANALYTICAL EPA METHOD

The harvested samples (PUF/QFFs) and their associated field blanks were shipped to EPA's Environmental Chemistry Laboratory for extraction, clean-up, and analysis by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) in accordance with a modification of EPA Method 1613 (U.S. EPA, 1994). The analytes measured in the study are shown in Table 3-1. They include 17 dioxin and furan congeners, 12 PCBs, and 8 dioxin and furan homologue groups. All samples had measurements of seven PCBs; it is noted that five dioxin-like PCBs were added in the summer of 2002: PCBs 81, 114, 123, 167, and 189.

The combined PUF and QFFs of the samples and field blanks were extracted with benzene or toluene using a Soxhlet apparatus. Prior to the initiation of the extraction period, the PUF was spiked with 100–400 pg of $^{13}C_{12}$-labeled analogs, one dioxin and one PCB analog, to monitor losses during the sampling period. The extract was collected and stirred with acidified silica gel, followed by acid/base silica gel clean-up and alumina and carbon chromatography. The final extract was concentrated to approximately 10:l and fortified with $^{13}C_{12}$ internal standards of all analytes prior to HRGC/HRMS analysis. The chromatographic separation was achieved on a DB-5MS capillary column, and the mass spectrometer was operated in the lock mass drift correction mode at a resolution of 10,000 atm/z. A set of samples consisted of 12 samples including: 10 field samples and/or field blanks, one method blank, and one laboratory control spiked sample fortified with native target analytes at twice the limit of quantitation (these limits are provided at the end of this chapter). All reagents were prepared according to procedures detailed in EPA Method 1613 (U.S. EPA, 1994), and the analyses and QA/QC procedures and thresholds were consistent with those described in EPA Method 1613, with several notable exceptions:

1. Standard calibration solutions were prepared at lower concentrations. For the NDAMN, the lowest calibration standard contained 50 fg of TCDD and 5 pg/µL of $^{13}C_{12}$-labeled surrogates; EPA Method 1613's lowest calibration standard contains 500 fg and 100 pg/µL of surrogates. The samples in this study were fortified to deliver 5-20 pg/µL (EPA Method 1613 delivers 100 pg/µL from the same 20 µL final volume). The lower $^{13}C_{12}$ surrogate fortification level allowed for a more realistic approximation of the actual recovery of native analytes at the subparts-per-trillion level and better approximated the behavior of trace levels of natives during sample processing and analyses.

2. A DB-5MS column was used in place of the DB-5 specified by EPA Method 1613. The DB-5MS has superior separation of the 2,3,7,8-TCDD from the other tetra isomers and better resolves the 2,3,7,8-Cl-substituted dioxins and furans.

3. EPA Method 1613 specifies an AX21/Celite® mixture of graphitized carbon where the NDAMN procedure used a mixture consisting of 0.5 g of BioSil-A® silica gel and 0.5 g of Amoco PX-21® carbon. The eluting solvents and fractionization are also different. The column was conditioned with 10 mL of 50/50 benzene/methylene chloride (MeCl), 10 mL toluene, and 5 mL hexane. The sample was added to the column in 0.5 mL hexane and following two 0.5 mL rinses of the sample. Fraction 1, containing most of the ortho PCBs, was eluted with 4.5 mL of 25/75 MeCl/hexane. Fraction 2, collected in one vessel, consisted of 5.5 mL of MeCl and contained the mono-ortho PCBs and 11.5 mL of benzene/MeCl, which contained the nonortho PCBs. The column was then reversed, and the dioxins and furans were collected with 13 mL of toluene. Fractions were reduced to less than 10 µL, and solvent was exchanged with hexane and stored in the freezer until analyzed. All analyses were performed on either a Kratos Concept® or a Micromass Autospec® high resolution mass spectrometer using isotope dilution. The HRMS was operated in the electron impact ionization mode using selected ion monitoring. Chromatographic separations were achieved using a Hewlett Packard 6890 Series II® high-resolution gas chromatograph, utilizing a 60 m × 0.32 mm (0.25 µm film thicknesses) DB-5MS capillary column. The gas chromatography conditions were optimized to completely separate the various 2,3,7,8-Cl-substituted dioxins/furans: initial oven temperature, 130ºC; injector temperature, 270ºC; interface temperature, 275ºC; temperature programming, time 1, 1.0 minute, rate 1, 5ºC/minute, time 2, 15.0 minute, rate 2, 6ºC/minute; temperature 3, 295ºC; injector, splitless, 1.0 minute; split flow, 30−40 mL/minute; purge flow, 1−2 mL/minute; and temperature equilibration time, 2 minute. A combination of 23 psi (constant pressure) and 1.5 mL/min (constant flow) were used throughout the project resulting in similar chromatography and retention times on the same column. The mass spectrometer was tuned and calibrated prior to all analyses. It was tuned to a minimum resolution of 10,000 ppm (10% valley) using m/z = 330.9792 (or any suitable reference peak) at full accelerating voltage of 8,000 V. Pertinent mass spectroscopy parameters were as follows: cycle time for each congener group, ~1.0 s; electrostatic analyzer sweep (analytes), 10 ppm; native ion dwell, ~100-200 ms; ^{13}C-labeled ion dwell, ~30-66 ms; lock mass sweep, 200 ppm; lock mass dwell, 50 ms; ionization voltage, ~35 eV; source temperature, 250ºC; accelerating voltage, 8,000 V; and trap current, 500-700 µA.

3.2. QUALITY CONTROL (QC) OF LAB SAMPLES AND CALIBRATION

Between four and six calibration standards with native analyte concentrations bracketing the expected analyte concentrations were analyzed prior to analyzing samples. The analyses of calibration standards permitted the response factors (RFs) to be determined as a function of concentration using linear regression. The RF for each native analyte at each concentration was calculated relative to its ^{13}C-labeled analog. The relative standard deviation (RSD) for the average RF for each of the native analytes had to be <20%. Similarly, the RF for each $^{13}C_{12}$ recovery surrogate relative to the appropriate internal standard was also calculated. The RSD for the average RF for each labeled surrogate had to be <35%. The calibration curves were considered linear under these conditions, and the analytical system was considered calibrated when these conditions had been satisfied. If these conditions could not be satisfied, corrective actions were taken. The average RFs were used for subsequent quantitations. Prior to sample analysis, the linearity of the calibration curve was verified by analyzing calibration solution 2 (200 fg of TCDD) and calculating the RF as described previously. The percentage difference between the new RF and the average had to be <20% for the native analytes and <35% for the $^{13}C_{12}$ recovery surrogates.

The chromatogram was also examined to ensure that all 2,3,7,8-Cl-substituted congeners were clearly separated. If the signal-to-noise (S/N) ratio values were >10, the ion abundance ratios were +15% of the theoretical (this ratio was relaxed to $\pm$ 25% if the mass quantified was less than 100 fg), and the RF and isomer separations were within specified limits, then sample analyses proceeded. Corrective actions were initiated if specified control limits were exceeded. These corrective actions included returning of the mass spectrometer and/or new calibration standards prepared and re-analyzed. On the days that samples were analyzed, 10 µL of the internal standard solution (20 pg/µL) was added to each sample, and the final volume was adjusted to 20 µL.

Once all QA/QC parameters had been verified to be within specified limits, sample analyses proceeded. The mass spectrometer was operated in a mass drift correction mode using perfluorokerosene to provide lock masses. The selected ion current profile areas for the characteristic ions for each native and labeled analyte were measured. Native analyte concentrations were determined by isotope dilution. Peak areas from the characteristic ions for each native analyte and its ^{13}C-labeled analog were used in conjunction with RFs from the

internal calibration data to determine concentrations directly. Labeled surrogate concentrations (expressed as percentage recovery) were similarly calculated using an internal standard EPA method. Samples were organized and analyzed in sets: method blank, laboratory control spike, and the ten field samples. Peak identification criteria were as follows: S/N > 3.5; the isotope ratio of the two characteristic ions for each congener class within 15% of the theoretical value; the peak maxima for the molecular cluster ions coincide within 2 seconds; and native analytes elute within ± 3 seconds of their corresponding $^{13}C_{12}$-labeled analogs. Method blanks were examined for the presence of interfering background. For furans, an ion for the appropriate chlorinated diphenyl ether was monitored, and the ion chromatogram was examined to ensure the absence of chlorinated diphenyl ether contamination. The amount of any native analyte detected was listed on the quantitation report, along with the recovery of its labeled analog. Recoveries of ^{13}C-labeled analogs for the samples were between 25 and 150%. Sample sets were reviewed by the QA/QC officer to ensure compliance with QA/QC guidelines/criteria.

The analytical DLs ranged from 0.5 pg for TCDD/TCDF to 20 pg for octochlorodibenzo-*p*-dioxin/octachlorodibenzofuran (OCDD/OCDF), and from 1 pg (PCB 169) to 500 pg (PCB 118) for the individual PCBs. Analyte-specific DLs are shown in Table 3-1. DLs expressed on a concentration basis are a function of the volume of the sample, and thus varied by sample. With a sample volume average of 6,827 m^3, DLs were less than 1 fg/m^3 for all PCDDs/PCDFs except OCDD at 3 fg/m^3, and were generally higher for PCBs than PCDDs/PCDFs, with a high of about 70 fg/m^3 for PCB 118.

3.3. REFERENCES

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U.S. EPA (Environmental Protection Agency). (1999) Compendium of methods for the determination of toxic organic compounds in ambient air second edition compendium method TO 9A. Determination of polychlorinated, polybrominated and brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans in ambient air. Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH; EPA/625/R-96/010b. Available online at http://www.epa.gov/ttnamti1/files/ambient/airtox/to-9arr.pdf.

Table 3-1. NDAMN analytes measured and their detection limits (DL, in pg)

PCDD	DL, pg	PCDF	DL, pg	PCB (IUPAC #)	DL, pg
2,3,7,8-TCDD	0.5	2,3,7,8-TCDF	0.5	3,3',4,4'-TCB (PCB 77)	20
1,2,3,7,8-PeCDD	1.5	1,2,3,7,8-PeCDF	1.5	3,4,4,5-TCB (PCB 81)	2
1,2,3,4,7,8-HxCDD	2.5	2,3,4,7,8-PeCDF	1.5	3,3',4,4',5-PeCB (PCB 126)	2
1,2,3,6,7,8-HxCDD	2.5	1,2,3,4,7,8-HxCDF	1.5	3,3',4,4',5,5'-HxCB (PCB 169)	1
1,2,3,7,8,9-HxCDD	2.5	1,2,3,6,7,8-HxCDF	1.5	2,3,3',4,4'-PeCB (PCB 105)	300
1,2,3,4,6,7,8-HpCDD	2.5	1,2,3,7,8,9-HxCDF	1.5	2,3,4,4',5-PeCB (PCB 114)	20
OCDD	20.0	2,3,4,6,7,8-HxCDF	1.5	2,3',4,4',5-PeCB (PCB 118)	500
Total TCDD	0.5	1,2,3,4,6,7,8-HpCDF	2.5	2',3,4,4',5-PeCB (PCB 123)	10
Total PeCDD	1.5	1,2,3,4,7,8,9-HpCDF	2.5	2,3,3',4,4',5-HxCB (PCB 156)	80
Total HxCDD	2.5	OCDF	4.0	2,3,3',4,4',5'-HxCB (PCB 157)	20
Total HpCDD	2.5	Total TCDF	0.5	2,3',4,4',5,5'-HxCB (PCB 167)	10
		Total PeCDF	1.5	2,3,3',4,4',5,5'-HpCB (PCB 189)	2
		Total HxCDF	1.5		
		Total HpCDF	2.5		

Notes: PCDD = polychlorinated dibenzo-*p*-dioxin; PCDF = polychlorinated dibenzofuran; PCB = polychlorinated biphenyl; TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl.

4. OVERVIEW OF RESULTS

This section provides a summary of results of measuring atmospheric PCDDs, PCDFs, and dl-PCBs from June 1998 through November 2004 at 35 NDAMN stations throughout the United States. Results are presented on a congener-specific basis and also for TEQ concentrations. The intent of this chapter is to present an overview of the results, rather than a comprehensive interpretive analysis. Researchers are encouraged to apply their own statistical models to the data provided in the NDAMN database that is released along with this report for more in-depth analysis.

Section 4.1 describes the breadth of the final data set. Section 4.2 provides a summary of the QA results for the study. Section 4.3 provides a summary of the results, with a look at some basic trends, including concentrations found, trends over time and land use, and some of the high concentrations found.

4.1. OVERVIEW OF NETWORK OPERATION STATUS

On June 16, 1998, 10 NDAMN stations became operational in the field at 9 rural locations, with Station 2 acting as a duplicate QA/QC sampler operating adjacent to Station 1. NDAMN was expanded to 23 sampling stations by the last sample moment in 1999, 30 stations at the end of 2000, 32 stations at the end of 2001, 34 stations at the end of 2002, and finally, 35 stations at the end of 2003 when the last one was added for the first sampling moment in 2003. The count of 35 stations includes QA/QC Station 2. Because this QA/QC station did not obtain data for the program but rather was a duplicate sampler serving as a quality measure, the full NDAMN data set is considered to be composed of 34 stations. A comparison of the results from this duplicate sampler and the regular NDAMN samplers is provided in Section 4.2.

Table 4-1 shows when each of the study stations were operational and when data were "not available," NA. If all 34 study stations operated for all moments following their initially collected sample, there would be a total of 736 samples. However, there were only 685 completed samples, and the remaining 51 samples were NA for the following reasons:

1. Station Not Operating: This was the most common cause, and it occurred 26 times.

2. QA Failure at the Lab, All Analytes: The station was operating and a volume in the sampler was recorded, but the laboratory recorded a QA Failure and did not develop any data for the sample. This occurred eight times, and seven of those occurrences were for Moment 28 samples, for Stations 12 and 14 through 19.

3. QA Failure at the Lab, PCDD/PCDFs: There were occasions where the laboratory reported QA failure for measurements of all dioxins and furans but did report measurements for the dioxin-like PCBs (or most dioxins and furans; one sample had reported some but not all dioxins and furans). Rather than count the PCBs in any of the results compilation for this chapter, none of the data from these samplers was used for the results generated in this chapter. The PCB data are available on the spreadsheet accompanying this report, if others wish to analyze it. This occurred seven times.

4. Volume Lost: The station was operating, and the laboratory reported measurements of analyte mass. However, the volume in the sampler was missing, so concentrations could not be developed. This occurred two times.

5. Low Volume: The station was operating, and the laboratory reported measurements of analyte mass. However, the volume was less than 2,000 m^3. According to the protocol for sampling (see Appendix B), a sample with less than this volume was to be rejected. While this rejection did not occur during the NDAMN program, these samples will not be included in the generation of results for this chapter. The results are reported in the raw data file, however, should others wish to analyze them. This occurred eight times in the NDAMN sample and once for the QA sampler.

The spreadsheet with final NDAMN results identified the cause for each of the NA samples. It is noted that the following dioxin-like PCBs were only first measured in the summer of 2002 (Moment 20): PCBs 81, 114, 123, 167, and 189. While the total "*n*" for all other analyte measurements was 685, the number of measurements per analyte for these congeners was 317.

4.2. QUALITY ASSURANCE (QA) MEASURES AND RESULTS

4.2.1. Blank Samples

There were three types of blanks employed in NDAMN: trip blanks, field blanks, and laboratory blanks. Trip blanks were found to be minimally contaminated during the first moment of sampling and were discontinued after that. Another reason trip blanks were discontinued was that they are not specified as part of Method TO 9A. Field blanks were only exposed to ambient air during sample setup and harvesting. Based on minimum background contamination found in field blanks, EPA decided that beginning with Moment 9

(November/December 1999), all field blanks did not need to be analyzed. From that point forward, at least one field blank per station per year was analyzed. Method blanks were used during the entire program consistently—one method blank per nine NDAMN samples. Their purpose, of course, was to determine if there was contamination of laboratory equipment or reagents.

Subsets of field and laboratory method blank results were used for analysis in this section. All field blanks through Moment 3 were collected, along with all field blanks for Moments 5, 7, and 9. This subset entailed 56 samples and was judged to be sufficient to characterize the NDAMN field blank results. All laboratory method blank results through Moment 13 were used in this analysis, along with all method blanks every other moment thereafter (Moments 15, 17, and 19 through 29). By this selection, there were 108 method blank results in the analysis, and this was judged as sufficient to characterize the overall results of method blanks.

Results comparing the average mass of congener found in the blanks with average mass of congener found in NDAMN study samples are shown in Table 4-2. All average masses were derived with non-detects set equal to 0.0. For NDAMN, average congener masses were presented for the three types of stations—remote, rural, and urban. This delineation was described in Chapter 2. Six stations were characterized as "remote" with 153 samples, 4 stations characterized as "urban" with 69 samples, and the remaining 24 stations of NDAMN were characterized as "rural" with 463 samples. Along with congener-specific average masses found in the blank samples (again counting non-detects as 0.0), Table 4-2 shows the program-specific "target" method DLs and the percent positive quantified congener in the blank samples. These targets were determined prior to the beginning of NDAMN. If a sample had less than this amount, in a sample or in a blank, generally speaking the result was characterized as ND. An examination of the blank results did show, however, that some blank samples had congener-specific measurements above the target levels, as well as some below the target levels, and then some were simply described as ND. In other words, these "targets" were not very rigidly observed, as the laboratory did quantify some congener masses from blank samples that were lower than these targets.

Several observations are made based on the results from Table 4-2:

1. The NDAMN categorization of remote, rural, and urban did appear to capture some differences in the levels of dioxins, furans, and PCB congeners in the air, particularly in that masses in the remote samplers were much lower than the other two categories. This is discussed later in Section 4.3.

2. The average mass of all tetra- through hexa dioxin and furan congeners in the blank samples, both the field and laboratory blanks, were significantly lower than the target levels, and similarly significantly lower than measured even in the remote samplers. The fact that it is lower than the target is because most samples were characterized as NDs, and NDs were counted as zero in the calculation of averages. Specifically, the percents of positive quantifications in the blanks were under 10% most of the time. The one exception to this generalization was 2,3,4,6,7,8-hexachlorodibenzofuran (HxCDF), found in 40% of the field blanks (and in 84% of the study samples). Also, the amount of this congener in the blanks was closer to the amount in the remote samples; the average of 1.1 pg in the laboratory blank was about one-fifth of the average amount found in the remote sampler, at about 5 pg. Other than this hexa furan congener, the average amounts of all other congeners found in the blank samples were an order of magnitude or more lower than found in the remote samples, and two or more orders of magnitude lower than in the rural or urban samplers.

3. The hepta- and octa dioxin and furan congeners were quantified more frequently in blank samples, with four of five such congeners found in 88% or more of the laboratory blanks samples. But, like the tetra- through hexa congeners, the average mass found in the field and laboratory blank samples was about an order of magnitude lower than the amount found, on average, in the remote samplers, and about two orders of magnitude lower than the amounts found in the rural and urban samplers.

4. Other than PCB 169, all PCB congeners were found in blank samples at high percentages, most above 90%, and for five of the seven congeners, it was found at either 98 or 99% of the blank samples. The average masses found in the blanks were close to expectations based on the target levels set, except for PCB 118. For that congener, the average amount found in the field blanks was about three times the target, and the amount in the method blanks was about twice the target.

5. For all PCBs, the average masses found in the field blanks were less than, but close to, the masses found in the remote samples, approximately lower by a factor of 2 (half as much in the blank as the remote sampler) to lower by a factor of 5. Comparing to the rural averages, the amount found in the blanks ranged from about a factor of 3 less to a factor of 10 less.

It can be concluded that PCBs are ubiquitous in the environment, as well as in the laboratory, as seen by their presence in the blank samples. The same might be said of the higher chlorinated dioxins and furans, however, not the lower chlorinated dioxins and furans, whose

presence was quantified in blank samples mostly less than 10% of the time. Even though found in blanks, the masses of higher chlorinated dioxins and furans are still well below levels found in the NDAMN samples: near an order of magnitude lower than samples in the remote areas and two orders of magnitude lower than levels found in the rural or urban samplers. The same cannot be said for PCBs. As noted above, levels of PCBs in the blanks were within factors of two and five of levels in the remote area and within a factor of 10 and less for levels in the rural areas. PCBs have been identified as a laboratory contaminant in environmental measurement studies (Ferrario et al., 1997). The fact that they were present was not unexpected in NDAMN, as evidenced by the DL targets established before the program began. But it is also clear that PCB results may be problematic for proper interpretation of NDAMN results.

One way that similar issues are dealt with is through subtraction of chemicals found in blanks from the amount found in study samples. This is termed, blank subtraction. However, there was no blank subtractions in the NDAMN samples, for either dioxins/furans or the PCBs. Blank subtraction is often a judgment call and not a required protocol, particularly for dioxin-like compounds. The exact protocol for blank subtraction is not established for dioxin-like compounds. One approach is to subtract the method blank concentration values within a single batch of samples. Another is to make corrections post-survey based on overall method blank statistics, such as subtracting the mean amount found in all study method blanks from all study samples. Subtracting PCB levels in blanks with either of these methods would have resulted in a large number of final concentrations being reported at values less than the stated DL, which is problematic for obvious reasons. Ideally, measured concentrations would be significantly larger than concentrations found in method blanks, and that appears to be the case with dioxin and furan congeners, but not with PCB congeners.

It might be observed, however, that the most toxic PCB congeners, PCB 126 and 169, appeared to be measured with the least laboratory contamination issues. The target DLs of 2 and 1 pg of mass for PCB 126 and 169, respectively, were achieved in both the field and method blanks. The average masses in remote samples were relatively close to these target DLs, with averages of 8 and 0 pg of mass for PCB 126 and 169, respectively. The rural and urban concentrations were over an order of magnitude higher, at 32 and 68 pg for PCB 126, and though not an order of magnitude higher, still much higher for PCB 169 at 5 and 6 pg. As discussed in Section 4.3, PCB 126 drives the PCB portion of the TEQ concentration, with PCB 169 the

second most toxic congener, even though it did not influence the TEQ as did PCB 126. From these perspectives, it is concluded that the PCB 126 and 169 measurements were reliable and useful.

4.2.2. Co-Located Sampler Results

Station 2 was designated as a QA station where measurements were taken concurrently in order to provide a duplicate field test of the sampling and analytical EPA methods. The sampling apparatus and procedures were exactly the same for this station as all regular NDAMN stations, and the operators were instructed to process the samples in the same manner. For the first 19 moments, this station was located adjacent to the Station 1 monitor at Penn Nursery, and for moments 20−29 (not including Moment 28, when the station was not operating) the monitoring equipment was moved to North Carolina at Clinton Crops, Station 3. Ideally, results from the side-by-side monitors should be similar. Table 4-3 provides congener averages, correlation coefficients, and relative percent differences (RPDs), in the side-by-side measurements. These results do not include a side-by-side measurement for moment 10, the winter sample of 1999-2000, when the volume on the QA sampler was 1,198 m^2. The implications of this low sample volume on the QA sampler are discussed later in this section. The RPD is a common method to characterize precision in co-located samples and has been used to evaluate co-located dioxin samplings in the long-term air sampling program in Connecticut (described previously in Chapter 2; Hunt, 2008). The RPD for each pair of (congener NDAMN sample, congener QA sample) is calculated as:

$$RPD = [ABS (C_{NDAMN} - C_{QA})/AVG (C_{NDAMN}, C_{QA})] * 100\%$$

where:

RPD	=	relative percent difference, %
C_{NDAMN}	=	concentration of congener in an NDAMN sample
C_{QA}	=	concentration of corresponding congener in QA sample
ABS	=	absolute value function
AVG	=	average of the two concentrations

Figures 4-1 and 4-2 graph the concentrations of specific congeners found in the side-by-side monitors to display the comparison between the NDAMN and the co-located samples.

For the most part, there was a high correlation between NDAMN station and QA station results for dioxins and furans (see Table 4-3 and Figure 4-1a). Correlation coefficients for the PCDDs/PCDFs were mostly in the 0.80 to 0.99 range, although a few lower correlations, even at negative values, occurred for the tetra- and penta dioxin congeners at the Clinton Crops station. The RPDs listed in Table 4-3 were the average of each congener pair; for example the RPD of 17% for 2,3,7,8-TCDD at Penn Nursery was the average of 18 individual RPDs for that station. These average RPDs were approximately 20% or less for all PCDD/PCDF congeners at both Penn Nursery and at Clinton Crops, except for OCDD which was above 30% at Penn Nursery. The congener-specific average RPD varied between 9% and 36% for the PCDDs and PCDFs, with an overall average of 18.9%. This is a bit higher than the 12.5% overall found by Hunt (2008) in co-located air samplings of dioxins. That program in Connecticut involved 24-day sampling, similar to NDAMN, and though the precision they achieved was superior to that found here, NDAMN is nonetheless judged to show adequate precision for the PCDDs/PCDFs in co-located samples. The Penn Nursery found consistently higher concentrations of dioxins as compared to Clinton Crops, and this was seen in the average concentrations in the two sets of results from Penn Nursery compared to the two sets of results from Clinton Crops. Also, interestingly, the reverse was mostly true for furans; they were uniformly higher in the Clinton Crops station, except for OCDF which appeared similar at the two locations. Figure 4-1a shows the high correlation in 2,3,7,8-TCDD concentrations and the nearness to the perfect correlation line of $y = x$, with, importantly, a uniform finding of a high concentration of about 3 fg/m^3 found in both the NDAMN and QA sampler. Figure 4-1b shows an example where there was a low correlation in the NDAMN and QA stations for a congener, also 2,3,7,8-TCDD. It is seen that most of the samples were similar, but there were two instances where a disparity was seen in 2,3,7,8-TCDD measurements. In one case, the NDAMN sampler showed a higher concentration, and in the second case, the QA sampler had the higher concentrations. These two results explain the low correlation coefficient of - 0.10. Overall, the average concentrations and the positive, mostly high, correlations speak to the ability of the protocol to obtain excellent duplication of results for dioxins and furans.

The same cannot be said about dioxin-like PCBs. There was a trend that the QA sampler consistently had higher results as compared to the NDAMN sampler (within but sometimes even higher than a factor of 2). The correlation coefficients were often less than 0.50 and the RPDs were also consistently higher for the PCBs as compared to the PCDDs/PCDFs, often in the 40-50% range. There did not seem to be any apparent trends in overall PCB concentrations between geographic locations, as there was for dioxins and furans (as discussed above). This is seen in Table 4-3, where similar concentrations were found in both locations from an examination of just the NDAMN sampler. Figure 4-2 shows the common trends found in the comparison between the NDAMN and QA sampler. In Figure 4-2a, most of the QA results were higher than the NDAMN results, with some exceeding NDAMN results by a factor of 10. In other instances, there appeared to be a higher correlation, but still a trend of higher concentrations was found in the QA sampler. This is seen in Figure 4-2b, where again, the majority of samples were higher in the QA sampler, but at least the highest concentrations found in the QA sampler were matched with the highest samples found in the NDAMN sampler. Although a high correlation coefficient, it is clear that even for this case, a different set of data was obtained from the QA sampler. It is not known why there is this difference. The same equipment was used at the two stations—the QA monitoring equipment was transferred from Station 1 to Station 3 starting at Moment 20. This might suggest some internal PCB contamination of the QA sampler. In any case, the reason for this discrepancy was never identified.

4.2.3. NDAMN Sample Volume

The target volume for NDAMN, based on the protocol, was 6,000 to 8,000 m^3; unfortunately, that target was not always met. Specifically, 32% of the final study samples were outside of this range, but only 7% were lower than 5,000 or more than 9,000 m^3, with a low of 2,655 m^3 and a high of 13,035 m^3. The average volume of air was 6,827 m^3, with a standard deviation of 1,074 m^3. As noted earlier, there were eight study samples with volumes less than 2,000 m^3, and these were not included in the final study results (although the raw data of NDAMN for these samples with low volumes are available on the spreadsheet and can be evaluated by others).

The issue of sample volume was evaluated with the co-located samplers. Ideally, the volumes in the NDAMN and co-located samples should be very similar, event-to-event,

however, this did not occur in all cases. Figure 4-3 compares the volume in co-located samples with the NDAMN samples for the 19 events when the co-located sampler was located at Penn Nursery in Pennsylvania. One of the co-located samples had a very low volume of 1,198 m^3, so it would have been rejected from the NDAMN data. Not counting the pair with this low volume, the average of the other 18 samples was 6,530 m^3 for NDAMN samples and 7,170 m^3 for the co-located sampler. The t-test for the 18 paired values had a *p*-value of 0.13, indicating the means were not significantly different. From Figure 4-3, it is seen that 11 of the 18 pairs were very close to the perfect correlation line, y = x, while 7 were somewhat outside of this range. The causes for the differences in volume are not known. Detailed records from the stations, which would have included instrument readings and perhaps other information to explain the differences, were not available for this report. One would suspect or presume that the individual cooperating with EPA at this research nursery harvested the GFF and PUF from both the NDAMN and the QA sampler at the same time. Differences therefore, could only be explained by different air flow rates between the samplers.

In any case, these differences provided an opportunity to look at the influence of sample volume on sample results. If, in a pair of these samples, the one with lower volume had proportionally lower mass measured, and hence the same concentration, then perhaps volume perturbations would not be a cause to invalidate NDAMN measurements. Two sample pairs were culled from this group of 19 for further analysis. One of them included the co-located sample with a volume under 2,000 m^3 and the second had a co-located volume that was about 2,000 m^3 less than the study sample. Table 4-4 compares the concentrations between these two pairs, the RPDs between these two pairs, and then the average concentrations and average RPDs for all other 17 co-located samples at the Penn Nursery. Looking at the raw data for mass of congeners (not shown on Table 4-4), it is seen that lower masses are found in the co-located QA sampler as compared to the study sample. This is expected—lower masses should be associated with lower volumes. However, the question is, are these lower masses proportionally lower considering the difference in volume? For the Spring 2000 sample, the NDAMN sample had a volume of 4,859 m^3, and the co-located sampler had about one-quarter as much volume at 1,198 m^3. For the concentrations to have been similar in this sampler, the masses would similarly need to be about one-fourth as much. In fact, they were not—they were more than one-fourth as much, and subsequently, the concentrations were higher for the co-located sampler. They are

about 30% higher for the lower chlorinated dioxins, and then about twice as high or more for the higher chlorinated dioxins, the furans, and the PCBs. The average RPD for all congeners within this sample was 66%. For the second sample pair shown in Table 4-4, the co-located sample concentrations were much more similar to the study samples, with an average RPD of 20%, which is similar to the RPD average for all other Penn Nursery samples. Some of the co-located sample concentrations were higher and some lower than the corresponding NDAMN sample.

This analysis suggests two conclusions: (1) that there quite possibly was a QA problem, in general, with samples that had low volume and their removal from the overall NDAMN sample was justified, and (2) samplers with lower (or possibly higher due to extended periods) volumes than the target volume would still accurately be characterizing the air concentration during the period of time they were operating.

On average, the volume of air collected in NDAMN samples was consistent with a second major use of this long-term sampling method for dioxin and furans. The CDEP monitoring program consists of 30-day sampling events (Hunt and Lihzis, 2011). Sample volumes during the 10-year period of 2002–2012 averaged 7,659 m^3. Sample collection flows ranged narrowly from 165 to 182 liters per minute, with an average flow of 177 liters per minute (telephone conversation between Gary Hunt and Matthew Lorber, March 2013). These volumes are lower than suggested by EPA TO 9A, which specifies a sample air volume range of 325 to 400 m^3 per 24-hour sampling period. This equates to a sample collection flow ranging from 225 to 275 liters per minute but the latter assumes a 24-hour sampling event. Lower flows are to be expected for a 30-day sampling period (telephone conversation between Gary Hunt and Matthew Lorber, March 2013). While the average 30-day volume in the CDEP program at 7,659 m^3 was higher than the NDAMN average of 6,827 m^3, a difference is to be expected as the monitor in the CDEP program ran for 30 continuous days, while in NDAMN, the monitor was shut down for 1 to 2 days per week per every 28-day sampling period. The reason that one-third of all NDAMN samples were outside the target range of 6,000 to 8,000 m^3 (although only 7% were outside the 5,000 to 9,000 m^3 range) remains unknown. Chapter 2 discussed the implementation of NDAMN, where monitors were located near existing networks, such that EPA could rely on operators to maintain and implement the NDAMN protocol for sampling. It seems possible that these cooperators could have deviated from the protocol, harvested the GFFs earlier or later than the 5- to 6-day protocol, to cause either higher or lower air volumes. It is also possible that log

sheets provided to EPA used to calculate final volumes contained missing or incorrect values, on occasion. These possibilities could not be evaluated. However, the analysis above with the co-located sampler showing similarity in concentrations despite a 2,000 m^3 volume difference suggested that volumes were generally valid. A scan of other stations in NDAMN shows differences in sample volumes, but similarities in concentration, supporting this finding.

4.2.4. A Comment on NDAMN Quality Assurance (QA)

Sections above addressed results from sample blanks (field and method), results from the co-located samples, and sample volumes. Quality issues were identified, but any judgment regarding overall validity of the NDAMN results should consider the context of the data and the intended uses. As a research project without a regulatory mandate or intended regulatory purposes, funding was limited. This resulted in some restrictions and had design implications. The decision was made to only characterize background air concentrations, and not venture into urban centers to any extent. Samplers were added to the program as funding permitted, and the program closed perhaps earlier than ideal. Cooperators were sought to implement EPA's sampling protocol rather than have the samplers consistently manned under a single contract. Issues were found with PCB measurements, both in terms of laboratory performance, and in the co-located samplers. In comparison, the CDEP program, which was operated by a single contractor over time, had sample volumes that were within a more desired narrow range. By contrast, NDAMN appeared to have a wider range in sample volumes than desired.

Still, measurements of dioxin and furan congeners appeared to have met QA expectations with regard to blank results and co-located comparisons. PCB results should be used cautiously, but it does appear that PCBs 126 and 169, the most toxic of the PCB congeners, appear to have been measured within target DLs and with a minimum of external contamination. For its intended purpose, which was to establish background levels of dioxin concentrations for research purposes, it is concluded that the NDAMN program performed adequately from a QA perspective.

4.3. OVERVIEW OF FINAL RESULTS FROM NDAMN

Table 4-5 provides congener- and homologue-specific survey-wide statistics. Several observations are made from this table:

1. Frequency of occurrence was very high, mostly above 95% and at 85% for 2,3,7,8-TCDD. The lowest detection frequency was 74% for 1,2,3,7,8,9-HxCDF. The protocol to obtain 4 weeks of air volume guaranteed low DLs and a high detection frequency. All results in this chapter have been generated assuming ND = 0, but a quick check on a few averages showed virtually no change if instead assuming ND = ½ DL. Sample-specific, congener-specific DLs can be generated by using the cogener-specific mass DLs provided in Table 3-1 with the volume in the sampler. For example, the congener-specific mass DL for 2,3,7,8-TCDD was 0.5 pg, and assuming a volume was 7,000 m^3 (as noted in Chapter 2, volumes typically range between 6,000 and 8,000 m^3), the concentration-based DL would be 0.07 fg/m^3.
2. The archetype dioxin and furan background air congener profile was seen in the survey averages and in most individual samples. Discussions below show that some of the higher samples did not follow this pattern. This archetype profile is characterized by low and similar concentrations for tetra through hexa dioxins and furan congeners, with elevations in 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF. Lorber et al. (1998) discuss this profile and show it to be present in urban as well as rural settings. A similar archetype profile of dioxin-like PCBs in air has not been elucidated in the literature, but the values found here could serve that purpose. The highest concentrations were found for PCBs 118 and 105, with concentrations in the hundreds to thousands of fg/m^3; the lowest mean concentrations, at less than 10 fg/m^3, were seen for PCBs 126, 169, and 189. PCB 126 is the most toxicologically significant of the dioxin-like PCBs, with a TEF at 0.1. It was detected 100% of the time at an average concentration of 6.9 fg/m^3.
3. The overall average TEQ was 11.1 fg/m^3 with dioxin-like PCBs contributing only 0.8 fg/m^3 (7%) of this total and with PCB 126 explaining most of this contribution (about 88%). The top six contributors explained 67% of the TEQ, and their percentage contributions to this TEQ were 1,2,3,7,8-PeCDD at 27.8%, 2,3,4,7,8-PeCDF at 11.4%, 1,2,3,4,6,7,8-HpCDD at 9.1%, 1,2,3,6,7,8-HxCDD at 6.5%, 1,2,3,7,8,9-HxCDD at 6.4%, and PCB 126 at 6.1%. The congener, 2,3,7,8-TCDD, contributed 5% to the TEQ. All dioxin-like PCBs excluding PCB 126 contributed about 1% to the TEQ.

Figure 4-4 shows the average TEQ concentrations for all NDAMN stations. Average TEQ concentrations throughout most of the Eastern Seaboard, into the central part of the United States, range between 5 and 20 fg/m^3. In the central part of the United States and into the western portion, as well as Alaska, excluding California, the average TEQ concentration appears to be near or less than 5 fg/m^3. Two of the stations in the Western Seaboard, one in California and one in Oregon, showed average TEQ concentrations just above 20 fg/m^3. The other four stations on the Western Seaboard showed average TEQ concentrations less than 10 fg/m^3. Station 20, Fond du Lac Indian Reservation in Minnesota, showed the highest average concentration at 47 fg TEQ/m^3, but this was skewed by a single outlier at 847 fg TEQ/m^3.

Without this concentration, the average for the station was 6.9 fg TEQ/m^3. Station 28, Rancho Seco (closed nuclear power plant), was also influenced by a single high concentration, although not as much. The station average concentration of 36 fg TEQ/m^3 was reduced to 21 fg TEQ/m^3 if the high concentration of 241 fg TEQ/m^3 is not considered in calculating the average. Two other stations had a single measured concentration above 100 fg TEQ/m^3, and these measurements will be discussed shortly.

As discussed in Chapter 2, stations were generally categorized as either urban (4 stations), rural (23 stations), or remote (7 stations). These characterizations were for purposes of this study and should not be considered representations of any of these three land-use categorizations, particularly for urban. For example, Station 13 in Beltsville, Maryland, is considered "urban" because it is near the Washington, DC urban area. Cities such as Chicago or New York would be expected to have higher air concentrations than were characterized by the urban sites in NDAMN due to proximity of air emission sources (industrial incinerator sources, vehicular emissions, other air sources). EPA (2003) summarized the literature on dioxins in air in the United States pertinent to the time frame of the late 1980s into the 1990s. While this time frame is a bit earlier than the time frame of NDAMN, nonetheless it reports on numerous studies, including those in California, Ohio, and New York, which show average air concentrations exceeding 100 fg TEQ/m^3, where "average" is over time for some temporal sampling or over several different monitors. As noted below, recent urban measurements in California averaged 30 fg TEQ/m^3. In any case, the average TEQ concentrations over all stations and moments within these categories were (1) urban at 15.9 fg TEQ/m^3, (2) rural at 13.9 fg TEQ/m^3, and (3) remote at 1.2 fg TEQ/m^3. Figure 4-5 shows the land-use averages over time. The difference between remote areas and the other two areas are clear from this figure. Otherwise, no unambiguous trends emerge from a visual examination of this figure. It might be observed that the rural stations, as a group, may show elevations during the fall or winter months as compared to the spring or summer months. Perhaps that could be said as well for urban stations, but the remote stations appear to show little variation during the course of a year. Over the 6-year period of NDAMN, there does not appear to be any significant upward or downward change that would occur as a result of a meaningful increase or decline in dioxin source emissions.

Concentrations found in NDAMN are comparable to or lower than similar studies undertaken within the United States and around the world. Among the early sampling

campaigns was one undertaken to study PCBs, polycyclic aromatic hydrocarbons, and PCDD/PCDFs in urban air in the United Kingdom (UK) in the early 1990s (Coleman et al., 1997). Between 1991 and 1995, they measured these semi-volatile compounds at sites in London and Manchester. Samples were taken every two weeks by hi-volume samplers. Declines in concentrations were observed at both locations between 1991 and 1994, with an upturn in 1995. Concentrations in Manchester ranged from about 100 to approximately 450 fg TEQ/m^3, while concentrations in London were between 50 and 150 fg TEQ/m^3. It is presumed that the values were determined using the 1994 TEF values as described in Van den Berg et al. (1994), although the authors did not provide a reference for their assignment of TEFs. A ten-year program monitoring dioxins in air in Catalonia, Spain, was reported by Abad et al. (2007). A total of 174 samples were taken between 1994 and 2004. Concentrations were highest in an industrial area, with a range of 50 to 1,196 fg TEQ/m^3 and a mean of 140 fg TEQ/m^3. They were second highest in a high traffic area, with a range of 10 to 357 fg TEQ/m^3 and a mean of 72 fg TEQ/m^3, and they were lowest in a rural area with a narrow range of 5 to 45 fg TEQ/m^3 and a mean of 28 fg TEQ/m^3. This is a bit higher than the rural results of NDAMN which averaged 13.9 fg TEQ/m^3. In the United States, California's Air Resources Board conducted a CADAMP consisting of 12 sites which operated from 2002 to 2006 (CADAMP, 2010). Measuring 30 dioxin-like congeners including PCDDs, PCDFs, and PCBs, their average concentration for urban sites was just above 30 fg TEQ/m^3, which was about twice the total TEQ found at the single rural site of the program. Their program was modeled after EPA's NDAMN program and also included measurements of polybrominated diphenyl ethers. Another study with longer-term air measurement similar to NDAMN and CADAMP occurred between November 2004 and December 2007, and entailed four sites around the Great Lakes of the United States (Venier et al., 2009). Individual samples were obtained over a 24-day continuous period for three rural and remote sites and for a 48-hour period for an urban site near Chicago, Illinois. A total of 185 samples showed similar concentrations as the California program, and a similar difference between the urban and remote sites: the average for Chicago was 35 fg TEQ/m^3 while it was 2.3, 7.4, and 13 fg TEQ/m^3 for the three remote and rural sites. The state of Connecticut has similarly conducted long-term air modeling for dioxin-like compounds, with results in rural areas in the low fg TEQ/m^3 as found in NDAMN (Hunt and Lihzis, 2011).

Table 4-5 shows a comparison of the four highest measurements with the station average, which is calculated for all other moments not including the high measurement. A very interesting trend emerges here. For Stations 3 and 20, the concentrations of all congeners and homologue groups in the anomalous reading are substantially higher than the station average, from 10 times higher to over 100 times higher. The only pattern for these two stations is that everything appears elevated. For Stations 28 and 29, a very different picture emerges. Here it is only the dioxin congeners and dioxin homologue group concentrations that are 10 to more than 100 times higher than the station average. For the furan congeners, furan homologues, and PCBs, the concentrations are only slightly elevated and even less than the station average. Upon further inspection, it is noted that the station averages of dioxins (congeners and homologues) in Stations 28 and 29 are also generally higher, by about a factor of 2, than station averages for Stations 3 and 20. Meanwhile, furan and PCB congener/homologue group averages are all about the same for all four stations. These trends suggest a source near Stations 28 and 29 that might generally elevate dioxin concentrations with the potential for very high dioxin concentrations occasionally. These sources would not appear to influence the general background of furans and PCBs. This pattern of exaggerated elevation in dioxins, while essentially background levels of furans, was also found in ball clay, which was discovered to be a contaminant in animal feed in the 1990s. As described in Ferario et al. (2000), samples of ball clay from animal feeds showed TEQ concentrations above 1,500 ppt (for comparison, soil concentrations are typically 10 ppt TEQ or less), explained in full by elevated dioxins while furan concentrations were either absent or at least 2 orders of magnitude lower than dioxin concentrations. Recently, Chinese investigators have observed this pattern of high PCDD and reduced or absent PCDF concentrations in air samples collected near six ceramic plants in China. Analyses of the exhaust gases indicate that these plants might be contributing significant concentrations of dioxin TEQ to the environment in China. Kaolinitic clays are the source materials for this manufacturing process (Lu et al., 2012). Investigations have not occurred to identify potential sources near Sites 28 and 29; certainly it is possible that combustion of a product high in PCDDs in comparison to PCDFs such as clays might explain the findings in these monitors. Thermal processes that preferentially emit dioxins over furans could also be the cause.

4.4. REFERENCES

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Table 4-1. Operating status of all stations over all moments

Station Number	Moment Number																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	TOTAL √
1	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**29**
3	**NA**	√	√	√	**NA**	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	**25**
4		√	√	**NA**	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	√	√	**NA**	**NA**	**NA**	**22**
5	√	√	√	√	√	√	√	√	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**28**
6	√	√	√	**NA**	√	**NA**	**NA**	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	**24**
7	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**29**
8	√	√	√	√	√	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**28**
9	√	√	√	√	√	**NA**	**NA**	**NA**	√	**NA**	√	√	**NA**	√	√	**NA**	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	**22**
10	√	√	√	√	√	√	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**28**
11								√	√	**NA**	√	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**20**
12							√	√	√	**NA**	**NA**	√	√	√	√	√	√	√	√	√	√	**NA**	√	√	√	√	**NA**	**NA**	√	**18**
13						√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	**NA**	**22**
14							√	√	√	√	**NA**	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	**20**
15							√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	**22**
16									√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	**19**
17											√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	**18**
18													√	√	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	**NA**	√	**15**
19									√	√	√	√	√	√	√	√	√	√	√	**NA**	√	√	**NA**	√	√	√	√	**NA**	√	**18**
20									√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**21**
21									√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**21**

Table 4-1. Operating status of all stations over all moments (continued)

Station Number	Moment Number																													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	TOTAL √
22										√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**20**
23										√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**20**
24									√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**21**
25									√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**21**
26									√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**21**
27									√	√	√	√	√	√	√	**NA**	√	√	√	√	√	√	√	√	√	√	√	√	√	**20**
28															√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**15**
29										√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	√	√	√	√	√	√	**19**
30												√	√	√	√	√	√	√	√	√	√	√	√	√	**NA**	√	√	√	√	**17**
31													√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**17**
32															√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	**15**
33																		√	√	**NA**	√	√	√	√	√	√	√	√	√	**11**
34																		√	√	√	√	√	√	√	√	√	√	√	√	**12**
35																						√	√	√	√	√	**NA**	√	√	**7**
TOTAL	**7**	**9**	**9**	**7**	**8**	**8**	**10**	**10**	**21**	**21**	**23**	**26**	**28**	**28**	**31**	**29**	**29**	**33**	**33**	**31**	**33**	**32**	**32**	**34**	**33**	**34**	**31**	**24**	**31**	**685**

Notes: Station 2 was a QA/QC station, located adjacent to Station 1 for most of the sampling program. Results for Station 2 not included on table.
Key: "√" = station operating; " " (blank) = station not yet operating; NA = data not available, due mostly to the station not operating but also, on occasion, to QA failures at the lab or lost sample (see text).

Table 4-2. Comparison of congener-specific results from laboratory blanks with those from remote, rural, and urban stations of NDAMN

Congener	NDAMN Results, pg[1]			Blank Results, pg				
				Target[2]	Field		Laboratory	
	Remote (n=153)	Rural (n=463)	Urban (n=69)		Actual[3] (n=56)	Percent Positive[4]	Actual[3] (n=108)	Percent Positive[4]
2,3,7,8-TCDD	0.4	4	5	0.5	<0.1	2	0.1	2
1,2,3,7,8-PeCDD	2	20	27	1.5	0.1	2	0.2	3
1,2,3,4,7,8-HxCDD	3	27	31	2.5	0.1	2	0.3	9
1,2,3,6,7,8-HxCDD	6	50	56	2.5	0.1	4	0.5	6
1,2,3,7,8,9-HxCDD	5	49	54	2.5	0.1	4	0.5	4
1,2,3,4,6,7,8-HpCDD	76	718	716	2.5	5.1	85	10.2	93
OCDD	265	2,521	2,356	20.0	32.1	6	43.3	99
2,3,7,8-TCDF	2	14	21	0.5	0.1	2	0.1	7
1,2,3,7,8-PeCDF	2	14	20	1.5	0.1	2	0.1	5
2,3,4,7,8-PeCDF	3	24	32	1.5	0.2	2	0.2	7
1,2,3,4,7,8-HxCDF	3	31	38	1.5	0.3	7	0.3	19
1,2,3,6,7,8-HxCDF	3	28	40	1.5	0.3	4	0.3	15
2,3,4,6,7,8-HxCDF	5	37	46	1.5	0.8	39	1.1	84
1,2,3,7,8,9-HxCDF	1	5	15	1.5	0.1	6	0.1	6
1,2,3,4,6,7,8-HpCDF	20	158	187	2.5	1.3	20	1.6	94
1,2,3,4,7,8,9-HpCDF	2	20	18	2.5	0.1	2	0.2	8
OCDF	29	139	119	4.0	1.5	37	3.3	88
PCB 77	238	448	942	20.0	43.1	98	31.7	99
PCB 105	1,260	2,401	6,408	500.0	518.6	98	271.6	99
PCB 118	3,316	6,650	17,191	300.0	1,017.3	98	556.8	99
PCB 126	8	32	68	2.0	2.5	65	1.3	71
PCB 156	214	375	895	80.0	124.1	98	72.6	99
PCB 157	48	80	191	20.0	26.6	98	15.7	99
PCB 169	0	5	6	1.0	<0.1	6	0.2	8

Notes: TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin;
HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin;
OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran;
HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran;
TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl.

Table 4-2. Comparison of congener-specific results from laboratory blanks with those from remote, rural, and urban stations of NDAMN (continued)

[1]Average measurement in pg, independent of volume (see text for more detail), assuming non-detects equal to 0.
[2]"Target" levels were the method detection limit levels determined in method development prior to NDAMN.
[3]"Actual" levels were the average mass measured in 56 field and 108 laboratory method blank samples during NDAMN, with non-detects equal to 0.
[4]"Percent Positive" was the percentage of field and method blanks with quantified measurements.

Table 4-3. Comparison of average concentrations in the NDAMN monitors, #1 and #3, with the adjacent QA sampler, #2, the correlation coefficient, *r*, between the set of measurements, and the average Relative Percent Difference, RPD, between the set of measurements (concentrations in fg/m^3; NA = no data available)

	Penn Nursery (*n* = 18)				Clinton Crops (*n* = 9)			
Congener	St #1	St #2	*R*	RPD	St #3	St #2	*R*	RPD
2,3,7,8-TCDD	0.88	0.82	0.95	17	0.52	0.58	−0.10	31
1,2,3,7,8-PeCDD	4.56	4.33	0.98	18	2.97	3.21	−0.05	24
1,2,3,4,7,8-HxCDD	5.02	4.96	0.99	16	3.34	3.19	0.69	20
1,2,3,6,7,8-HxCDD	8.30	8.19	0.97	19	6.32	5.99	0.68	21
1,2,3,7,8,9-HxCDD	7.41	7.38	0.97	20	5.73	5.37	0.80	18
1,2,3,4,6,7,8-HpCDD	118.72	113.17	0.98	23	71.44	69.59	0.98	9
OCDD	533.86	417.23	0.88	36	253.37	282.76	0.88	16
2,3,7,8-TCDF	2.30	2.40	0.84	18	3.12	2.87	0.74	15
1,2,3,7,8-PeCDF	2.19	2.20	0.83	16	3.62	3.32	0.75	13
2,3,4,7,8-PeCDF	3.53	3.64	0.91	16	6.69	5.89	0.81	17
1,2,3,4,7,8-HxCDF	4.35	4.23	0.85	16	8.28	7.38	0.84	17
1,2,3,6,7,8-HxCDF	4.42	4.39	0.72	16	7.72	5.85	0.59	16
2,3,4,6,7,8-HxCDF	5.16	5.06	0.87	16	10.31	9.30	0.83	18
1,2,3,7,8,9-HxCDF	0.93	0.99	0.96	21	0.82	0.72	0.96	33
1,2,3,4,6,7,8-HpCDF	28.74	26.97	0.81	17	37.78	35.70	0.85	16
1,2,3,4,7,8,9-HpCDF	2.70	2.69	0.93	17	4.63	4.19	0.92	20
OCDF	29.32	26.41	0.93	24	27.16	27.15	0.97	14
PCB 77	58.38	81.15	0.61	33	93.93	102.17	0.89	24
PCB 81	NA	NA	----		7.17	6.68	0.57	20
PCB 105	267.41	500.91	0.27	39	377.50	487.73	0.79	16
PCB 114	NA	NA	----		31.06	35.48	0.87	25
PCB 118	761.72	1,318.11	0.15	39	877.40	1,141.23	0.87	30
PCB 123	NA	NA	----		17.82	21.16	0.87	27
PCB 126	7.14	8.46	0.92	23	7.04	17.91	−0.26	44
PCB 156	48.28	90.75	0.22	39	52.24	86.37	0.85	45
PCB 157	10.85	20.38	0.25	38	11.49	19.03	0.83	46
PCB 167	NA	NA	----		21.58	48.19	0.57	56
PCB 169	0.85	0.82	0.94	38	1.61	2.70	−0.24	37
PCB 189	ND	ND	----		4.24	7.01	−0.15	40

Table 4-3. Comparison of average concentrations in the NDAMN monitors, #1 and #3, with the adjacent QA sampler, #2, the correlation coefficient, *r*, between the set of measurements, and the average Relative Percent Difference, RPD, between the set of measurements (concentrations in fg/m^3; NA = no data available) (continued)

Notes: TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl.

Table 4-4. Comparison of congener concentrations in co-located samplers in Pennsylvania for two occurrences with discrepencies in volume (Spring and Summer, 2000) and all co-located samples in Pennsyania (concentrations in fg/m^3; ND = no data, NA = not applicable, RPD = relative percent difference)

Congener	Spring 2000			Summer 2000			All Other Samples (n=17)		
	St #1	St #2	RPD	St #1	St #2	RPD	St #1	St #2	RPD
2,3,7,8-TCDD	1.5	1.5	3	0.33	ND	NA	0.9	0.9	17
1,2,3,7,8-PeCDD	9.4	10.6	12	1.70	1.31	26	4.7	4.5	18
1,2,3,4,7,8-HxCDD	12.9	15.5	19	2.11	1.56	30	5.2	5.2	16
1,2,3,6,7,8-HxCDD	22.8	30.1	28	5.14	3.95	26	8.5	8.4	19
1,2,3,7,8,9-HxCDD	22.0	28.7	27	3.67	3.24	12	7.6	7.6	20
1,2,3,4,6,7,8-HpCDD	318.4	606.6	62	89.09	63.39	34	120.5	116.1	22
OCDD	1,325.9	3,303.8	85	507.08	287.25	55	535.4	424.9	35
2,3,7,8-TCDF	5.6	11.1	66	2.82	3.02	7	2.3	2.4	19
1,2,3,7,8-PeCDF	4.7	9.4	66	2.23	1.78	23	2.2	2.2	16
2,3,4,7,8-PeCDF	8.6	16.8	65	3.38	2.98	13	3.5	3.7	17
1,2,3,4,7,8-HxCDF	8.2	16.7	68	3.94	3.05	25	4.4	4.3	16
1,2,3,6,7,8-HxCDF	7.4	14.4	64	3.52	3.05	14	4.5	4.5	16
2,3,4,6,7,8-HxCDF	10.1	21.3	71	4.93	4.44	11	5.2	5.1	17
1,2,3,7,8,9-HxCDF	0.9	1.8	59	1.18	1.23	4	0.9	1.0	33
1,2,3,4,6,7,8-HpCDF	41.2	87.9	72	23.22	17.73	27	29.1	27.5	17
1,2,3,4,7,8,9-HpCDF	5.7	11.9	70	2.48	1.73	36	2.7	2.7	16
OCDF	46.5	106.2	78	28.42	21.01	30	29.4	26.7	24
PCB 77	36.1	82.3	78	46.67	45.24	3	59.1	83.3	34
PCB 105	205.8	683.8	107	252.58	280.96	11	268.3	513.9	41
PCB 118	548.3	1,846.9	108	745.44	790.33	6	762.7	1,349.2	41
PCB 126	8.0	17.0	72	6.03	5.73	5	7.2	8.6	24
PCB 156	46.8	147.2	104	53.17	64.97	20	48.0	92.3	40
PCB 157	11.1	32.6	98	13.00	15.94	20	10.7	19.9	39
PCB 169	1.5	2.0	28	0.76	0.64	18	0.9	0.8	39
PCB 189	1.5	1.5	3	0.33	ND	NA	0.9	0.9	17
Average RPD			66			20			25
Volume, m^3	4,859	1,198		5,564	3,474		6,585	7,368	

Table 4-4. Comparison of congener concentrations in co-located samplers in Pennsylvania for two occurrences with discrepencies in volume (Spring and Summer, 2000) and all co-located samples in Pennsyania (concentrations in fg/m^3; ND = no data, NA = not applicable, RPD = relative percent difference) (continued)

Notes: TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl.

Table 4-5. Survey-wide statistics for all congeners and homologue groups (concentrations in fg/m^3)

Congener	Percentage Detected	Mean	SD	95% CI	Median	Max
2,3,7,8-TCDD	85	0.6	1.2	0.5−0.7	0.3	23
1,2,3,7,8-PeCDD	89	3.1	5.9	2.7-3.6	1.7	87
1,2,3,4,7,8-HxCDD	94	4.2	10.4	3.4−5.0	2.1	209
1,2,3,6,7,8-HxCDD	97	7.3	15.3	6.1−8.4	3.8	257
1,2,3,7,8,9-HxCDD	96	7.2	15.3	6.1−8.3	3.5	305
1,2,3,4,6,7,8-HpCDD	100	102.3	243.6	85.4−120.5	52.8	5,487
OCDD	100	352.8	973.4	28−425	187.4	23,953
2,3,7,8-TCDF	96	2.1	9.6	1.4−2.8	1.1	249
1,2,3,7,8-PeCDF	94	2.4	14.1	1.3−3.4	1.1	361
2,3,4,7,8-PeCDF	96	4.3	28.8	2.1−6.4	1.7	738
1,2,3,4,7,8-HxCDF	98	5.6	41.4	2.6−8.7	2.2	1,056
1,2,3,6,7,8-HxCDF	98	4.9	31.1	2.6−7.2	2.0	787
2,3,4,6,7,8-HxCDF	99	6.4	41.3	3.3−9.5	2.6	1,031
1,2,3,7,8,9-HxCDF	74	1.5	22.3	0−3.1	0.3	597
1,2,3,4,6,7,8-HpCDF	100	27.3	178.1	14.0−40.6	11.3	4,498
1,2,3,4,7,8,9-HpCDF	91	3.5	25.2	1.6−5.4	1.2	644
OCDF	99	21.9	142.8	11.2−32.5	9.8	3,721
Total TCDF	99	75.4	263.2	55.7−94.9	44.1	6,300
Total TCDD	98	18.4	69.9	13.2−23.6	9.0	1,732
Total PeCDF	98	57.2	303.4	34.6−79.8	26.6	7,619
Total PeCDD	94	40.0	132.5	30.1−49.8	18.1	2,962
Total HxCDF	99	58.2	262.7	38.9−77.8	26.9	6,467
Total HxCDD	99	102.1	220.2	85.7−118.5	52.3	3,293
Total HpCDF	99	43.9	232.7	26.6−61.3	19.2	5,735
Total HpCDD	98	241.6	520.0	202.8−281.3	131.1	10,975
PCB 77	100	157.2	1,286.7	61.3−253.0	36.9	31,167
PCB 81	100	12.5	104.8	1.0−24.1	2.9	1,539
PCB 105	99	629.8	3,601.8	361−898	188.3	80,653
PCB 114	100	47.4	375.3	6.4−88.9	13.9	6,895
PCB 118	99	1,430.3	6,248.5	965−1,896	489.5	134,846
PCB 123	100	32.8	273.8	2.7−62.9	9.1	4,923

Table 4-5. Survey-wide statistics for all congeners and homologue groups (concentrations in fg/m^3) (continued)

Congener	Percentage Detected	Mean	SD	95% CI	Median	Max
PCB 126	100	6.9	32.7	4.5−9.3	3.0	758
PCB 156	99	67.7	168.6	55.1−80.2	30.2	2,633
PCB 157	99	14.9	37.9	12.1−17.7	6.8	590
PCB 167	100	22.2	67.4	14.8−29.6	9.9	1,083
PCB 169	83	0.9	9.7	0.2−1.7	0.3	260
PCB 189	100	2.7	4.6	2.2−3.2	1.7	50
TEQ DF		10.5	33.2	8.1−12.9	5.9	773
TEQ P		0.8	3.7	0.6−1.1	0.4	84
TEQ DFP		11.3	36.1	8.7−13.9	6.5	857

Notes: TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl.; DF=dioxins and furans when used in TEQ DF; P = PCBs when used in TEQ P; DFP = dioxins, furans, and PCBs when used in TEQ DFP.

n = 685 except for PCBs 81, 114, 123, 167, and 189, where *n* = 318. See Section 3.1 for more detail.

Table 4-6. Comparison of the four highest concentrations measured with the station average where that concentration was measured (for each station, the date given as month/year—1/2000—is compared to the station average—AVG; all concentrations in fg/m^3)

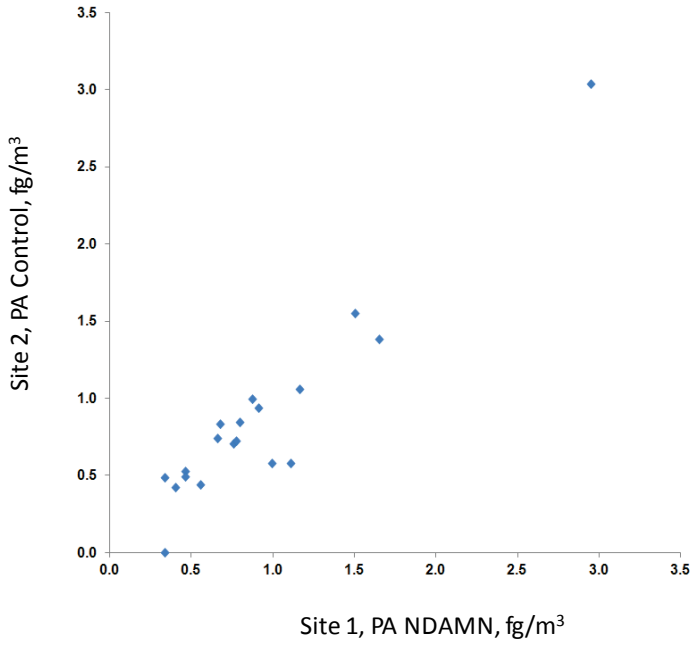
Congener	Station 20, MN		Station 3, NC		Station 29, OR		Station 28, CA	
	1/2000	AVG	11/2001	AVG	9/2000	AVG	2/2003	AVG
2,3,7,8-TCDD	5.6	0.3	6.3	0.5	22.6	1.2	7.0	2.1
1,2,3,7,8-PeCDD	55.9	1.8	42.5	2.8	68.3	8.5	86.5	9.7
1,2,3,4,7,8-HxCDD	118.9	2.9	57.6	3.4	55.8	13.6	209.0	8.2
1,2,3,6,7,8-HxCDD	191.4	4.4	125.0	6.0	100.6	22.5	257.0	14.1
1,2,3,7,8,9-HxCDD	98.4	4.9	105.5	5.6	99.3	22.2	304.9	13.8
1,2,3,4,6,7,8-HpCDD	1,336.8	73.6	860.7	69.8	1,046.5	321.6	5,487.4	180.7
OCDD	2,892.5	297.4	1,185.3	235.0	2,627.0	914.0	23,953.0	582.3
2,3,7,8-TCDF	249.0	2.0	48.1	3.2	2.1	1.9	2.5	2.0
1,2,3,7,8-PeCDF	361.3	1.7	95.2	3.5	2.6	1.8	5.5	1.8
2,3,4,7,8-PeCDF	738.0	3.0	213.3	6.6	5.0	3.4	7.4	3.0
1,2,3,4,7,8-HxCDF	1,055.9	3.6	330.4	7.9	6.7	3.9	13.8	3.8
1,2,3,6,7,8-HxCDF	786.7	3.0	256.4	7.3	4.8	3.6	14.2	3.7
2,3,4,6,7,8-HxCDF	1,030.5	3.9	386.5	10.2	5.8	4.5	12.9	4.6
1,2,3,7,8,9-HxCDF	596.9	0.8	43.9	1.6	1.7	0.6	2.7	0.3
1,2,3,4,6,7,8-HpCDF	4,498.2	16.1	1,532.3	39.3	37.8	20.0	74.0	21.5
1,2,3,4,7,8,9-HpCDF	644.4	2.2	193.1	4.6	3.5	2.5	28.8	2.1
OCDF	3,721.4	12.7	815.8	29.1	24.4	20.5	85.4	16.8
Total TCDF	6,299.9	61.0	2,749.3	132.9	91.9	63.2	110.3	65.7
Total TCDD	327.9	13.9	1,732.2	32.7	441.1	27.2	120.5	20.4
Total PeCDF	7,619.2	36.6	2,557.0	91.9	63.8	41.5	118.8	55.1
Total PeCDD	1,153.5	22.7	2,962.4	51.9	968.2	97.7	643.1	57.3
Total HxCDF	6,467.3	34.0	2,363.8	89.3	96.2	53.2	130.2	66.9
Total HxCDD	2,235.0	63.7	3,293.2	100.1	1,819.5	333.1	2,758.2	164.7
Total HpCDF	5,735.3	26.0	2,224.8	58.0	103.2	41.3	164.0	40.8
Total HpCDD	2,907.2	166.0	2,302.0	171.1	2,997.1	799.6	10,974.8	392.1

Table 4-6. Comparison of the four highest concentrations measured with the station average where that concentration was measured (for each station, the date given as month/year—1/2000—is compared to the station average—AVG; all concentrations in fg/m^3) (continued)

Congener	Station 20, MN		Station 3, NC		Station 29, OR		Station 28, CA	
	1/2000	AVG	11/2001	AVG	12/2000	AVG	8/2001	AVG
PCB 77	452.9	27.0	357.0	91.8	65.8	52.6	58.0	93.2
PCB 81							3.8	3.0
PCB 105	702.7	124.3	3,017.0	447.1	618.1	513.1	238.1	580.3
PCB 114							21.2	29.7
PCB 118	967.7	304.0	8,207.5	1,096.6	2,443.6	1,313.0	736.0	1,659.6
PCB 123						7.0	12.0	17.4
PCB 126	758.2	3.2	144.0	7.6	6.2	4.4	4.0	8.6
PCB 156	724.6	23.6	599.0	72.1	131.3	124.2	32.3	89.6
PCB 157	262.5	5.4	156.2	16.1	27.7	26.9	7.3	20.0
PCB 167					0.0	12.8	13.7	26.2
PCB 169	260.4	0.6	ND	1.4	0.3	0.4	0.4	0.5
PCB 189						1.0	1.9	2.0
TEQ DF	773.3	6.6	277.5	11.1	131.8	21.8	240.7	20.0
TEQ P	83.8	0.4	14.8	0.9	0.7	0.5	0.4	1.0
TEQ DFP	857.1	6.9	292.3	11.9	132.6	22.3	241.2	21.0

Notes: TCDD = tetachlorodibenzo-*p*-dioxin; PeCDD = pentachlorodibenzo-*p*-dioxin; HxCDD = hexachlorodibenzo-*p*-dioxin; HpCDD = heptachlorodibenzo-*p*-dioxin; OCDD = octochlorodibenzo-*p*-dioxin; TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCB = tetrachlorobiphenyl; PeCB = pentachlorobiphenyl; HxCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl; DF=dioxins and furans when used in TEQ DF; P = PCBs when used in TEQ P; DFP = dioxins, furans, and PCBs when used in TEQ DFP.

a. Moments 1 through 19 at Penn Nursery in Pennsylvania.



b. Moments 20 through 29 (excluding 28) at Clinton Crops, NC.

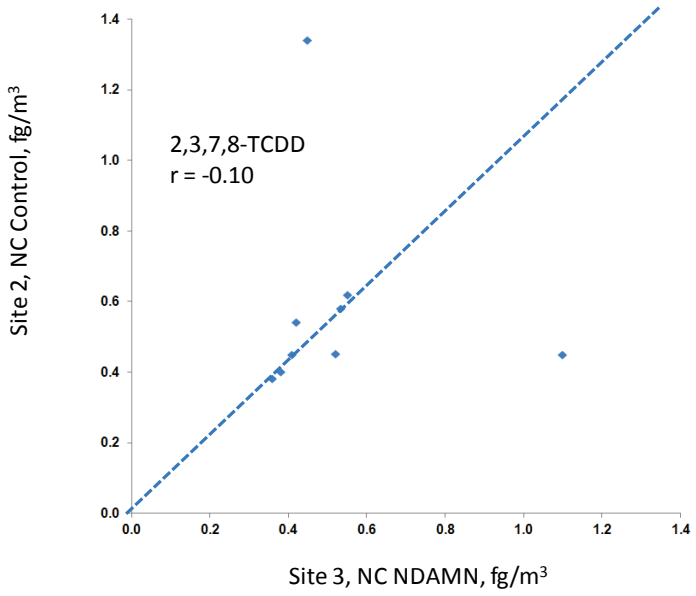
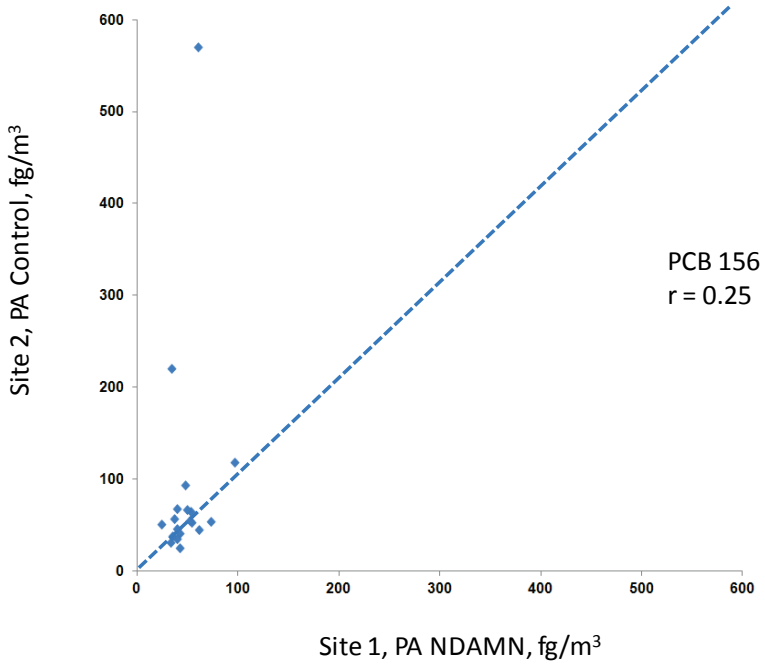


Figure 4-1. Comparison of control and NDAMN results for 2,3,7,8-TCDD (the perfect correlation $y = x$ is shown as dashed line).

a. Moments 1 through 19 at Penn Nursery in Pennsylvania.



b. Moments 20 through 29 (excluding 28) at Clinton Crops, NC.

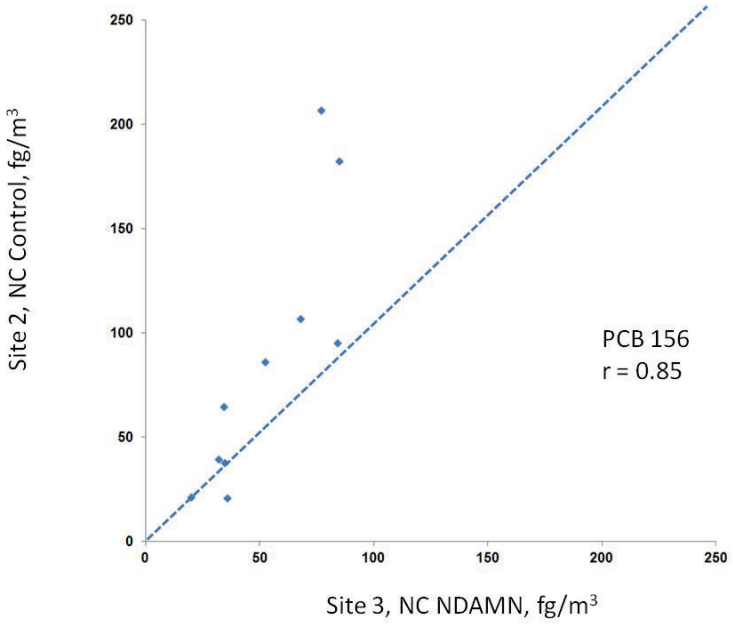


Figure 4-2. Comparison of control and NDAMN results for PCB 156 (the perfect correlation *y* = *x* is shown as dashed line).

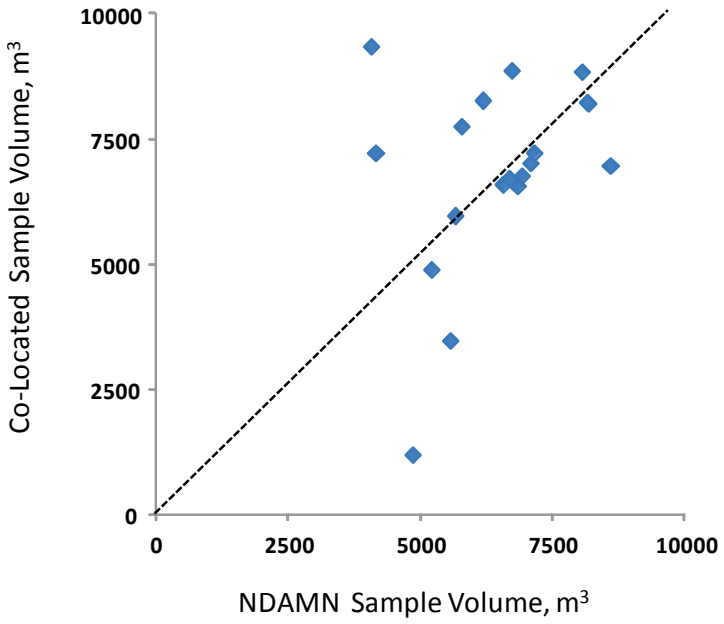


Figure 4-3. Comparison of control and NDAMN sample volumes (the perfect correlation $y = x$ is shown as dashed line).

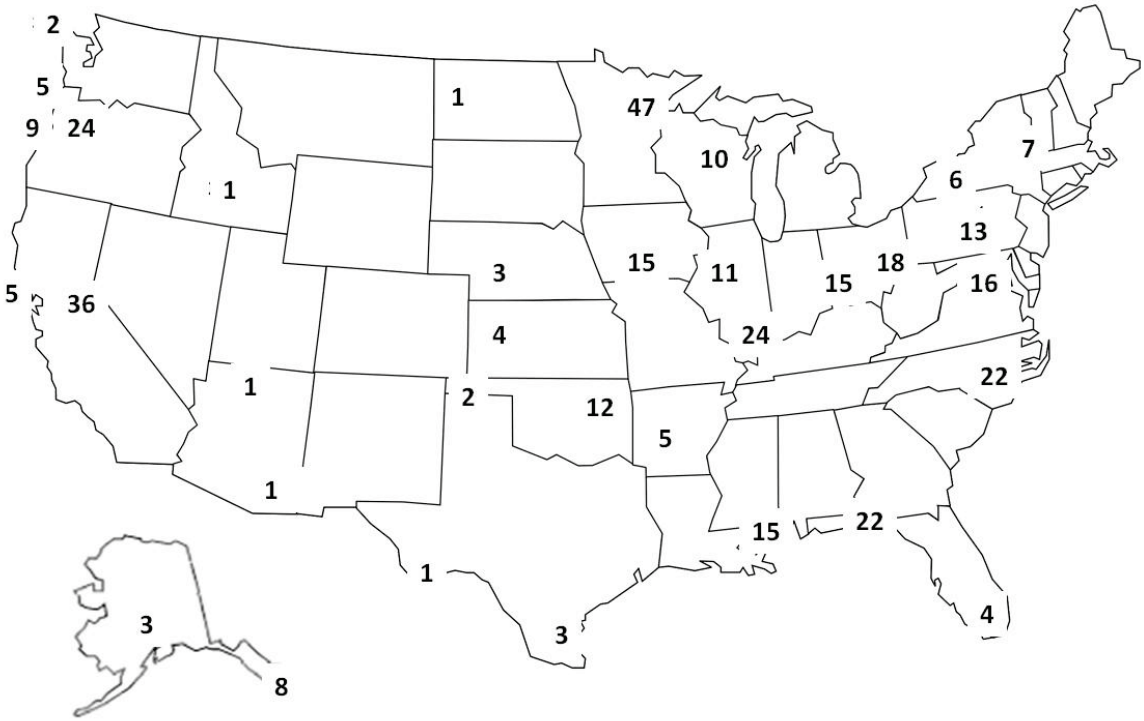


Figure 4-4. Average TEQ concentrations found at all NDAMN stations.

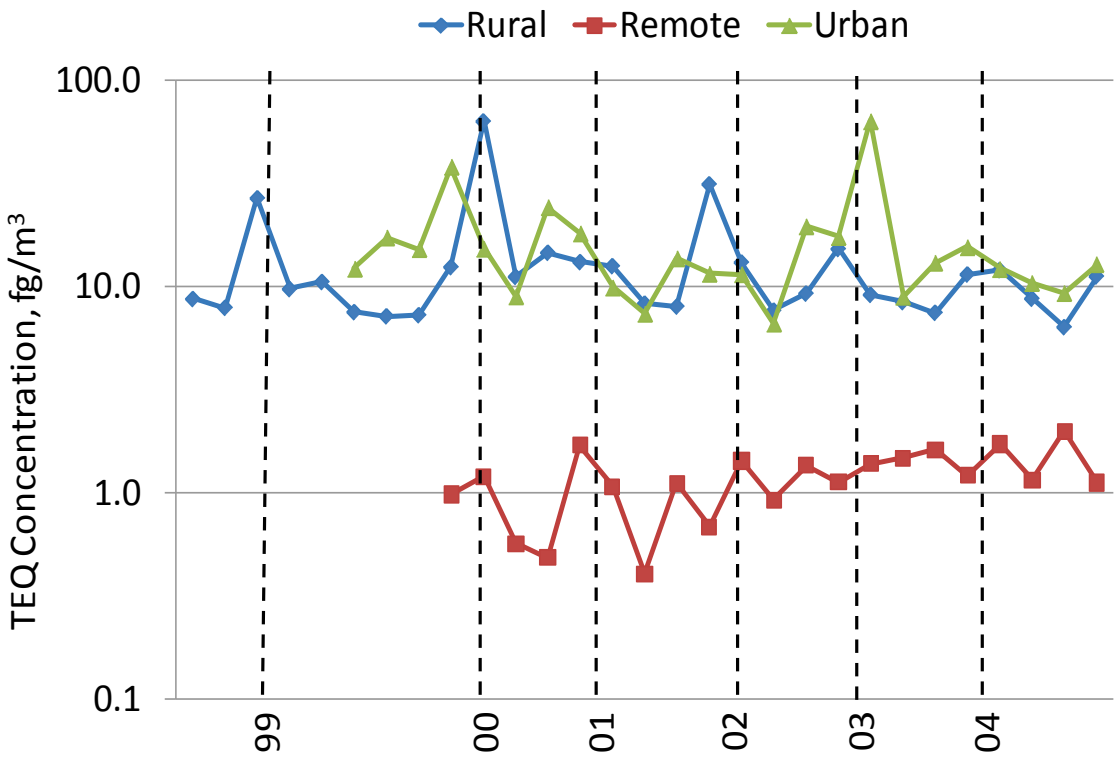


Figure 4-5. Temporal variability of TEQ concentrations averaged by station characterization (note: calendar year 1999 had six sample moments, 1998 had three moments, and all other years had four moments. Each year identified on the x-axis corresponds to January of that year).

APPENDIX A. DESCRIPTION OF EXCEL WORKBOOK CONTAINING NDAMN DATA

The NDAMN Workbook contains three worksheets: (1) Title Page, (2) All NDAMN Raw Data 1998 to 2004, and (3) NDAMN concentrations at non-detect (ND) equal to zero. The following comment and column descriptions are included for each worksheet:

Title Page: This contains a brief description of the database, a map showing station locations, a legend to the map providing location names, the full citation of the report, and contact information.

All NDAMN Raw Data: This worksheet contains the raw data, including sample identification information, sample volumes, and all analytical data as reported by the laboratory for each sample. The column definitions, mostly self explanatory, are as follows:

Column A: Station name
Column B: Nearest town
Column C: Type of station, characterized as either "rural," "urban," or "remote." See Chapter 2 for further discussion on the study design.
Column D: Latitude
Column E: Longitude
Column F: Station number
Column G: Sampling moment. There were 29 sampling moments in the study. See Chapter 2 for further discussion on the study design.
Column H: Dates of sampling including month/day to month/day (06/16–07/14); formatted as text.
Column I: Year of sampling
Column J: Season of sampling
Column K: Operating Status. There are three conditions of operation: (1) "Operating" meaning that the sampler was fully operational and samples were delivered to the laboratory, (2) "Not Operating" meaning that for some reason, the sampler did not obtain a sample for analysis (it may have been operating a part of the time but then a failure resulted; for logistical or other reasons, it may not have been operating at all during the sampling moment, or some other reason), and (3) "QA Failure" meaning a sample was obtained and shipped to the laboratory where a quality assurance failure resulted in no or only partial data being developed. The analytical result fields provide more information on the status of measurements.
Column L: Sample volume, m^3
Columns M–AW: Laboratory analytical results for: 7 dioxin congeners, 10 furan congeners, 8 dioxin and furan homologue group concentrations, and 12 dioxin-like PCB measurements. See Table 3-1 for a complete list of the analytes measured in the study. The information in each cell can take these forms: (1) picograms of analyte measured by the laboratory (reported in 2 or 3 places after the decimal point), the concentration is simply these picograms divided by the sample volume; (2) blank—in some cases, this analyte was not measured in the sample—this was the case for several PCB congeners which were measured starting later in the program. In other cases, the sampler was not operating so there is nothing to report, (3) ND—this analyte not detected in the sample (see Table 3-2 for the analyte-specific detection limit in pg). To get the

sample- and analyte-specific detection limit, simply divide the analyte specific detection in Table 3-2 with the sample-specific volume provided in Column L; and (4) QA Failure—no value can be reported due to a quality assurance failure at the laboratory.

NDAMN Concentrations, ND = 0: This is the complete set of data where concentrations were derived by dividing the picograms reported by the laboratory by the sample volumes, with zero values substituted for non-detects. This was the data set upon which all of the results in this report were derived. The column definitions, mostly self-explanatory, are as follows:

Column A: Station name
Column B: Station number
Column C: Sample moment number
Column D: Dates of sampling
Column E: Year of sampling
Column F: Season of sampling
Columns G through AQ: Final concentrations, in fg/m^3, for each of 7 dioxin congeners, 10 furan congeners, 8 dioxin and furan homologue group concentrations, and 12 dioxin-like PCB measurements. The information in each cell can take these forms: (1) the concentration calculated as the mass of analyte reported by the laboratory, in picograms, divided by the sample volume (both of these on the previous worksheet), with conversion to arrive at the concentration in fg/m^3. The concentration is formatted to report concentrations two places after the decimal point; (2) blank—there are three possible reasons for a blank: (a) the analyte was not measured in the sample while others may have been measured, (b) the sampler was not operating so no analytes were measured in the sample, and (c) there was a QA failure for this analyte (in some cases, the QA failure pertained to all analytes, but in others, a portion of the analytes were measured and reported); and (3) the value "0." Non-detects were replaced by zeros.
Column AR, AS, and AT: It is noted that row 9, columns G through AI, contain TEF values for each of the congeners in columns G through AI. There is no TEF value associated with the homologue group concentrations reported in columns AJ through AQ. Rows AR, AS, and AT provide calculations for TEQ concentrations of dioxins and furans (Column AR), dioxin-like PCBs (Column AS), and Total (sum of columns AR and AS).

APPENDIX B. QUALITY ASSURANCE PROJECT PLAN FOR NDAMN

Two Quality Assurance Project Plans (QAPPs) are included in this Appendix:

1. A QAPP for field implementation procedures prepared by Battelle dated April 2001 and titled "Dioxin Exposure Initiative Implementation, Operation, and Maintenance of the National Dioxin Air Monitoring Network (NDAMN)" that was signed by principals from EPA and Battelle.

2. A QAPP for the analytical methods prepared by the Environmental Chemistry Laboratory of EPA dated July 2001 and titled "Quality Assurance Project Plan for the Dioxin Exposure Initiative: National Dioxin Air Monitoring Network" that had signature blocks but was not signed.

It should be noted that these are provided here as examples of the documents developed over the course of NDAMN that were used in the implementation of the study. For example, before Battelle was the primary contractor for NDAMN implementation, that task was performed by Versar, Inc, of Springfield, Virginia. There were documents associated with siting of the samplers on public lands and maintenance of samplers. There were sample transmittal forms and lab receipt information. There were also documents associated with shutdown of the field samplers and disposition of equipment. These examples are provided simply to give readers a sense of the complexity and the procedures used in NDAMN for sampling and analysis.

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