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## An Exploratory Study: Assessment of Modeled Dioxin Exposure in Ceramic Art Studios

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National Center for Environmental Assessment Office of Research and Development U.S. Environmental Protection Agency Washington, DC

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#### ABSTRACT

The purpose of this report is to describe an exploratory investigation of potential dioxin exposures to artists/hobbyists who use ball clay to make pottery and related products. Dermal, inhalation and ingestion exposures to clay were measured at the ceramics art department of Ohio State University in Columbus, OH. The measurements were made in two separate studies, one in April 2003 and one in July 2004. This assessment combines the results of these two studies. Estimates of exposure were made based on measured levels of clay in the studio air, deposited on media representing food and on the skin of artists. Dioxin levels in the clay were based on levels reported in the literature for commercial ball clays commonly used by ceramic artists.

Hypothetical dioxin dose estimates were calculated for each subject assuming that all used a 20% ball clay blend with 162 pg TEQ/g. The single-day total doses across the 10 subjects were estimated to range from 0.49 to 20.81 pg TEQ/day, with an average of 3.45 pg TEQ/day. The dermal dose was the major contributor to total dose, exceeding 78% for all subjects. A Monte Carlo simulation suggested that ball clay exposures in a broad population of artists could extend to levels lower or higher than the levels estimated for the 10 subjects. Comparing US average background intakes (adjusted to an absorbed basis) to the 10 subject average dose from ball clay use, indicates that the average ball clay dose is 10% of the background CDD/CDF dose (34.4 pg TEQ/day).

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## LIST OF ABBREVIATIONS AND ACRONYMS

°C	degrees Centigrade
CDD	Chlorinated dibenzo- <i>p</i> -dioxin
CDD/F	Chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans
CDF	Chlorinated dibenzofuran
cm	centimeter
d	day
DI	Deionized
EDS	Energy dispersive spectroscopy
EPA	U.S. Environmental Protection Agency
ET	Extrathoracic
FDA	U.S. Food and Drug Administration
g	gram
GFF	Glass fiber filters
HpCDD	Heptachlorodibenzo-p-dioxin
hr	hour
HRMS	High-resolution mass spectrometry
HxCDD	Hexachlorodibenzo-p-dioxin
IRB	Institutional Review Board
kg	kilogram
Kow	Octanol-water partition coefficient
L	liter
L/min	liters per minute
LRB	Laboratory record book
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
MMAD	Mass median aerodynamic diameter
ND	Nondetect
ng	nanogram
NR	Not reported

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## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

OCDD	Octachlorodibenzo- <i>p</i> -dioxin
OSHA	Occupational Safety and Health Administration
OSU	Ohio State University
OZ	ounces
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxin
PCDF	Polychlorinated dibenzofuran
PCD/F	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PeCDD	Pentachlorodibenzo-p-dioxin
pg	picogram
PU	Pulmonary
QA	Quality assurance
QC	Quality control
$r^2$	Regression coefficient squared
SD	Standard deviation
SEM	Scanning electron microscopy
TB	Tracheobronchial
TCDD	Tetrachlorodibenzo-p-dioxin
TEF	Toxic equivalency factor
TEQ	Toxic equivalent
TOC	Total organic carbon
TWA	Time-weighted average
USGS	U.S. Geological Survey
WHO	World Health Organization
wt	Weight
μg	microgram
μL	microliter
μm	micrometer

#### PREFACE

Dioxins were discovered in ball clay in 1996 as a result of an investigation to determine the sources of elevated dioxin levels in two chicken samples from a national survey of poultry. The investigation indicated that the contamination source was ball clay added to chicken meal as an anti-caking agent. The purpose of this study is to evaluate another potential exposure scenario associated with ball clay, namely its use in ceramic art studios. This exploratory investigation makes preliminary exposure estimates that can be used to evaluate whether more detailed follow-up analyses are needed. Hypothetical dioxin exposure estimates were calculated using an assumption of dioxin levels in the ball clay based on measurements from other studies. The study was conducted during 2003 and 2004 by the National Center for Environmental Assessment with contract support provided by Battelle in Columbus, Ohio.

### AUTHORS, CONTRIBUTORS, AND REVIEWERS

#### **Principal Author**

John Schaum, National Center for Environmental Assessment, U.S. Environmental Protection Agency, Washington, DC (EPA Project Manager)

#### Authors

Ryan James, Battelle (Battelle Project Manager)

James Brown, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dwain Winters, Office of Pollution Prevention and Toxic Substances, U.S. Environmental Protection Agency, Washington, DC

#### Contributors

Ian MacGregor and Christine Lukuch of Battelle served as the technicians for the project.

#### Reviewers

Mark F. Boeniger, National Institute for Occupational Safety and Health, Cincinnati, OH

David Crawford, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC

Mike Dellarco, Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC

Kim Hoang, Region 9, U.S. Environmental Protection Agency, San Francisco, CA

Chong Kim, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Sid Soderholm, National Institute for Occupational Safety and Health, Washington, DC

Dan Stralka, Region 9, U.S. Environmental Protection Agency, San Francisco, CA

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1 2

#### **1. INTRODUCTION AND BACKGROUND**

Ball clay is a natural clay mined commercially in the United States, primarily in
Kentucky, Tennessee, and Mississippi. A total of 1.21 million metric tons was mined in the
United States in 2005. Its plasticity makes ball clay an important commercial resource for a
variety of commercial uses. In 2005, it was used as follows: floor and wall tile - 40%, sanitary
ware (sinks, toilets, etc.) - 25%, exports - 17%, ceramics - 11%, fillers, extenders and binders 4%, pottery - 1.5%, and miscellaneous purposes - 1.9% (USGS, 2007).

9 Dioxins were discovered in ball clay in 1996 as a result of an investigation to determine 10 the sources of elevated dioxin levels in two chicken samples from a national survey of poultry 11 (Ferrario et al., 1997). The investigation indicated that soybean meal added to chicken feed was 12 the source of the dioxin contamination. Further investigation showed that the dioxin 13 contamination occurred when ball clay was mixed with the soybean meal as an anti-caking agent 14 (Ferrario et al., 2000b; U.S. FDA, 2000). In 1997, the Food and Drug Administration (FDA) 15 asked producers or users of clay products in animal feeds to cease using ball clay in all animal 16 feeds and feed ingredients (U.S. FDA, 1997).

17 The purpose of this study is to characterize the possible dioxin exposures of artists using 18 ball clay in ceramic art studios. This exploratory investigation makes preliminary exposure 19 estimates that can be used to evaluate whether more detailed follow up analyses are needed. The 20 limited resources available for this study required a strategy to base the analysis on existing data 21 to the fullest extent possible.

22 Dioxin exposure is primarily a function of the dioxin concentration in the clay and an 23 individual's level of exposure to the clay. Although studies in the literature provided 24 information about dioxin levels in clay, no information could be found on clay exposure levels in 25 ceramic art studios. Therefore, this study was designed to measure total clay exposures in a 26 ceramic art studio. No dioxin measurements were made in this study, rather the dioxin levels in 27 ball clay were assumed based on measurements from other studies. Three exposure pathways 28 were evaluated: inhalation, dermal contact, and incidental ingestion. The evaluations involved 29 measuring levels of clay particulates in air, clay residues on skin, and clay deposition on media 30 representing food and beverages. These data provided a basis for estimating potential dioxin 31 exposures and resulting doses, conducting an initial analysis of which exposure pathways 32 contribute most to total dose, and evaluating how individual behaviors affect exposure/dose. 33 Ultimately, the data helped develop distributions for input parameters for conducting a Monte

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Carlo analysis to estimate how dioxin exposure/dose may vary across a wide population of
 artists.

3 An alternative way to evaluate dioxin exposures is by blood testing. While this provides 4 a direct measure of dioxin exposure, it represents exposures from all sources, not just work in an 5 art studio. Also, a blood study would not have provided any insights about how dioxin 6 exposures may occur in an art studio. Normal background exposures vary widely and factors 7 such as diet and age are known to have large impacts on dioxin body burden. Accordingly a 8 blood study would require a large number of subjects with controls to reduce the effects of these 9 factors. Also blood tests have very high analytical costs. On the basis of costs alone, blood 10 testing was beyond the scope of this effort. The clay exposure testing done here provided a low 11 cost way to explore the problem and gives future researchers an informed basis for deciding if 12 blood testing or other types of follow-up work are needed.

13 Dioxin concentrations and exposures are presented in terms of toxic equivalents (TEQs). 14 TEQs allow concentrations of dioxin mixtures to be expressed as a single value computed by 15 multiplying each congener concentration by a toxicity weight (toxic equivalency factor or TEF) 16 and summing across congeners. TEFs are expressed as a fraction equal to or less than 1 with 1 17 corresponding to the most toxic dioxin congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin 18 (2,3,7,8-TCDD). The TEQ data presented here are based on TEFs from the 1998 World Health 19 Organization (WHO) recommendations (Van den Berg et al., 1998). In 2005, WHO updated the 20 TEFs (Van den Berg et al., 2006). As discussed in Section 4, these updates had little impact on 21 the literature values used here, so no adjustments were made. 22 The term "dioxins" is used in this study to refer collectively to the tetra- through

octa-chlorinated dibenzo-*p*-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) with chlorine
substitutions in all of the 2,3,7,8 positions. This term is commonly defined to include the 12 coplanar pentachlorobiphenyls (PCBs) which also demonstrate dioxin-like toxicity. However,
PCBs are not addressed in this study. PCBs have been shown to make up a small fraction of the
total TEQs in a wide variety of background soils (U.S. EPA, 2007) and therefore are probably
not important contributors to TEQs in ball clay.

1 2

#### 2. APPROACH OVERVIEW

While working in a ceramics studio, artists may be exposed to dioxin-contaminated clay via three pathways: dermal contact, particle inhalation, and incidental ingestion. Exposure could also occur via open cuts or eyes and this possibility is discussed in Section 9 on uncertainty. The general strategy and procedures used to characterize each pathway are described below.

7 8

## 2.1. GENERAL STRATEGY

9 The site selected for this study was the Ceramics Area in Hopkins Hall at Ohio State 10 University (OSU) in Columbus, OH. The Ceramics Area, housed in the basement of Hopkins 11 Hall, has eight rooms, including classrooms, studios, a storage area, a glaze-mixing area, a clay 12 recycling area, and a furnace room. This facility was selected because it offered a convenient 13 location for assessing exposures during a variety of typical ceramic art activities.

14 The exposure measurements were carried out in two separate studies. The first study was 15 conducted in April 2003 and the second in July 2004. The results of both studies have been 16 combined in this report. Seven artisans and one nonartisan staff member in the OSU Ceramics 17 Department were recruited to serve as subjects for the first study, and two additional artisans 18 were recruited for the second study. An open solicitation was presented to the students and 19 departmental staff, and the first volunteers were selected. The subjects included three males and 20 seven females ranging in age from about 20 to 40 years. Approval for human subjects was 21 obtained via the Battelle Institutional Review Board (IRB) and EPA. Upon approval by the 22 Battelle IRB and EPA, OSU determined that review by their IRB was not necessary. The testing 23 was conducted while the subjects conducted a variety of unscripted tasks, including clay 24 mixing/preparation, sculpting, pottery wheel work, and molding.

To assess dioxin exposure levels, it is necessary to estimate dioxin levels in the various exposure media (i.e., clay used by the artists, dust particles suspended in the studio air, and dust settled onto surfaces). No actual dioxin measurements were made in this study. Rather, dioxin levels were estimated using literature-reported concentrations of dioxins in ball clay and information about the amount of ball clay in the clay mixtures used by the artists. Details about this procedure are discussed in Section 4.

A questionnaire was administered to subjects during the first study to gather information
 on their routines involving clay artwork. The questionnaire data are presented in Appendix A
 and summarized in Section 6.

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#### 1 2

3

## 2.2. CHARACTERIZATION PROCEDURES

The following procedures were used to characterize each exposure pathway.

## 4 **2.2.1. Dermal Contact**

5 Dermal contact with clay can occur via direct handling of the clay, deposition from the 6 air onto exposed skin, transfer from surfaces, and splashing during wheel operations. The 7 amount of clay on skin was measured using rinsing procedures. Additionally, surface wipes 8 were collected in work areas to evaluate dermal exposures via transfers from surfaces. To 9 further evaluate dermal exposure, a dermatologist examined the condition of the stratum 10 corneum, the outermost layer of skin, before and after each subject worked with clay. The 11 primary focus of this examination was to determine if any damage to skin may have occurred 12 that would affect dermal absorption.

13

## 14 **2.2.2. Inhalation**

15 Both personal and area air-monitoring techniques were used to assess inhalation 16 exposures. Personal air samplers provide data most representative of an individual's exposure 17 because they sample the air in a person's breathing zone and reflect changes in concentration due 18 to their movement. An area sampler provides a general indication of exposure for people in its 19 vicinity and also can achieve lower detection levels. Both the personal and area-monitoring 20 techniques provided particle size-selective data, so that the deposition site of the particles in the 21 respiratory tract (nose/mouth, tracheobronchial airways, and alveolar region) could be 22 determined.

23 Two types of personal air samplers were used: real-time and time-integrating. Similarly, 24 two types of area air samplers were used: real-time and time-integrating. The real-time air 25 samplers provided data on particle levels on a nearly continuous basis (every minute). The 26 integrating samplers collected particles over the entire time period of a work activity, yielding a 27 time-weighted average (TWA) concentration. In this sampling design, the real-time exposure 28 monitoring was used to assess frequency, magnitude, and duration of peak exposures as well as 29 TWA across the entire sampling time, while the integrating samplers provided information on 30 average exposures.

31

## 32 **2.2.3. Ingestion**

Inadvertent ingestion of clay or dust can occur in several ways. Clay particles in the air
 can deposit on food or in beverages. Deposition onto surrogate food samples (a quartz filter was
 used to represent food and a beaker of water was used to represent a beverage, see Section 3.1.5

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- 1 for further details) was measured to evaluate this pathway. Ingestion can also occur via transfers
- 2 from hands to food or cigarettes and via transfers to the mouth resulting from wiping the hands
- 3 or licking the lips. These possibilities were evaluated qualitatively through observations about
- 4 individual behaviors. Finally, ingestion can also occur via particle deposition in the nose, mouth,
- 5 and tracheobronchial airways; clearance to the throat; and swallowing. This process was
- 6 evaluated using inhalation modeling (Appendix G).

1 **3. SAMPLING METHODS** 2 3 Methods used for collecting, preparing, and analyzing samples are described below. 4 5 **3.1. SAMPLE COLLECTION** 6 Samples were collected from personal air, area air, skin rinses, surface wipes, and 7 surrogate food and beverages. 8 9 3.1.1. Personal Air Sampling 10 The Respicon model 8522 particle sampler (TSI Incorporated, Shoreview, MN) is a two-11 stage virtual impactor with a three-stage gravimetric filter sampler. The sampler sorts airborne 12 particulate matter into three size ranges. Each size range is collected on a 37-mm glass fiber 13 filter (GFF). The particle size collection ranges are as follows: stage 1, aerodynamic particle 14 diameter ( $D_{ae}$ ) < 4 µm; stage 2, 4 <  $D_{ae}$  < 10 µm; and stage 3, 10 <  $D_{ae}$  < 100 µm. 15 Before the start of sampling, three preweighed GFFs were removed from their protective 16 polystyrene containers (47-mm Millipore petri slides) and loaded into the Respicon using 17 nonmetallic filter forceps. A unique laboratory record book (LRB) identification number was 18 assigned to each GFF during tare weighing, and this weight was recorded onto the sampling data 19 sheet at that time. The Respicon was then assembled, and the total flow checker head was 20 installed. A personal sampling pump (SKC model no. 224-PCXR4, Eighty Four, PA) was 21 attached to the total flow head, and the flow rate through the Respicon was adjusted to 3.11 liters 22 per minute (L/min)  $\pm$  2%, according to the manufacturer's specifications. All flows were 23 verified by employing a calibrated National Institute of Standards and Technology (NIST)-24 traceable Buck calibrator (Model M5, A.P. Buck, Orlando, FL). After confirmation of the 25 manufacturer's suggested flow rates at each stage of the sampler, the total flow checker was 26 replaced with the standard (100 µm) inlet head. A nylon chest harness (TSI Incorporated, 27 Shoreview, MN) was used to place the Respicon in each subject's breathing zone, approximately 28 15-20 cm below the chin. The personal sampling pump was attached to the subject's belt and 29 connected to the Respicon. Sampling was initiated by starting flow through the Respicon and 30 continued throughout a subject's entire work shift, typically 2 to 2.5 hours. The average 31 sampling volume was 387 L. Following sampling, the pump was turned off, the Respicon was 32 disassembled, and the filters were returned to their polystyrene petri dish containers for 33 transportation back to the laboratory for gravimetric analysis. Quality control samples, such as 34 field blank samples and matrix spike samples, were collected and analyzed for each sampling 35 technique (see Section 3.2.3).

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1 The personal DataRAM-1000 (pDR-1000, Thermo Electron Corporation, Franklin, MA) 2 sampler was also used to measure personal particle exposure passively. No pump is required for 3 this instrument; instead, the air surrounding the sampler circulates freely through the open 4 sensing chamber by natural convection, diffusion, and background air motion. Particle 5 concentrations are measured using a light-scattering (nephelometry) technique. This instrument 6 responds optimally to particles with diameters in the range of 0.1 to 10 µm but will also respond 7 to a lesser extent to larger diameter particles. Via internal calibration, the sampler converted 8 particles/ $m^3$  to  $mg/m^3$  as final data units.

9 Before the start of sampling, the instrument sensor was zeroed by placing it in a 10 resealable bag into which particle-free (filtered) air was pumped. All zero operations were 11 performed successfully. To begin sampling, the instrument was clipped to the subject's waistline 12 (on the belt or strap holding the SKC pump) and the unit was activated. The pDR-1000 collected 13 data at 1 Hz and was programmed to record these data as 1-minute averages over the duration of 14 the sampling period. At the conclusion of sampling (typically 2–2.5 hours), data logging was 15 stopped and the instrument was turned off. The data were then uploaded to a personal computer 16 using software provided by the manufacturer and an RS-232 serial port connection.

17

#### 18 **3.1.2.** Area Air Sampling

19 To assess the particle size and concentration in the ceramic studio's air, a six-stage 20 Delron cascade impactor (Delron Research Products, Powell, OH) was employed. Each stage 21 filters out successively smaller particles so that the following particle sizes are collected in 22 successive stages: >32  $\mu$ m, 16–32  $\mu$ m, 8–16  $\mu$ m, 4–8  $\mu$ m, 2–4  $\mu$ m, and 0.5–2  $\mu$ m; the final GFF 23 collects all particles smaller than 0.5 µm in diameter. Particles accumulate on glass slides 24 underneath each impactor orifice. To prevent particle loss due to bouncing, a small amount of 25 vacuum grease was applied to each glass slide. The area coverage of the grease on the slide was 26 determined by the approximate size of the impactor nozzle below which the slide was to be 27 placed. Correct airflow rate through the impactor ensures that the correct particle sizes are 28 collected on each stage. A carbon-vane pump (Gast Co., Benton Harbor, MI), with a critical 29 orifice that provides a pressure drop of at least 430 mm of mercury, was used to ensure the flow 30 rate of 24 L/min.

Before the start of sampling, preweighed glass slides were removed from their protective polystyrene petri slide containers and loaded into the impactor using clean forceps or tweezers. Unique LRB numbers, assigned to each slide during tare weighing, were recorded on sample data forms. The impactor tower was then assembled and flow was initiated to verify the required pressure drop. For each sample, the pressure drop was between 480 and 510 mm of mercury.

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Flows were also verified using the Buck calibrator. Sampling times were approximately 2–2.5
 hours, giving an average sample volume of approximately 2,900 L. Following sampling, the
 impactor was disassembled and all slides were returned to their respective petri dish containers

4 for transportation back to the laboratory for gravimetric analysis.

5 The Climet CI-500 innovation laser particle counter (Redlands, CA) was a second 6 sampling device used to measure area particle concentrations. In a manner similar to the pDR-7 1000, the Climet CI-500 measures particle number concentration using nephelometry. A self-8 contained pump sampled air at a constant flow rate of approximately 3 L/min. In the count 9 mode, the Climet CI-500 measures particles in six particle size ranges:  $0.3-0.5 \,\mu\text{m}$ ,  $0.5-1 \,\mu\text{m}$ , 10  $1-2.5 \,\mu\text{m}, 2.5-5 \,\mu\text{m}, 5-10 \,\mu\text{m}, \text{and} > 10 \,\mu\text{m}$ . The sampling frequency for the instrument is 1 Hz, 11 and the data were logged as 1-minute averages. The particle counts were converted from particles/m<sup>3</sup> to mg/m<sup>3</sup> as final data units. The particle counts did not exceed the manufacturer's 12 recommended maximum (200–250 counts/cm<sup>3</sup> at 3 L/min) at any time except for a few minutes 13 14 during two of the sampling periods. No instrument zero or span checks were necessary. 15 Following sampling, the data were uploaded to a computer using an RS-232 serial cable and 16 software provided by the manufacturer. The Climet CI-500 was located in close proximity to the 17 cascade impactor and generally very near the subject. For example, when the subject was 18 working with clay at a wheel, the two air samplers were placed on the side of the wheel opposite 19 the subject at a height and distance from the wheel similar to the subject's mouth and nose. The 20 inlet to the Climet was oriented in a vertical direction.

21

## 22 **3.1.3. Skin Sampling**

23 The total skin area of hands, arms, face, feet, and legs was estimated using a combination 24 of direct measurements and regression models based on body weight and height (U.S. EPA, 25 1997). The subject's exposed body parts were rinsed with a dilute soap solution ( $\sim 2\%$  soap in 26 deionized [DI] water, by weight). Approximately 100–150 mL of the soap solution was used to 27 rinse each exposed body part. After each body part was rinsed, the washbasin contents were 28 transferred to a polypropylene bottle with small amounts of deionized (DI) water rinses. The 29 bottle was labeled and sealed with a screw-top cap. The washbasin was then rinsed again, wiped 30 out, and reused. Between the first and second studies, the procedures differed as described 31 below.

April 2003. All subjects wore short-sleeved shirts, long pants, socks, and shoes.
Therefore, the only exposed skin areas were the hands and forearms, and the rinsing was limited
to these body parts. At three times during each subject's work session, the subject's exposed
skin was examined for clay residue. When clay was observed visually, the affected areas of the

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1 subject's body were rinsed. Rinses were performed at approximately equally spaced intervals,

- and the last rinse usually coincided with the conclusion of the sampling period. The average of
  the three measurements was used to represent the session.
- July 2004. Both subjects wore short-sleeved shirts, short pants, and sandals. Therefore, the exposed skin areas included the hands, arms, legs, and feet, and the rinsing was expanded from the first tests to include all of these body parts. The subjects' faces were also rinsed during these tests. Although no visible residues were apparent on the faces, this area was included for the sake of completeness.
- 9 The rinse samples were collected in a washbasin using a squirt bottle of soap solution 10 while the subjects used their hands to gently wipe off the affected area. Rinses were conducted 11 in the following manner:
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- **Hands.** Moving downward from the wrist, the technician rinsed the residual clay off both sides of the artisans' hand; the residual clay from each hand was rinsed into separate containers and analyzed separately.
  - **Arms.** Moving downward from the elbow, the artisans rinsed the residual clay from their arms.
  - **Feet.** Moving downward from the ankle, the artisans rinsed the residual clay from their feet.
    - **Legs.** Moving downward from the top of the exposed area of the legs, the artisans rinsed the residual clay from their legs.
      - **Face.** The artisans rinsed the residual clay from their faces.

28 Skin rinse samples were collected at the close of each work session. In addition, if at any 29 point during the work session the subject indicated the need to wash an exposed body part, it was 30 rinsed into a sample container reserved for that body part.

31

## 32 **3.1.4. Surface Wipe Sampling**

- A 20 cm by 20 cm horizontal surface near the subject's workspace was selected and
- 34 cleaned with dilute soap solution before the subject began working with any clay. Wipe samples
- 35 of this area were taken immediately after cleaning (to confirm that low levels were present
- 36 before starting the work session) and at the end of the work session. The wipe sampling
- 37 procedure consisted of the following steps. The selected area was wiped with 10 cm x 10 cm
- rayon gauze wipes wetted with ~5 mL isopropanol using the following procedure. The wipe was *This document is a draft for review purposes only and does not constitute Agency policy*.
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secured between the thumb and forefinger of one hand, and the surface was wiped five times in one direction using evenly applied pressure. The soiled side of the wipe was folded to the inside and, in an orthogonal direction, the surface was wiped five more times. This soiled side of the wipe was again folded to the inside and the wipe was placed into its prelabeled, resealable bag for transportation back to the laboratory for gravimetric analysis. The entire wiping process above was then repeated using one additional wipe.

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## 3.1.5. Surrogate Food and Beverage

9 An 85-mm diameter quartz fiber filter and a 125-mL polypropylene jar filled with 10 100 mL DI water served as surrogates for food and beverage samples, respectively. Before clay 11 work began, both were placed in a location where the artisan indicated he or she might normally 12 place food or drink. In most cases, this location was away from the direct work area but still in 13 the same room. However, occasionally clay workers placed food and beverage directly adjacent 14 to their work. To begin sampling, the lid of the polycarbonate petri dish containing the food 15 surrogate and the screw-cap lid on the beverage surrogate were removed. Following the 16 conclusion of sampling, the lid to the petri dish was replaced and sealed with Teflon tape, and 17 the polypropylene jar was secured for transportation back to the laboratory for gravimetric 18 analysis.

19

## 20 **3.2. SAMPLE PREPARATION AND ANALYSIS**

21 Procedures used for sample preparation, analysis, and quality control are described22 below.

23

## 24 **3.2.1. Filtration and Drying**

25 To collect the clay rinsed from the subject's skin during the skin rinse sampling 26 procedure and the clay deposited into the surrogate beverage sample, the clay-liquid suspensions 27 were filtered through a preweighed 85-mm diameter quartz fiber filter in a Buchner funnel using 28 vacuum filtration. Any remaining clay in the sample container was rinsed with several small 29 aliquots of DI water to ensure complete transfer of the clay to the filter. All filters from the 30 vacuum filtration procedure were subsequently placed on clean 10-cm watch glasses and dried 31 overnight at 100°C. The gauze wipes for surface residues were dried in this fashion as well. No 32 drying was required for the 37-mm Respicon filters or glass slides.

#### 1 **3.2.2.** Gravimetric Analysis

2 The accuracy of the analytical balance (AT-20, Mettler-Toledo) used for all gravimetric 3 analyses was confirmed daily with weights approved by NIST. The calibration weights ranged 4 from 0.001 mg to 100 g. All 37-mm GFFs, 85-mm quartz fiber filter paper, 37-mm glass slides, 5 and gauze wipes were conditioned in a temperature- and humidity-controlled balance room 6 (temperature 22–23° C, relative humidity 46–56%) for a minimum of 24 hours before tare and 7 final weights were recorded. For conditioning, the lid of the container holding the filter or slide 8 was left slightly ajar, and the reseatable bags containing the gauze wipes were left open. For 9 both kinds of filters and glass slides, three separate weights were recorded to the nearest 10 microgram. The weight was acceptable if the range of the three independent measurements was 11 less than 10 µg. For gauze wipes, the three separate weights were recorded to the nearest tenth 12 of a milligram and the acceptability criterion was that the range of the measurements be less than 13 1 milligram.

14

## 15 **3.2.3. Quality Control Samples**

16 At least one field blank sample was collected for each type of gravimetric sample, 17 including the Respicon, cascade impactor, food and beverage, and surface wipe samples. Such 18 samples were collected by transporting the sampling media to the field location and placing them 19 into their respective sampling device or position for sampling. As soon as the medium was ready 20 for sampling, it was collected as if the sampling time had come to a close and transported back to 21 the laboratory for gravimetric analysis. The detection limits for the gravimetric measurements 22 were determined by multiplying the standard deviation of the field blank net weights by 3. The 23 detection limits for each type of gravimetric measurement were as follows:  $0.0025-0.015 \text{ mg/m}^3$ for each stage of the cascade impactor,  $0.878 \text{ mg/m}^3$  for each stage of the Respicon, 10.6 mg for 24 25 the surface wipes, 0.6-1 mg for the food/beverage deposition samples, and 0.6-1.6 mg for the 26 dermal rinse samples.

As a quality control check, the skin rinse, surface wipe, and food and beverage sampling 27 28 and analysis methods were tested in a controlled laboratory setting. For the skin rinse method 29 evaluation, approximately 3 g of clay (obtained from one of the artisan subjects) was handled 30 carefully without dropping any until the entire sample was spread over the hands and forearms of 31 a Battelle researcher. The skin rinse and analysis method described above was performed, and 32 recoveries of  $87 \pm 3\%$  of the clay applied were obtained. This compares favorably with Kissel et 33 al. (1996), who obtained 93% recovery when rinsing wet soil from the skin of human subjects 34 using a similar sampling method. Similarly, for the surface wipe method, approximately 1 g of 35 clay was deposited onto a precleaned laboratory bench, the wipe method described above was

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- 1 performed, and recoveries of  $94 \pm 5\%$  were obtained. For the food and beverage samples,
- 2 approximately 50 mg of clay was added to those sampling matrices and recoveries of 90 and
- 3 95%, respectively, were obtained using the gravimetric analysis procedures described above.

1 2

#### 4. DIOXIN CONTENT OF CLAY AND STUDIO RESIDUES

3 As discussed earlier, this study made no dioxin measurements in clays, dust residues, or 4 other materials from the Ohio State University ceramics studio. Instead, the possible levels were 5 estimated on the basis of other studies. A number of studies have measured dioxin levels in raw 6 and processed ball clay. Raw clay is the clay as it comes out of the ground. Processed clays are the result of the initial processing, which is usually conducted at or near the mining site before 7 8 shipping. This processing typically involves drying with hot air at 120°C and pulverizing in a 9 series of milling stages (Ferrario and Byrne, 2002). The following studies describe dioxin levels 10 in raw and processed clay:

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• Ferrario and Byrne (2000, 2002). Both papers present data for processed ball clay used at one ceramics manufacturer. The mean of seven samples of processed ball clay was 3,172 pg/g TEQ. Additional data are presented on dioxin levels in clay mixtures and fired products. The authors noted that dioxin levels in the dust samples collected at the facility were the same as those in the unfired clay mixtures.

- 19 • Ferrario et al. (2000a). This study compared the mean levels in eight raw clay 20 samples from Mississippi (see Table 1) to the mean levels in four processed ball 21 clay samples. This comparison showed that the processed clays had much lower 22 levels of 2,3,7,8-TCDD and higher levels of 1,2,3,4,7,8-hexachlorodibenzo-p-23 dioxin (HxCDD), 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (HpCDD), and octachlorodibenzo-p-dioxin (OCDD) than the raw clay. The mean total TEQ of 24 25 the processed clay (977 pg/g TEQ) was 37% lower than the raw clay (1,513 pg/g TEQ). 26
  - **Ferrario et al. (2000b).** This study also presents the data for raw and processed clay described in Ferrario et al. (2000a). In addition, it presents dioxin levels in a variety of other types of clays and discusses the evidence of a natural origin for their presence.
- 33 Ferrario et al. (2004, 2007). These studies collected processed ball clay directly • 34 from four art-supply retailers. All ball clay types sold by these retailers were purchased in 22.7 kg (50 pound) bags. One type of ball clay was sold by all four 35 retailers, five types were sold by two of the retailers and seven types were sold by 36 only one retailer. Thus a total of 21 bags representing 13 different types of ball 37 38 clays were purchased and sampled. A ceramics expert confirmed that the most 39 commonly used ball clays for making artware and pottery were represented in 40 these samples. These data are summarized in Table 2.
- 41
- 42

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## Table 1. Raw ball clay dioxin concentrations

	PCDD concentration (pg/g dry weight)			ht)
Congener	Range	Median	Mean	Mean TEQ
2,3,7,8-TCDD	253-1,259	617	711	711
1,2,3,7,8-PeCDD	254–924	492	508	508
1,2,3,4,7,8-HxCDD	62–193	134	131	13
1,2,3,6,7,8-HxCDD	254–752	421	456	46
1,2,3,7,8,9-HxCDD	1,252–3,683	1,880	2,093	209
1,2,3,4,6,7,8-HpCDD	1,493–3,346	2,073	2,383	24
OCDD	8,076–58,766	4,099	20,640	2
Total				1,513

TEQ = toxic equivalent

Source: Ferrario et al. (2000a).

9 Since the data from Ferrario et al. (2004, 2007) represented the types of clays most likely 10 used in ceramic art studios, these data were selected as the most representative ones to be used in 11 this study. Accordingly, it was assumed here that the dioxin TEQ levels in clay could range 12 from 289 to 1,470 pg/g with an average of 808 pg/g. As shown in Table 2, the TEQs from this 13 study were calculated on the basis of the WHO-98 Toxicity Equivalecy Factors or TEFs (Van 14 den Berg et al., 1998). In 2005, WHO updated the TEFs (Van den Berg et al., 2006). These 15 updates increased the TEF for OCDD from 0.0001 to 0.0003. None of the TEFs for the other six 16 congeners used to estimate the ball clay TEQs were changed by the WHO update. The increase 17 in the OCDD TEF would cause the overall average to increase by 6%. It was decided to use the 18 TEQ estimates for ball clay as originally reported instead of updating it on the basis of the 2005 19 WHO TEFs. This was based on two reasons, first the change would have been relatively minor 20 and second it would have complicated comparisons to exposure estimates which have not yet 21 been updated on the basis of the new TEFs.

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## Table 2. Processed ball clay dioxin concentrations (pg/g)

	Average	Standard deviation	Median	Minimum	Maximum	WHO- TEF <sup>a</sup>	Avg TEQ
PCDDs							
2,3,7,8-TCDD	76	60	63.5	21.8	291	1	76.0
1,2,3,7,8-PeCDD	374	144	387	125	588	1	374
1,2,3,4,7,8-HxCDD	335	141	313	142	636	0.1	33.5
1,2,3,6,7,8-HxCDD	526	204	523	167	944	0.1	52.6
1,2,3,7,8,9-HxCDD	1,480	608	1,570	394	2,550	0.1	148
1,2,3,4,6,7,8-HpCDD	9,780	4,480	8,600	3,940	19,500	0.01	97.8
OCDD	254,000	88,200	233,000	118,000	471,000	0.0001	25.4
Total							
TCDD	1,450	606	1,600	412	2,370		
PeCDD	4,600	1,890	4,880	1,560	7,140		
HxCDD	13,500	5,710	12,800	4,800	21,900		
HpCDD	25,000	11,700	24,400	9,320	44,900		
Total TEQs <sup>b</sup>	808	318	771	289	1,470		808

<sup>3456789</sup> 10 11 12 13 14 15 16

<sup>a</sup>World Health Organization Toxic Equivalency Factors (WHO-TEFs) based on Van den Berg (1998)

<sup>b</sup>The overall average presented by Ferrario et al. (2007) is based on averaging the mean congener levels across samples. An alternative approach is to compute the average on the basis of the TEQ for each sample. This approach yields an average of 819 pg/g (SD = 303 pg/g). Similarly the median TEQ is 810 pg/g based on the individual samples. The minimum and maximum TEQ values are reported on the basis of the individual samples. TEQ = toxic equivalent

Source: Ferrario et al. (2004, 2007).

All of these studies indicate that ball clay has relatively high levels of CDDs and very low levels of CDFs. Based on Ferrario et al. (2004, 2007), about 95% of the TEQs in processed clay are contributed by four congener groups: TCDDs (9%), pentachlorodibenzo-p-dioxin 17 (PeCDDs) (46%), HxCDDs (28%), and HpCDDs (12%).

18 Artists commonly use a mixture of clays to achieve various physical properties and visual 19 effects. The percentage of ball clay in the mixture can vary widely. The amount of ball clay in This document is a draft for review purposes only and does not constitute Agency policy. DRAFT-DO NOT CITE OR QUOTE

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1 the mixtures used on days when the testing occurred ranged from 0 to 100% with an average of 2 21.5% (Table 3). Although 4 of the 10 subjects used mixtures containing no ball clay on the test 3 days, on other days these subjects would likely use mixtures that do contain ball clay. This is 4 because students are required to conduct a variety of projects, and some of these are better suited 5 to using ball clay and others are not. Accordingly, it was assumed here that the ball clay portion 6 of clay mixtures used by artists can range from 0 to 100% with an average of 20%. Furthermore, 7 it was assumed that the dioxin levels in the non-ball clays were negligible. This is supported by 8 Ferrario et al. (2000b), who analyzed 15 different mined clays and concluded their dioxin levels 9 were significantly lower than levels in ball clay.

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 Table 3. Percentage ball clay in the clay mixtures used during this study

Subject	Percentage ball clay
1	0
2	27
3	48
4	0
5	20
6	0
7	0
8	15
9	100
10	5

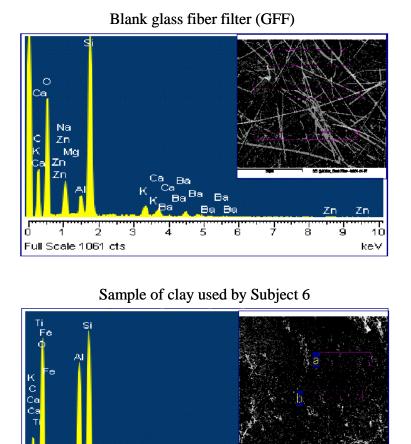
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- 15

Finally, it was assumed that the dusts suspended in the air and settled onto food or skin would have the same dioxin levels as the clay. Material other than clay may contribute to these dusts, further diluting dioxin concentrations. This possibility was evaluated using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). These techniques were applied to four types of samples:

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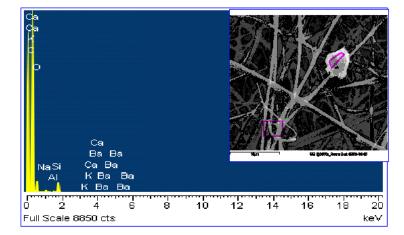
1 2	•	Blank GFF.				
3 4	•	Dust on a GFF collected from a storeroom at the Battelle Laboratory (not impacted by clay).				
5 6 7	•	Air particles on a Respicon GFF collected in the studio.				
, 8 9	•	Clay used by subjects.				
10	SEM	photographs and elemental spectra of samples associated with Subject 6 are shown				
11	in Figure 1. A visual comparison of the SEM photographs suggests that the particles on the					
12	Respicon filter appear to differ from those in the storeroom dust. Also, the spectra of the					
13	particles on the Respicon filters resemble clay more than those of storeroom dust. The clay					
14	samples and l	Respicon filter samples had high abundances of titanium, iron, and aluminum,				
15	which were n	ot seen in the GFF blank or in the storeroom dust sample. Similar results were				
16	found for all	eight subjects in the April 2003 tests, as shown in Appendix E. The analysis was				
17	not repeated i	n the July 2004 tests. These observations suggest that clay dominates the air				
18	particles colle	ected in the studio. On this basis, it was assumed that the studio dust was				
19	dominated by	clay and no further dilution factor was needed to adjust dioxin concentrations.				



к<sup>Са</sup> К Са Ті Ті

Full Scale 2136 cts

#### Dust particles on GFF in Battelle storeroom



Clay particles on Respicon filter used by Subject 6

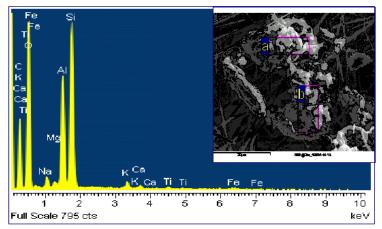


Figure 1. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) data.

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#### 5. DOSE ESTIMATION PROCEDURES

3 This section presents the procedures used to estimate the dioxin dose to artisans from all 4 three routes of exposure: dermal contact, inhalation, and ingestion. Because the dermal dose is 5 expressed on an absorbed basis, the dose by other pathways must also be expressed on an 6 absorbed dose basis. This provides an equivalent basis for comparison and addition across 7 pathways. All doses are presented as daily estimates. No adjustments are made for the 8 frequency with which artists work with clay. Therefore, these dose estimates should be 9 interpreted as the dose that could occur on a day that clay work is conducted, rather than as a 10 long-term average.

11

1

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### 12 **5.1. DERMAL CONTACT**

13 A fraction absorbed approach is used to estimate dermal absorption. This method has 14 been widely used to assess dermal exposures to solid residues and is endorsed in current Agency 15 guidance (U.S. EPA, 2004, 1992). Bunge and Parks (1998) have proposed an alternative 16 approach based on a more mechanistic model. This model has had only limited testing and is not 17 addressed in Agency guidance. Therefore, it was not chosen as the primary basis for this 18 assessment, but Appendix I discusses how it could be applied to this situation. This new model 19 suggests similar estimates of absorbed dose to those presented here using the traditional 20 absorption fraction approach.

21

#### 22 **5.1.1. Estimating Particle Loading on Skin**

As described earlier, rinsing procedures were used to determine the total amount of clay on exposed skin. This mass was divided by the exposed skin area to derive a loading in units of mg/cm<sup>2</sup>.

26

#### 27 **5.1.2. Estimating Monolayer Load**

The monolayer is the layer of particles immediately adjacent to the skin. According to the monolayer theory, the only significant dermal absorption comes from chemicals contained in this first layer (U.S. EPA, 2004, 1992). Experimental evidence supporting the monolayer theory has been published by Duff and Kissel (1996) and Touraille et al. (2005). To properly apply the dermal absorption fractions, it was necessary to determine whether residue loads on skin exceeded monolayer loads. The monolayer load for a specific soil can be estimated on the basis

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1	of the median particle size. Assuming spherical particles and face-centered packing, the
2	monolayer loads can be calculated as follows (U.S. EPA, 2004):
3	
4	$L_{mono} = \rho \ d_p / 6 \tag{1}$
5	
6	where:
7	$L_{mono} = monolayer load (mg/cm^2)$
8	$\rho = \text{particle density (mg/cm}^3)$
9	$d_p = physical particle diameter (cm)$
10	
11	The average particle density of the processed clays analyzed by Ferrario et al. (2004) was
12	2.64 g/cm <sup>3</sup> . Clays typically have very small particles relative to other components of soil. The
13	U.S. Department of Agriculture (USDA) defines clays as having less than $2 \mu m$ diameter
14	particles (Brady, 1984). The particle size specifications for a Tennessee ball clay is shown in
15	Table 4 (Ceramics Materials Info, 2003). Reviewing the specifications for a variety of
16	commercial ball clays, median particle sizes ranged from about 0.5 to $1.0 \mu m$ (Ceramics
17	Materials Info, 2003).
18	

- 19
- 20 21

 Table 4. Particle size distribution of Tennessee ball clay

Particle diameter (µm)	20	10	5	2	1	0.5	0.2
% finer than	99	97	93	81	72	56	35

22

23 Source: Ceramics Materials Info (2003).

24

25

The particle sizes found in the studio air had median physical diameters ranging across subjects from 8 to 27  $\mu$ m (this is derived from the mass median aerodynamic diameter [MMAD] range of 13 to 44  $\mu$ m described in Appendix G and converted to physical diameters using the procedure in Appendix G, footnote 1). These airborne particles appear larger than what would be expected from the original clay product. This may be explained by the bonding of particles caused by the addition of water to the clay or the firing process, which fuses particles. Particles that accumulate on the skin primarily from air deposition are likely to resemble the air particles

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1 more than the original clay particles. Particles that transfer to skin primarily from direct 2 handling of the clay should more closely resemble the original clay product than the airborne 3 particles. Accordingly, the particle sizes of the clay residues on skin could vary widely, with 4 medians ranging from 0.75 to 27  $\mu$ m. For purposes of the central exposure estimates, the 5 geometric mean of this range is assumed, i.e., 4.5  $\mu$ m. This implies a monolayer load of 6 0.62 mg/cm<sup>2</sup>. The uncertainty resulting from this assumption is discussed further in Section 9.

7

8

## 5.1.3. Estimating Fraction Absorbed

As discussed in U.S. EPA (1992), three teams of investigators have examined dermal
absorption of TCDD from soil (Roy et al., 1990; Shu et al., 1988; Poiger and Schlatter, 1980).
The Roy et al. (1990) data (also described in U.S. EPA, 1991) were selected as the best basis for
estimating dermal absorption fractions applicable to the ceramics studio. This was because the
test soil was most fully described allowing comparisons to the clay, and multiple exposure times
were used allowing evaluation of how dose varies with time.

15 Roy et al. (1990) conducted a variety of experiments in which TCDD was applied to soil 16 on human skin in vitro, rat skin in vitro, and rat skin in vivo. The experiments were conducted 17 with both a low organic carbon soil and a high organic carbon soil. Ferrario et al. (2004, 2007) 18 studied 21 samples of processed ball clay used in ceramics studios. They found that the organic 19 carbon content of these samples ranged from 0.06% to 1.1% with a median and geometric mean 20 of approximately 0.4%. This level is very similar to the level in the low organic carbon soil used 21 by Roy et al. (0.45%). Accordingly, this discussion focuses on the Roy et al. results for the low 22 organic carbon soil.

23 Roy et al. (1990) calculated the percentage absorbed at various times over the 96-hour 24 experiment (Table 5). The second column shows the results for the human skin in vitro 25 experiments. The percentage absorbed includes the amount measured in the skin at the end of 26 the experiment. These values were adjusted in two ways. First, as recommended in U.S. EPA 27 (1992), they were multiplied by the ratio of the percentage absorbed for rat skin in vivo (16.3%)28 to percentage absorbed for rat skin in vitro (7.7%). Second, they were adjusted to reflect the 29 assumption that the absorption occurs exclusively from the monolayer. In the low organic 30 carbon soil tests, Roy et al. (1990) used "Chapanoke" soil, which is composed of 15.1% sand, 31 68.2% silt, and 16.7% clay. Chapanoke soil has an organic matter content of 0.77% (0.45% 32 organic carbon). Based on the USDA soil classification system, this composition is a silty loam. 33 Silty loams have a median particle size of about 10 µm (Brady, 1984), which corresponds to a theoretical monolayer load of 1.3 mg/cm<sup>2</sup>. Roy et al. applied a soil load of 6 mg/cm<sup>2</sup>, exceeding 34

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the monolayer load by a factor of 4.6. Accordingly the percentage absorbed was also multiplied by this factor. The results of these two adjustments are shown in the third column of Table 5.

Time (hr)	Percentage absorbed - human in vitro	Percentage absorbed - adjusted <sup>a</sup>	Percentage absorbed - best fit <sup>b</sup>
1	0.19	1.85	1.01
2	0.25	2.43	1.24
4	0.24	2.34	1.69
8	0.19	1.85	2.59
24	0.45	4.38	6.19
48	1.08	10.52	11.59
72	1.71	16.65	16.99
96	2.42	23.57	22.39

Table 5. Adjustments to Roy et al. (1990) dermal absorption data

10

11 12 <sup>a</sup>These values were adjusted first by multiplying by the ratio of the percentage absorbed for rat skin in vivo (16.3%) to percentage absorbed for rat skin in vitro (7.7%) and second by multiplying by 4.6 to reflect the assumption that the absorption occurs exclusively from the monolayer.

<sup>b</sup>These values were derived using eq. 2 and converting to percent.

13 The Roy et al. (1990) data show a strong linear correlation between percent absorbed and 14 time ( $r^2 = 0.98$ ). The scatter plot for these data and the best fit line are shown in Figure 2. The 15 equation for this line is as follows (converting percent to fraction):

16

17

 $AF_{dermal} = 0.00225t + 0.00787, t < 96hr$ (2)

18

19 where:

20  $AF_{dermal} = dermal absorption fraction$ 

21 t = time (hr)

22

This equation was adopted in this study for purposes of estimating dermal absorption of
dioxin. The percentage absorbed values based on this equation are shown in the last column of
Table 5.

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1 2 3

4

5

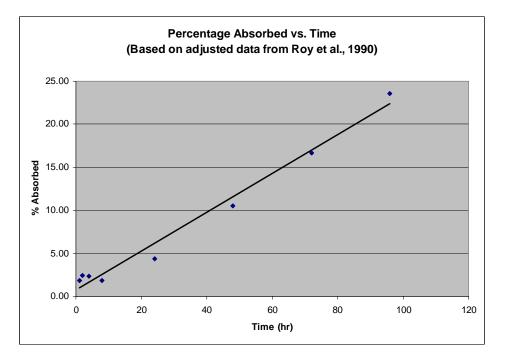


Figure 2. Scatter plot of adjusted absorption data versus time with linear trend line.

Source: Adapted from Roy et al. (1990).

#### 5.1.4. Calculating Dermal Dose

9 The rinsing experiments indicated that clay loading exceeded the monolayer load in 10 some, but not all, cases. The dermal absorption fractions presented above were applied to the 11 measured loads where these were less than or equal to monolayer loads. At soil loadings greater 12 than monolayer, the dermal absorption fraction was applied to only the monolayer load. 13 Accordingly, the dose of dioxins absorbed through the skin of the artisan subjects during this 14 study was estimated using the following equation for each body part and then summed: 15

$$D_{dermal} = SA \ L \ C \ AF_{dermal} \tag{3}$$

18 where:

16 17

19 $D_{dermal} = dermally absorbed dose (pg TEQ/d)$ 20 $SA = skin area exposed (cm^2)$ 21L = daily clay loading on skin (measured or monolayer, whichever is less) (mg/cm<sup>2</sup>-d)22C = dioxin concentration in clay (pg TEQ/g)23 $AF_{dermal} = dermal absorption fraction$ 

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#### 1 **5.2. INHALATION**

2 The portion of particles that enter the respiratory tract through the nose or mouth 3 (inhalability) depends mainly on particle size, route of breathing (through the nose or mouth), 4 wind speed, and a person's orientation with respect to wind direction. Inhaled particles may be 5 either exhaled or deposited in the extrathoracic (ET), tracheobronchial (TB), or pulmonary (PU) 6 airway. The deposition of particles in the respiratory tract depends primarily on inhaled particle 7 size, route of breathing, tidal volume, and breathing frequency (ACGIH, 2004; ICRP, 1994). 8 Appendix G presents a detailed discussion of how to consider these factors and estimate the 9 amount of particulate that deposits in various regions of the respiratory tract. 10 The absorbed inhalation dose is estimated as follows: 11 12  $D_{inhalation} = D_r C A F_r (1g/1000 mg)$ (4)13 14 where: 15  $D_{inhalation} = inhalation dose (pg TEQ/d)$ 16  $D_r = dose of particles to region r of the respiratory tract (mg/d)$ 17 C = dioxin concentration on particles (pg/g) $AF_r$  = absorption fraction for region r of the respiratory tract 18 19 20 This equation is used to estimate the absorbed dose to the three regions of the respiratory 21 tract (ET, TB, and PU) and then summed to derive total inhalation dose. In general, particles 22 deposited in the ET and TB regions clear rapidly (within 1-2 days) to the throat and are 23 swallowed. Accordingly, the absorption of dioxin from particles deposited in these regions is 24 treated as if the particles had been ingested with an absorption fraction of 0.3 (U.S. EPA, 2003). 25 The particles depositing in the PU region remain there a long time, and most of them are 26 ultimately absorbed directly into the body (assumed absorption fraction of 0.8 based on U.S. 27 EPA, 2003). 28 29 5.3. INGESTION 30 The ingestion dose is estimated by assuming that all particles deposited on the surrogate 31

32 33 using the equation below:

34

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 $D_{ingestion} = (F + B) C A F_{ingestion}$ (5)

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food and beverage samples are ingested. For both types of samples, the dose was calculated

1	where:
2	$D_{\text{ingestion}} = \text{ingestion dose (pg TEQ/d)}$
3	F = deposited clay on food (g/d)
4	B = deposited clay on beverage (g/d)
5	C = dioxin concentration in clay (pg TEQ/g)
6	$AF_{ingestion} = absorption fraction for ingestion$
7	
8	AF <sub>ingestion</sub> was assumed to equal 0.3 based on recommendations in U.S. EPA (2003) for
9	ingestion of dioxin in soil. The ingestion of dioxin from inhaled particles is included in the
10	inhalation dose as discussed above.
11	
12	5.4. TOTAL DOSE
13	The total absorbed dose was estimated to be the sum of the dermal absorption, inhalation,
14	and ingestion doses as shown below:
15	
16	$D_{total} = D_{dermal} + D_{inhalation} + D_{ingestion} $ (6)
17	
18	where:
19	$D_{total} = total dose (pg TEQ/d)$
20	$D_{dermal}$ = dermally absorbed dose (pg TEQ/d)
21	$D_{inhalation} = inhalation dose (pg TEQ/d)$
22	$D_{\text{ingestion}} = \text{ingestion dose (pg TEQ/d)}$

#### 6. QUESTIONNAIRE RESULTS

3 The complete questionnaire and all responses are presented in Appendix A. The 4 questionnaire focused on characterizing each subject's work with clay in terms of 5 frequency/duration, type of activity, clothing worn, and impact on skin. Table 6 summarizes the 6 questionnaire results for the amount of time that the subjects spent working directly with clay. 7 The subjects worked with clay, on average, for 30 hours per week and 38 weeks per year over a 8 6-year period. The times varied widely, however, reflecting the types of students involved. A 9 student obtaining an advanced degree in ceramics is likely to work with clay daily over many 10 years. In contrast, a student who takes a pottery class to fulfill a general education requirement 11 is likely to experience similar exposures, but only for 1–3 hours per day over the duration of the 12 class (9 months or less).

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# Table 6. Questionnaire questions on duration and frequency of subject'sclay work

Question (n = 8)	Mean (SD)	Median	Max	Min
Approximately how many hours per week do you work with clay?	30 (21)	23	70	10
Approximately how many weeks per year do you work with clay?	38 (10)	38	52	20
How long (years) have you been doing clay work with this level of intensity?	6 (8)	3	24	1

18

19

20 Table 7 summarizes the participants' answers to several questions about their clay work. 21 Some of the questions address the types of clothing worn, how often the subjects wash their 22 hands, and whether the subjects could correlate any skin health effects with working with clay. 23 All eight subjects answered that they have dry skin because of the clay work. In general, the 24 subjects wash their hands soon after working with clay, their face and arms within a few hours, 25 and the rest of their body within 24 hours. The responses indicated that one subject gets a rash 26 when using the wheel for throwing, another subject has nasal congestion due to clay work, and 27 another subject's fingernails do not grow well.

28 29

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# Table 7. Questionnaire questions about clay work

Question (n = 8)	Summary of answers (number of subjects with similar answers)
What type of clay artwork do you do?	Hand building/sculptural work (7), throwing on wheel (3), mixing clay and maintenance work (1)
What types of clothing do you wear while you work?	In general, long sleeves and pants in cool weather and short sleeves and pants or shorts in warm weather; both closed- toe shoes and sandals are worn at times
What areas of skin typically are exposed to the clay while you work?	Always face and hands; arms, legs, and feet when exposed
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Soon after: hands (8), arms (1), face (1) Within a few hours: arms (2), face (6) Within 24 hours: face (1), rest of body (4)
How do you wash your skin after you work with clay?	Soap and water or just water (8)
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Dryness (8), rash on hands when using wheel (1), nasal congestion (1), fingernails do not grow well (1)

3

1 2

# 7. COMPARING EXPOSURES ACROSS SUBJECTS

3	In this	section, a hypothetical dioxin dose is estimated for each subject and used to				
4	evaluate which pathways and activities contribute most to total dose. This is done by assuming					
5	that each subject uses clay with the same level of dioxin. More specifically, it is assumed that					
6	each subject uses a clay mixture with 20% ball clay and that the ball clay contains 808 pg TEQ/g					
7	•	ical values as discussed in Section 4). Accordingly, the dioxin levels in the clay				
8	were assumed to be 20% of 808 pg TEQ/g or 162 pg TEQ/g. This concentration was also					
9	-	oply to inhaled dust and dust settled onto food. A variety of other factors were also				
10	held constant	across subjects to facilitate this analysis:				
11						
12	•	Exposure duration. The questionnaire results presented in Section 6 indicate a				
13		median weekly time for clay work of 23 hours. Assuming a 5-day work week,				
14		this would correspond to about 4 hours/day. This value was applied to all				
15 16		subjects.				
10	•	Monolayer load. The monolayer load varies depending on particle size but is				
18	-	assumed here to be $0.62 \text{ mg/cm}^2$ for all subjects. This is based on the geometric				
19		mean of the range of possible median particle sizes, i.e., 0.75 to 27 $\mu$ m (see				
20		Section 5.1 for further discussion of this issue).				
21						
22	•	<b>Dermal absorption fraction.</b> This will depend on exposure time, as discussed in				
23 24		Section 5.1. The time that the skin is exposed to clay will vary with individual behaviors and body parts. Some body parts (such as hands and faces) are likely to				
24 25		behaviors and body parts. Some body parts (such as hands and faces) are likely to be washed more frequently than others (such as feet, legs, and arms), resulting in				
26		longer exposure times. The questionnaire data collected during this study (see				
27		Section 6) suggest that the artists generally wash their hands soon after working				
28		with clay, wash their faces and arms within a few hours, and wash the rest of their				
29		body within 24 hours. Accordingly, the exposure time for feet and legs was				
30		assumed to be 24 hours, and the absorption fraction corresponding to 24 hours				
31 32		was applied (6.2%). The exposure time for hands, arms, and face was assumed to be 4 hours with a corresponding 1.7% absorption.				
33		be 4 nours with a corresponding 1.7% absorption.				
34	•	<b>Ingestion absorption fraction.</b> This was set to 0.3 based on recommendations in				
35		U.S. EPA (2003) for ingestion of dioxin in soil.				
36		-				
37	•	Inhalation absorption fraction. This was set to 0.3 for ET and TB regions based				
38		on the assumption that the area is rapidly cleared to the gastrointestinal tract. It				
39 40		was set to 0.8 for the PU region based on recommendations in U.S. EPA (2003) for inhalation of dioxin in air.				
40 41						
11						

1 The hypothetical dioxin dose for each subject is calculated using the constant values 2 described above and their individual exposure conditions (e.g., dust level in air, clay load on 3 skin, clay load on food). The dose estimates are considered to be hypothetical because they are 4 based on assumed dioxin levels in the various exposure media rather than on studio-specific 5 measurements. Section 8 presents an analysis of the possible variability in dose resulting from a 6 range of dioxin levels in clay, ball clay mixtures, and exposure factors (Monte Carlo 7 simulations).

8 This section first addresses each pathway separately (dermal contact, inhalation, and 9 ingestion) and then addresses total dose. Individual exposures vary widely, and it is important to 10 consider the subject's activity and clothing in evaluating the results. Table 8 is provided as a 11 reference for this purpose with summaries of each participant's activities and clothing.

12

# 13 **7.1. DERMAL CONTACT**

14 As described in Section 5.1, the mass of clay rinsed from the skin was used to estimate 15 clay loadings on the skin for each exposed body part. The rinsing data are presented in 16 Appendix H. Section 5.1 also explains that the skin loading is compared to the monolayer load, 17 and the absorption fraction is applied to the lower amount. The dermal absorption estimate for 18 each subject is shown in Table 9. Subjects 1 through 8 wore clothing that limited their exposures 19 to only hands and arms (although arm exposure was detected on only Subjects 1 and 6). The 20 estimates for Subjects 9 and 10 include hands, arms, legs, and feet because they wore clothing 21 allowing exposure to these areas. All subjects could have had exposure to the face, but this was 22 evaluated only for Subjects 9 and 10. Pictures of the clay residues on skin are shown in 23 Appendix B. Table 9 shows that 5 of the 10 subjects had skin exposures exceeding the 24 monolayer. The absorbed dose ranged from 0.41 to 20.80 pg TEQ/d with a mean of 3.37 pg 25 TEQ/d (SD = 6.18). 26 The relationships between the activities of the subjects and their dermal exposure, as

27 presented in Table 9, are discussed below:

28

Wheel work (Subjects 6 and 9). This activity led to the highest dermal
 exposures. The high exposures were caused by the close proximity of the subjects
 to the wheel, the splashing of wet clay onto their bodies, and the use of both hands
 to mold the clay. The total dermal dose for Subject 9 was about 6 times greater
 than that for Subject 3, resulting primarily from their clothing difference. Both
 had similar hand and arm exposure, but Subject 9 had high exposure to legs and
 feet and Subject 6 had no exposure in these areas.

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	Table 8.	Artisan	activities	of each	subject
--	----------	---------	------------	---------	---------

Artisan/staff (minutes sampled)	Description of activity	Clothing		
Test 1, April 2003				
Subject 1/male (153 min)Wedged clay on a wedging board to remove air from the clay before kneading and shaping clay by hand. Used a wooden press to press the clay into flat, approximately 2.5 		Short-sleeved shirt, long pants, socks, shoes		
Subject 2/male, nonartisan staff (84 min)	Poured powdered components into large mixer for clay manufacture while wearing dust mask and while the dust removal system was operational. Weighed out portions of clay, and bagged and stored them. Subject moved to gas kiln room, where he cut blocks, built the kiln up a bit, and vacuumed. Finally, subject used compressed air to clean the dust off himself.	Short-sleeved shirt, long pants, socks, shoes		
Subject 3/female (124 min)	Subject wedged clay and covered a prefabricated mold with clay using her hands to mold and shape the clay.	Short-sleeved shirt, long pants, socks, shoes		
Subject 4/female (121 min)	Subject cut pre-wedged and formed blocks of clay into 5 cm thick pieces, loaded the blocks into a pneumatic press, pressed a pattern into each and cut blocks to the proper shape, and then stacked the finished pieces to be fired.	Long-sleeved shirt (rolled up), long pants, socks, shoes		
Subject 5/male (136 min)	Subject hand rolled clay into 60 cm long "snake-like" cylinders, which he then hand-formed into conical pots.	Short-sleeved shirt, long pants, socks, shoes		
Subject 6/female (123 min)	Subject threw a variety of clay items, including a pitcher, a vase, pots, and bowls on the pottery wheel.	Short-sleeved shirt, long pants, socks, shoes		
Subject 7/female (124 min)	Subject wedged, rolled, cut, and hand-built a variety of items.	Short-sleeved shirt, long pants, socks, shoes		
Subject 8/female (138 min)	Subject wedged, rolled, shaped, cut, and hand-built large pieces of clay and placed them on a mold.	Short-sleeved shirt, long pants, socks, shoes		
Test 2, July 2004				
Subject 9/female, five sessions (295–476 min)	Subject threw a variety of clay items, including plates, bowls, vases, and cups, on the pottery wheel.	Short-sleeved shirt, short pants, sandals		
Subject 10/female, three sessions (406–438 min)	Subject sculpted detailed designs into clay tiles and plaques; also chipped small bits of excess clay off pieces of art that had already been fired.	Short-sleeved shirt, 3/4 length pants, sandals		

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# Table 9. Hypothetical estimates of dermal dose

Body part	Clay load on skin (mg/cm <sup>2</sup> ) <sup>c</sup>	Skin area (cm <sup>2</sup> ) <sup>e</sup>	Fraction uncovered	Absorbed dioxin dose (pg TEQ/day) <sup>a,b,d</sup>
Subject 1				
Hands	0.38	970	1.0	1.00
Arms	0.15	2,406	0.5	0.49
Total				1.50
Subject 2				
Hands	[2.01]	970	1.0	1.65
Subject 3				
Hands	0.51	865	1.0	1.2
Subject 4				
Hands	0.17	855	1.0	0.41
Subject 5				
Hands	[2.61]	1,005	1.0	1.71
Subject 6				
Hands	[9.25]	790	1.0	1.34
Arms	[2.99]	2,005	0.6	2.04
Total				3.38
Subject 7				
Hands	0.26	785	1.0	0.57
Subject 8				
Hands	[1.90]	715	1.0	1.21

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## Table 9. Hypothetical estimates of dermal dose (continued)

Body part	Clay load on skin (mg/cm <sup>2</sup> ) <sup>c</sup>	Skin area (cm <sup>2</sup> ) <sup>e</sup>	Fraction uncovered	Absorbed dioxin dose (pg TEQ/day) <sup>a,b,d</sup>
Subject 9				
Hands	[10.12]	857	1.0	1.45
Arms	[1.50]	2,265	0.75	2.88
Lower legs	[0.72]	2,161	1.0	13.44
Feet	0.26	1,151	1.0	2.99
Face	0.03	374	1.0	0.03
Total				20.80
Subject 10				
Hands	0.20	783	1.0	0.42
Arms	0.04	2,271	0.9	0.22
Lower legs	0.11	2,095	0.1	0.23
Feet	0.03	1,109	1.0	0.30
Face	0.04	368	1.0	0.04
Total				1.22

<sup>3456789</sup> 

<sup>a</sup>Absorption = skin load (mg/cm<sup>2</sup>-day) × skin area (cm<sup>2</sup>) × fraction uncovered × dioxin concentration in clay (pg TEQ/g) ×  $10^{-3}$  mg/g × absorption fraction.

<sup>b</sup>All calculations assume dioxin concentration in clay = 162 pg TEQ/g and absorption fraction is 6.19% for feet and legs, and 1.69% for hands, arms, and face.

<sup>c</sup>All bracketed loads exceed monolayer of 0.62 mg/cm<sup>2</sup> and were reduced to this value in absorption calculation. <sup>d</sup>Results from Subjects 1 through 8 are based on one work session, from Subject 9 are based on average of five

10 sessions, and from Subject 10 are based on average of three sessions.

<sup>11</sup> <sup>e</sup>Skin area is for total body parts; for two-sided parts, it is the sum of right and left sides.

12 TEQ = toxic equivalent

- 13
- 14

15 16 17 • **Mixing (Subject 2).** Subject 2 was involved in the mixing and handling of dry clays and furnace/kiln maintenance during the work session. This activity produced relatively large hand loadings.

- 1 Wedging and molding (Subjects 1, 3, 4, 5, 7, and 8). Wedging clay involves 2 kneading and hitting clay against a tabletop to purge air pockets from the clay. 3 During the wedging process, the clay is firm and dry as compared with clay used on the wheel. This activity produced a wide range of hand loadings (from 0.17 to 4 5  $2.61 \text{ mg/cm}^2$ ). 6 7 Sculpting (Subject 10). This involved sculpting activities on dry clay. At times, • 8 fine detailing tools were used that involved very little contact with the clay, 9 resulting in low hand loading. 10 11 Table 10 shows the percent contribution to the dermal dose by body part for Subjects 9 12 and 10. Subjects 9 and 10 were tested in July 2004 and wore summer clothing, which allowed 13 exposure to their legs and feet. Leg and foot exposure accounted for 79% of the total dose for Subject 9 and 44% of the total dose for Subject 10. This reflects the relatively large surface 14 15 areas and higher absorption fraction (due to longer exposure time) for these parts. The 16 uncovered portion of Subject 10's lower legs was only 10%, so the leg contribution to total dose 17 was much less than that of Subject 9. Facial exposures were low, accounting for only 0.1–3% of 18 total dose. 19
- 20
- 21

### Table 10. Percent contribution to dermal dose by body part

	Percentage of dose		
Body part	Subject 9 (wheel)	Subject 10 (sculpture)	
Hands	7	34	
Arms	14	18	
Legs	65	19	
Feet	14	25	
Face	0.1	3	

23 24

#### 25 7.1.1. Clay Loads on Surfaces

26 The horizontal surfaces in ceramic art studios can have high dust loads resulting from air 27 deposition. Most clay on the hands of artisans probably results from direct contact with clay, but 28 some could also result from contact with surfaces. In the interest of exploring this issue, wipe

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1 samples were collected from the work surface of each subject. These results are shown in

- Table 11. The surface dust loads ranged from 0.2 to 7  $mg/cm^2$ , which are high compared with 2
- dust loads on floors in residences (i.e., 0.005 to 0.7 mg/cm<sup>2</sup>) (Lioy et al., 2002). The efficiency 3
- 4 of transfers from surfaces to hands will vary depending on the type of surface, type of residue,
- 5 hand condition, force of contact, etc. Rodes et al. (2001) conducted hand press experiments on
- 6 particle transfer to dry skin and measured transfers with central values of about 50% from hard
- 7 surfaces. Several of the ratios of hand loads to surface loads given in Table 11 exceed 50% by a
- 8 wide margin. Subject 6 was working on a wheel and clearly had hand loads resulting from direct
- 9 contact with clay. Similarly, Subjects 5 and 8 had very high hand loads that must have resulted
- 10 from direct clay contact. The other subjects had ratios ranging from 0.05 to 0.30, which are in
- 11 the range that could result from surface transfers. Observation of the subjects indicated that
- 12 almost all contact with the work surface also involved some contact with the clay. Therefore, the
- 13 hand residues are most likely derived from a combination of direct clay contact and transfers
- 14 from surfaces.
- 15
- 16
- 17

Table 11.	Comparing clay	y loads on surface	es to clav loads o	on hands
	Comparing cia	y iouus on suitace	b to ciay ioaub (	ii iiaiias

18

Subject	Clay loading on surface (mg/cm <sup>2</sup> )	Clay load on hand (mg/cm <sup>2</sup> )	Ratio of hand load to surface load
1	7.002	0.38	0.05
2	NA	2.01	NA
3	2.966	0.51	0.17
4	0.572	0.17	0.30
5	0.774	2.61	3.4
6	0.238	9.25	38.9
7	1.206	0.26	0.22
8	0.419	1.90	4.5

19

NA = Nonartisan subject was not working at a surface during sampling, so this type of sample 20 21 was not collected.

- 22
- 23

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#### 1 7.1.2. Dermatologist Report

The dermatologist did not diagnose any serious skin health problems among the subjects.
Small abrasions and common skin conditions such as dryness and cracking, as the subjects
reported on the questionnaires, were noted, but changes in these conditions could not be detected
based on before and after observations.

6 7

### 7.2. INHALATION

8 Estimating the inhalation dose involved measuring particle concentrations in air and
9 modeling deposition to various regions of the respiratory system. Classroom exposures were not
10 estimated.

11

## 12 **7.2.1. Particle Levels in Air**

13 As described in Section 3, four different sampling techniques were used during the April 14 2003 tests to measure clay particle concentrations in air: two personal monitors and two area 15 monitors. The data from all four devices are shown in Appendixes C and D. The Respicon 16 personal air sampler normally would have been the best indicator of individual exposures, but 17 the blanks were high, resulting in a high detection limit and a high frequency of nondetects in the 18 data. Instead, the cascade impactor was chosen as the best indicator of daily exposure. Although 19 this is an area sampler, it was located near the subjects and the subjects were generally stationary 20 during the test. Thus, it should have been a reasonable indicator of individual exposures. Also, 21 the cascade impactor uses deposition collectors and gravimetric techniques to estimate air 22 concentrations; consequently, it is a more direct measurement technique than the other two 23 instruments (pDR-1000 and Climet), which use light scattering to estimate particle 24 concentration. These optical devices provide a nearly continuous readout of concentration 25 levels, making them better suited to evaluating short-term fluctuations in particle levels rather 26 than long-term concentrations. 27 Only the cascade and Climet monitors were used in the July 2004 tests. The instruments 28 were located even closer to the individuals, i.e., within 30 cm of their breathing zones. The data

29 were used in a fashion consistent with the April 2003 tests, i.e., daily exposures were based on 30 the cascade data and the Climet was used to evaluate short-term fluctuations.

- 31 Table 12 presents the air data for each subject on the basis of the cascade measurements.
- 32 The MMADs were estimated by fitting the data to log-normal distributions (see the discussion in
- Appendix G). Table 12 indicates that the range for total particulate matter is 0.084 to 0.99
- $34 \text{ mg/m}^3$ . Note that the upper end of this range is less than the Occupational Safety and Health
- 35 Administration (OSHA) standard for total particulates of 15 mg/m<sup>3</sup> (OSHA, 2004). Subject 3's
- 36 concentration was the highest because students were cleaning the floor near the area samplers
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(see the discussion below). Subject 9's concentration was the lowest as a result of a relatively
low activity level during the testing. Subject 5's concentration was also low, likely because a
steady breeze entered through an open window in the room in which sampling was occurring.
All of the other subjects had fairly similar concentrations.

- 4 5 6 7 8
- 9

Table 12. Particle concentrations in air and mass median aerodynamic
diameter (MMAD) based on cascade impactor

Subject	MMAD (µm)	Total concentration (mg/m <sup>3</sup> )
1	26.9	0.35
2	44.6	0.47
3	18.5	0.99
4	$25.0^{a}$	0.37
5	$25.0^{a}$	0.13
6	20.2	0.61
7	13.0	0.51
8	26.7	0.64
9	32.6	0.084
10	16.0	0.24

10 11

<sup>a</sup>Nondetects prevented calculation of the MMAD for these subjects; they were assumed equal to the average over the remaining first eight subjects.

12 13 14

15

The two subjects using wheels (Subjects 6 and 9) had very different air exposures.

16 Because a great deal of water is used to moisten clay during wheel molding (the clay was

17 saturated with water and a pan of water was placed directly next to the artisans for their use), this

18 setting would not be expected to produce much clay dust, which was observed for Subject 9.

19 Subject 6, however, had fairly high air levels. Subject 6 was located near a classroom that, as

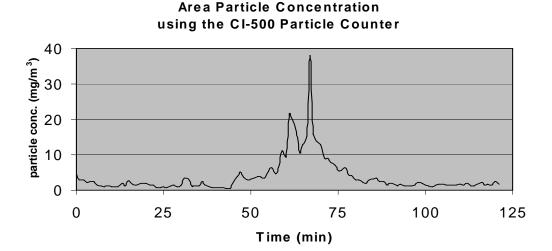
20 discussed below, had high activity levels. Therefore, this subject's high air levels may have been

21 associated more with the classroom activities than the wheel activities.

Figure 3 shows the plot of concentration versus time (based on the Climet CI-500 area particle counter) for Subject 3, who worked in an area designated for graduate student work

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- 1 adjacent to a large classroom. Approximately 50 minutes into the sampling session, about 20
- 2 students from the adjacent classroom began sweeping and wiping down the surfaces. This
- 3 activity continued for approximately 15 minutes and generated a significant cloud of dust. As
- 4 shown in Figure 3, particle levels began rising at about 50 minutes, peaked sharply at 60–70
- 5 minutes, and declined to low levels at about 80 minutes.
- 6 7



10

11 12

Figure 3. Real-time particle concentration for Subject 3 using the CI-500 particle counter.

13 During two of Subject 10's sculpture work sessions, a small dog was present. The dog's 14 movement disturbed dust on the floor of the ceramics studio and, in turn, increased the particle 15 concentration. Figures 4 and 5 are the real-time traces for the Climet monitor for the sculpting 16 work sessions during which the dog was present. The dog was present for the entire first 17 sculpting work session. This was reflected in the relatively constant variation in the particle 18 concentration throughout the work session. During the second sculpting work session, the dog 19 did not arrive until 138 minutes into sampling. Note the increase in overall particle 20 concentration and increase in variability of particle concentration after arrival of the dog. The 21 presence of a dog in the studios and classrooms is not likely to be a common occurrence, 22 especially during the regular school year. Therefore, the particle concentrations during the work 23 sessions when the dog was present (1 and 2) were not used to estimate the exposures for this

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1 subject. It should be noted, however, that pets, which may be present in many ceramic art

2 studios, can have a large influence on the suspended dust levels and spread dust to other areas.

3

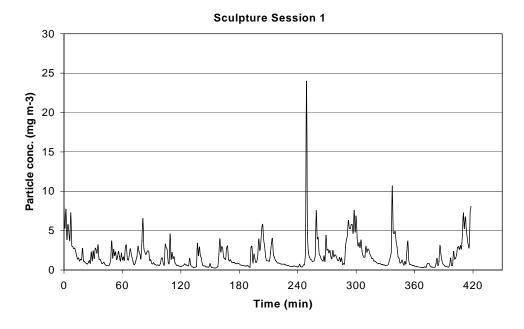
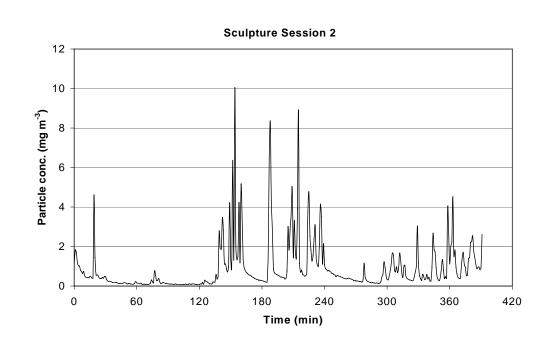


Figure 4. Sculpture session 1 with dog present.



8 9

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Figure 5. Sculpture session 2 with dog present.

### 1 7.2.2. Inhalation Dose

Table 13 shows the absorbed dose in various regions of the respiratory system for all 10 subjects. The total inhalation doses ranged from 0.006 to 0.09 pg TEQ/d with an average of 0.04 pg TEQ/d. Most particle deposition was found to occur in the extrathoracic region. The modeling to support these estimates is presented in Appendix G.

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9

	Absorbed dose (pg TEQ) <sup>a</sup>			
Subject	ET <sup>b</sup>	TB <sup>b</sup>	PU <sup>c</sup>	Total
1	0.032	0.001	0.003	0.035
2	0.033	0.001	0.003	0.036
3	0.082	0.002	0.010	0.094
4	0.028	0.001	0.002	0.031
5	0.012	0.000	0.001	0.014
6	0.054	0.001	0.004	0.059
7	0.049	0.001	0.006	0.057
8	0.048	0.001	0.003	0.052
9	0.005	0.000	0.001	0.006
10	0.022	0.001	0.002	0.025

## Table 13. Hypothetical estimates of inhalation dose

10 11 12

<sup>a</sup>Dose calculated using procedures in Appendix G for nasal breathing; subject exposure concentrations from Appendix D; 4-hour exposure duration and dioxin concentration of 162 pg TEQ per gram clay.

<sup>b</sup>Absorption fraction of 0.3 assumed, since these regions rapidly clear into the gastrointestinal tract.

14 <sup>c</sup>Absorption fraction of 0.8 assumed, in part, due to slow particle clearance from this region. 15

16 TEQ = toxic equivalent; ET = extrathoracic; TB = tracheobronchial; PU = pulmonary

- 17
- 18 19

The inhalation exposure estimates assume that no respiratory protection was used.

20 Generally this was true, however, Subject 2 used a dust mask while pouring powdered clay into a

21 mixer for clay preparation. This reduced his inhalation exposures relative to levels reported here.

22

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#### 1 **7.2.3. Classroom Exposure**

2 Estimating student exposures in a classroom setting was not an objective of this study. 3 However, some insight on this issue can be gained from the data for Subjects 1, 3, and 6. These 4 subjects performed their clay activities adjacent to the undergraduate classroom during times 5 when undergraduate classes of 20–25 students were participating in clay-related activities. The 6 area particle samples collected for these subjects are generally representative of the inhalation 7 exposure of students in those classes. As discussed above, students in this class swept the floor 8 during Subject 3's testing period, producing elevated particle concentrations for about 9 30 minutes.

10

# 11 **7.3. INGESTION**

12 The ingestion dose was calculated by assuming that all deposited material on the 13 surrogate food and beverage samples was ingested. As Table 14 shows, clay deposition onto the 14 food and beverage samples reached detectable levels in only 5 out of 16 total samples. The 15 deposition amounts for the nondetects were assumed to equal half the detection limit. The 16 resulting ingestion doses ranged from 0.03 to 0.1 pg TEQ/d. The field technicians did not 17 observe hand-to-mouth activities for any of the subjects. Also, none of the subjects ate food or 18 smoked without first washing the clay from their hands. No deposition samples were collected 19 for Subjects 9 and 10.

20

# 21 **7.4. TOTAL DOSE**

Table 15 lists the hypothetical estimates of total dioxin dose derived by summing across exposure pathways for each subject. The total doses ranged from 0.49 to 20.81 pg TEQ/d with an average of 3.45 pg TEQ/d. Table 16 shows the percentage contribution of each exposure pathway to the total dose of each subject. Dermal absorption is the major contributor to total dose for all subjects, exceeding 78% for all subjects. Ingestion and inhalation contribute similar amounts, generally in the range of 1–10%.

Table 17 shows the dose estimates by activity. The highest total doses were associatedwith wheel activities.

Subject	Clay deposited onto food (mg)	Clay deposited into beverage (mg)	Ingestion dose (pg TEQ/day) <sup>a,b</sup>
1	0.71	0.66	0.07
2	<dl< td=""><td><dl< td=""><td>0.03</td></dl<></td></dl<>	<dl< td=""><td>0.03</td></dl<>	0.03
3	<dl< td=""><td><dl< td=""><td>0.03</td></dl<></td></dl<>	<dl< td=""><td>0.03</td></dl<>	0.03
4	<dl< td=""><td>0.72</td><td>0.05</td></dl<>	0.72	0.05
5	<dl< td=""><td><dl< td=""><td>0.03</td></dl<></td></dl<>	<dl< td=""><td>0.03</td></dl<>	0.03
6	<dl< td=""><td><dl< td=""><td>0.03</td></dl<></td></dl<>	<dl< td=""><td>0.03</td></dl<>	0.03
7	1.66	<dl< td=""><td>0.1</td></dl<>	0.1
8	1.50	<dl< td=""><td>0.09</td></dl<>	0.09

6

7

8 9 <sup>a</sup>Ingestion dose (pg TEQ) = (deposited clay on food (mg) + deposited clay on beverage (mg)) × dioxin concentration in clay (pg TEQ/g) × absorption fraction × (1 g/1,000 mg).

<sup>b</sup>All calculations assume dioxin concentration in clay = 162 pg TEQ/g, absorption fraction =

0.3, all deposited clay is ingested, and nondetects were set equal to half the detection limit.

TEQ = toxic equivalent; DL = Detection limit (0.60 mg).

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Table 15. Hypothetical	estimates of total dioxin dose (pg TEQ/day)
------------------------	---

		Estimated dioxi	in dose (pg TEQ/day)	
Subject	Inhalation	Ingestion	Dermal absorption	Total
1	0.035	0.07	1.50	1.61
2	0.036	0.03	1.65	1.72
3	0.094	0.03	1.20	1.32
4	0.031	0.05	0.41	0.49
5	0.014	0.03	1.71	1.75
6	0.059	0.03	3.38	3.47
7	0.057	0.1	0.57	0.73
8	0.052	0.09	1.21	1.35
9	0.006	NM	20.80	20.81
10	0.025	NM	1.22	1.25
Mean (SD)	0.041 (0.025)	0.05 (0.03)	3.37 (6.18)	3.45 (6.15)
Median	0.036	0.04	1.36	1.48
Minimum	0.006	0.03	0.41	0.49
Maximum	0.094	0.10	20.80	20.81

TEQ = toxic equivalent; NM = not measured; SD = standard deviation

	Percentage of dose			
Subject	Inhalation	Ingestion	Dermal absorption	
1	2.2	4.4	93.4	
2	2.1	1.7	96.2	
3	7.1	2.3	90.7	
4	6.3	10.2	83.5	
5	0.8	1.7	97.5	
6	1.7	0.9	97.4	
7	7.8	13.8	78.4	
8	3.9	6.7	89.5	
9	0.0	NM	100.0	
10	2.0	NM	98.0	

### Table 16. Percent contribution to total dioxin dose

3 4

NM = not measured

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1 2

# Table 17. Dose estimates by activity

Activity	Subject	Inhalation dose (pg TEQ/day)	Ingestion dose (pg TEQ/day)	Dermal dose (pg TEQ/day)	Total dose (pg TEQ/day)
Wedging and	1	0.035	0.07	1.50	1.61
molding	3	0.094	0.03	1.20	1.32
	4	0.031	0.05	0.41	0.49
	5	0.014	0.03	1.71	1.75
	7	0.057	0.1	0.57	0.73
	8	0.052	0.09	1.21	1.35
Mixing	2	0.036	0.03	1.65	1.72
Wheel	6	0.059	0.03	3.38	3.47
	9	0.006	NM	20.80	20.81
Sculpting	10	0.025	NM	1.22	1.25

#### 3 4

NM = not measured; TEQ = toxic equivalent

#### 8. MONTE CARLO SIMULATION OF THE EXPOSURE DATA

Section 7 presented hypothetical dose estimates for each subject, assuming that all were
using typical amounts of ball clay with average dioxin levels. In this section, Monte Carlo
simulations are used to explore the doses that could occur in a broad population of artists with a
wide range of behaviors using ball clay with differing levels of dioxin.

7 The general strategy for selecting input value distributions was as follows. The 8 distribution of skin surface areas across adults in the general population was assumed to be log-9 normal with mean and standard deviation from the Exposure Factors Handbook (U.S. EPA, 10 1997). Similarly, the dioxin concentration in clay was assumed to have a log-normal distribution 11 with mean and standard deviation from Ferrario et al (2004, 2007). The rationale for choosing 12 log-normal distributions was that physiological parameters and environmental media 13 concentrations are commonly found to have these types of distributions. The distributions were 14 truncated at the minimum and maximum data points to eliminate the chance that some simulation 15 trials could use unreasonable values. The remaining exposure factor parameters were based on 16 observations from this study. These were generally assumed to have triangular distributions with 17 ranges based on minimum and maximum values and peaks based on means. The rationale for 18 choosing a triangular distribution was that (1) the small sample sizes associated with the study 19 observations prevented fitting the data to standard distributions and (2) it reflected the likelihood 20 that a central value would occur most often. In some cases (e.g., clay load on face), only two 21 data points were available and a uniform distribution was assumed. The distributions assumed 22 for all input variables are listed in Table 18. 23 Crystal Ball 7 software was used to conduct 1,000 trial simulations. For each simulation 24 trial, a set of parameter values was obtained by randomly sampling the parameter distributions as 25 listed in Table 18 and then computing the dioxin dose. The dose was calculated using the 26 equations presented in Section 5. All simulation trials first select a set of values for the dioxin 27 concentration in ball clay, the fraction of ball clay in the blend used by the artist, and the 28 exposure duration. These are shown as general parameters in Table 18. The simulation then 29 calculates the dose from the dermal, inhalation, and ingestion pathways, as discussed below: 30

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- 32 33 34

37

34percentage of total surface area. These percentages were obtained from U.S. EPA35(1997): hands, 5.2%; arms, 14%; legs, 31.8%; feet, 6.8%; and face, 2.5%36(assumes face area equals one-third of head area). This approach ensures that

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**Dermal.** The simulation was designed to first select a total body surface area

from a log-normal distribution. Subsequently, skin surface areas for individual

body parts were calculated by multiplying the total surface area by the average

simulation trials have realistically matched body part areas. Since the body part

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Parameter	Distribution	Basis
General parameters		
Dioxin concentration in ball clay (pg TEQ/g)	Log-normal (mean = $808$ , SD = $318$ )	Ferrario et al. (2004, 2007) (n = 21); truncated at range limits
Fraction of ball clay in blend	Triangular (0, 0.2, 1.0)	Data in this study $(n = 10)$
Exposure duration (hr/d)	Triangular (1, 4, 10)	Judgment and data from this study $(n = 8)$
Dermal absorption parameters		
Total body surface area (cm <sup>2</sup> )	Log-normal (mean = 18,000, SD = 37.4)	<i>Exposure Factors Handbook</i> (U.S. EPA, 1997); truncated at range limits (n = 32)
Clothing selector	Uniform (0, 1.0)	Judgment and data from this study $(n = 8)$
Clay load on hand (mg/cm <sup>2</sup> )	Triangular (0.1, 3.0, 10)	Range and mean based on observations from this study $(n = 10)$
Clay load on arm (mg/cm <sup>2</sup> )	Triangular (0.04, 0.35, 3.0)	Data in this study $(n = 4)$
Clay load on leg (mg/cm <sup>2</sup> )	Uniform (0.1, 0.70)	Data in this study $(n = 2)$
Clay load on feet (mg/cm <sup>2</sup> )	Uniform (0.03, 0.3)	Data in this study $(n = 2)$
Clay load on face (mg/cm <sup>2</sup> )	Uniform (0.03, 0.04)	Data in this study $(n = 2)$
Ingestion parameters		
Clay load on food (mg)	Triangular (0.3, 0.7, 1.66)	Range and mean based on observations from this study $(n = 8)$
Clay load on beverage (mg)	Triangular (0.3, 0.5, 0.72)	Range and mean based on observations from this study $(n = 8)$
Inhalation parameters		
Particle concentration in air (mg/m <sup>3</sup> )	Triangular (0.08, 0.44, 0.99)	Range and mean based on observations from this study $(n = 10)$
Median particle size (µm)	Triangular (13, 25, 45)	Judgment and data from this study (n = 10)
Lung parameters	Male, 30%; female, 70%	Male/female split based on data in this study (n = 10)
Fraction of time engaged in light vs. moderate exertion.Uniform (0, 1.0)Judgment		Judgment
Breathing type	Oronasal, 13%; nasal, 87%	Brown (2005)

# Table 18. Monte Carlo simulation input parameters and sampling distributions

area calculations give total areas, a fraction unclothed was used to reduce this to the exposed area. These fractions were based on four clothing scenarios as shown in Table 19. These clothing scenarios were based on questionnaire responses and This document is a draft for review purposes only and does not constitute Agency policy. DRAFT-DO NOT CITE OR QUOTE 46

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judgment about typical apparel for a moderate climate. A clothing scenario was selected randomly for each simulation trial according to the time fractions shown in Table 19. Distributions were also assumed for the clay loads on skin. These were assumed to be spread uniformly over the entire unclothed area. As discussed in Section 5.1, dermal absorption was assumed to be limited to the monolayer that was held constant at the median value of 0.62 mg/cm<sup>2</sup> (the impact of changing this value is discussed as an uncertainty issue in Section 9). Finally, the absorption fractions (as presented in Section 5.1) were applied to derive the absorbed dose from exposed body parts and then summed to derive total dermal dose.

		Fraction unclothed		
Clothing scenario	Time fraction	Arms	Legs	Feet
Long-sleeved shirt, long pants, shoes	0.2	0	0	0
Short-sleeved shirt, long pants, shoes	0.6	0.67	0	0
Short-sleeved shirt, short pants, shoes	0.1	0.67	0.67	0
Short-sleeved shirt, short pants, sandals	0.1	0.67	0.67	1.0

#### Table 19. Clothing scenarios based on questionnaire responses

 • Inhalation. The inhalation dose was calculated using the procedures summarized in Section 5.2 and presented in detail in Appendix G. Distributions were used to represent the variability in total particulate concentration in air and median particle size (see Table 18). Breathing was assumed to be either oronasal (13%) or nasal (87%), based on Brown (2005). Inhalation parameters (see Appendix G) were based on an average female for 70% of the trials and an average male for 30% of the trials. The rate of breathing was determined by the fraction of time engaged in light versus moderate exertion. These fractions were varied randomly from 0 to 1.0 using a uniform distribution. Depositions to various parts of the respiratory system were modeled as described in Appendix G, multiplied by the absorption fraction, and summed to derive the total inhalation dose.

• **Ingestion.** The variability in ingested dose was simulated using distributions for the levels of clay in the food and beverages as shown in Table 18. As discussed in Section 5.3, all deposited material was assumed to be ingested.

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1 Two Monte Carlo stimulations were conducted. The first simulation was designed to 2 evaluate the influence of clay use only. Accordingly, it was conducted using the distributions for 3 dioxin concentration in the clay and the fraction of ball clay in the blend used by the artists. All 4 other inputs were held constant at their central values. The summer clothing scenario was used 5 (i.e., short-sleeved shirt, short pants, sandals). This simulation produced a mean total dose of 6 39 pg/d, median of 33 pg/d, and 90th percentile of 73 pg/d. These results are best compared to 7 the hypothetical dose estimate for Subjects 9 and 10 (presented in Section 7) because they wore 8 summer clothing matching the simulation assumption. Subject 9 had a dose estimate of 21 pg/d, 9 corresponding to about the 30th percentile of the simulation. Subject 10 had a dose of 1.5 pg/d, 10 corresponding to about the 2nd percentile of the simulation. This simulation suggests that clay 11 choice alone can account for a wide range of exposures with the potential to elevate exposures 12 above the hypothetical estimates for the 10 subjects.

13 The second simulation used the distributions for all parameters as shown in Table 18. 14 This simulation produced a mean total dose of 16 pg/d, median of 8 pg/d, and 90th percentile of 37 pg/d. The standard deviation exceeds the mean indicating that the results have a wide spread 15 16 as shown in Figure 6. The hypothetical dose estimates of most subjects would have 17 corresponded to low percentiles of this simulation except Subject 9 (80th percentile). Table 20 18 shows the simulation results for each pathway. The simulation means for each pathway 19 exceeded by 3 to 4 times the means of the hypothetical dose estimates for the 10 subjects. As 20 observed during the field study, the ingestion and inhalation doses are much smaller than the 21 dermal dose. The frequency diagram for total dose is shown in Figure 6. This figure shows a 22 highly skewed distribution with a peak around 3 pg TEQ/d and a long tail to the right extending 23 to about 70 pg TEQ/d. A detailed report showing all inputs and outputs for this simulation is 24 presented in Appendix F.

A sensitivity analysis was performed using the Crystal Ball 7 software. Each input parameter was evaluated using contribution to variance and rank order correlation (Figures 7 and 8). These analyses showed that clothing selected contributed most to variance (37.9%), followed closely by fraction of ball clay in blend (37.7%), dioxin concentration (16.6%), and exposure duration (5%).

30 Overall, the simulation suggests that higher exposures than those reflected in the 31 hypothetical dose estimates of the 10 subjects may occur. This results from the skewed input 32 distributions, which generally have long right-hand tails. Also 6 of the 10 subjects had hand 33 exposure only, and the simulation uses a range of clothing that will result in more skin exposure 34 in most trials.

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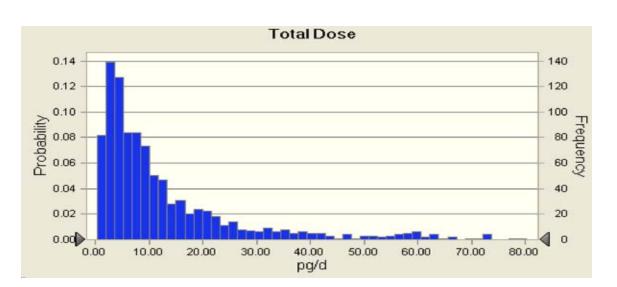
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1 2 3

# Table 20. Descriptive statistics of dioxin doses from ball clay use, based on a **Monte Carlo simulation**

Pathway	Mean	Standard deviation	Median	90th Percentile
Dermal dose (pg TEQ/d)	15.5	22.91	7.92	36.15
Ingestion dose (pg TEQ/d)	0.14	0.10	0.11	0.28
Inhalation dose (pg TEQ/d)	0.12	0.13	0.08	0.27
Total dose (pg TEQ/d)	15.76	23.01	8.12	36.63

4 5



6 7

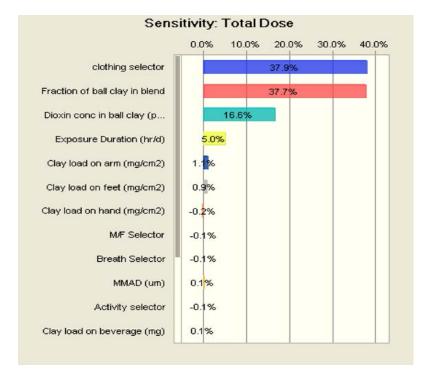
Figure 6. Frequency distribution of total dose (pg TEQ/day) based on Monte Carlo simulation.

9 10

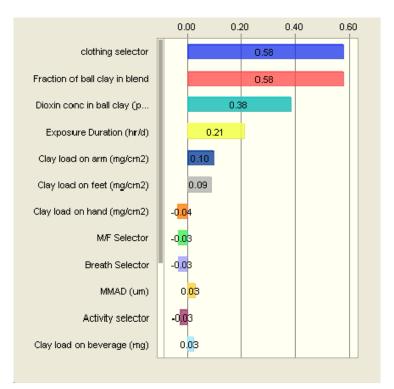
8

11 Many of the input distributions used in this simulation were based on very limited data or 12 judgment. A number of the distributions were based on data from this study, and the degree to 13 which the study subjects represented a broader population of artists is unknown. Similarly, the 14 degree to which the studio conditions observed in this study represent a broader set of studios is 15 unknown. The simulation should be interpreted as a preliminary indication of how to extrapolate 16 the study results to a broader population of artists.

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# Figure 7. Sensitivity analysis based on percent contribution to variance.



# Figure 8. Sensitivity analysis based on rank correlation.

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1	9. UNCERTAINTY
2	
3	This section discusses general uncertainty issues and uncertainties related to the three
4	exposure pathways: dermal, inhalation, and ingestion.
5	
6	9.1 GENERAL UNCERTAINTY ISSUES
7	
8	The sensitivity analyses showed that the dioxin concentrations in clay and the fraction of
9	ball clay used account for a large part of the overall variance in the exposure estimates. Thus it
10	is important to consider the uncertainty in the assumptions regarding these two parameters.
11	The dioxin levels in ball clay were assumed on the basis of the study by Ferrario et al.
12	(2004, 2007). An important uncertainty issue is whether the ball clay sampled by Ferrario is
13	representative of the ball clay used in the studio and by the broader community of ceramic
14	artists. Ferrario et al. (2004, 2007) explained that the major mining companies market a total of
15	32 ball clay products of which 13 were sampled. Although marketing data were not available to
16	do true statistical sampling, a ceramics expert confirmed that the most commonly used ball clays
17	were included in this study. The samples were collected from 22.7 kg (50 pound) bags in the
18	same form as delivered to ceramic studios. Four of the 21 samples analyzed by Ferrario et al.
19	matched exactly the primary type of ball clay used in the OSU ceramics studio.
20	As explained earlier, ceramic artists use a wide range of clay blends with ball clay
21	contents ranging from 0 to 100%. The hypothetical dose estimates were based on the assumption
22	of 20% ball clay in the blend, which is the average fraction used by the 10 subjects in this study.
23	It is unknown how representative this is of the wider population of ceramic artists. The ball clay
24	fraction assumption may also affect other exposure factors. For example, it could affect how
25	much clay adheres to skin. Soil adherence to skin has been shown to be influenced by moisture
26	content and particle size. Ball clay is similar to other clays in terms of these properties. The
27	primary way that ball clay is unique from other clays is its high plasticity. It is not known how
28	this property would affect skin adherence.

### 30 9.2. DERMAL EXPOSURE UNCERTAINTIES

A fraction absorbed approach is used to estimate dermal absorption based on current Agency guidance. As discussed in Section 5.1, this method has acknowledged weaknesses, but the uncertainties are difficult to assess. Appendix I presents an alternative approach using a more mechanistic model. This model predicts an absorbed dose that is similar to the fraction

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absorbed approach. The mechanistic model has had limited testing, and it is not yet clear
 whether it provides more reliable estimates.

3 The exposures in the studio are caused by clay, but the dermal absorption fraction is 4 derived from soil experiments. An important uncertainty issue is whether clay has properties 5 that differ significantly from soil and consequently make the soil-derived absorption estimates 6 invalid for clay. The soil used by Roy et al. (1990) was 16.7% clay. This fraction of the soil 7 should have properties similar to those of the studio clay. The organic carbon content of the clay 8 is approximately the same as that of the low organic soil used by Roy et al. In terms of particle 9 size, clays typically have lower particle sizes than soil and would be expected to more strongly 10 sorb organic contaminants (e.g., dioxins) as compared with normal soils, all other factors being 11 equal. As discussed in Section 5, commercial ball clay specifications report a median particle 12 size of about 0.75  $\mu$ m, which is smaller than that of the Roy et al. soil (median diameter of about 13  $10 \,\mu\text{m}$ ). The particle sizes measured in the studio air had median diameters ranging from 8 to 14  $27 \,\mu\text{m}$ , which are larger than those of the soils used by Roy et al. This may be explained by the bonding of particles caused by the addition of water to the clay or the firing process, which fuses 15 16 particles. Thus, it appears that the particle size of the soil used by Roy et al. falls within the 17 range present in the studio.

The studies on dermal absorption of dioxin from soil by Roy et al. and other investigators 18 19 have exclusively used TCDD. It is important to consider whether results for TCDD can be 20 extrapolated to the other dioxin congeners found in clay. As mentioned previously, the 21 compounds of concern in the clay are the tetra- through octa-CDD congener groups, as listed in 22 Table 21. This table indicates that molecular weight and the octanol-water partition coefficient 23  $(K_{ow})$  increase with chlorine substitution. Molecular weight and  $K_{ow}$  have been identified as key 24 chemical properties affecting dermal absorption (U.S. EPA, 1992). These properties also relate 25 to how tightly bound chemicals are to soils and their release kinetics. The higher chlorinated 26 congeners would be released from soils more slowly and permeate skin more slowly than TCDD. 27 Thus, use of TCDD experiments to represent the penta - octa dioxin congeners found in clay 28 probably leads to some overestimates of dermal absorption, but it is uncertain to what degree. 29 A related question is whether TCDD-derived dermal absorption values can be applied to 30 TEQs. As shown in Table 21, only about 9% of the TEQ in processed clay is derived from 31 TCDD. The TEFs used to determine TEQs discount the hepta- and octa- congeners much more 32 than the tetra- and penta- groups. The overestimates of dermal absorption for the higher 33 chlorinated congeners due to their higher molecular weights and Kow values will be compensated 34 to some extent by the large discounts during the TEQ calculation and thus make extrapolation of 35 dermal absorption data from TCDD to TEQs more reasonable.

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Table 21. Physical pro	operties of dioxin congeners and concentra	ation in processed
clay		

Congener	Molecular weight	Log K <sub>ow</sub> ª	Concentration in processed clay <sup>b</sup> (pg/g)	Concentration in processed clay <sup>b</sup> (pg TEQ/g)	% of total TEQ
TCDD	322	6.1 to 7.1	76	76	9
PeCDD	356.4	6.2 to 7.4	374	374	46
HxCDD	390.9	6.85 to 7.8	2,341	234	28
HpCDD	425.3	8.0	9,780	97.8	12
OCDD	459.8	8.2	254,000	25.4	3
Total				808	

> 6 7

<sup>a</sup>U.S. EPA (2000)

<sup>b</sup>Average values from Ferrario et al. (2004, 2007)

8
9 The amount of chemical that is dermally absorbed has been shown to be related to skin
10 thickness and whether the skin is dead or alive (U.S. EPA, 1992). Skin thickness varies across
11 body parts and across individuals. No information was found that could be used to account for
12 these factors in this analysis.

13 As discussed in Section 5.1, the monolayer calculation is also an important source of 14 uncertainty for the dermal absorption estimates. The monolayer load is estimated on the basis of 15 the median particle size and assumption of ideal packing. Actual monolayers will be composed 16 of a mix of sizes with complex packing that could result in loadings higher or lower than this 17 theoretical estimate. It is also uncertain how to best characterize the size distribution of particles 18 on the skin. The particles in the original clay product have a median particle size of about 19  $0.75 \,\mu\text{m}$ , and the airborne particles have medians ranging from 8 to 27  $\mu\text{m}$ . The particles on the 20 skin could more closely resemble either the airborne particles or the clay particles, depending on 21 the deposition mechanism. Accordingly, particle sizes of the clay residues on skin could vary 22 widely, with medians ranging from 0.75 to 27 µm. For purposes of the central exposure 23 estimates, the geometric mean of this range was assumed, i.e., 4.5 µm. This implies a monolayer load of  $0.62 \text{ mg/cm}^2$ . The monolayer loads corresponding to the upper and lower ends of the 24

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1 2 3

particle size range are 0.1 to  $3.7 \text{ mg/cm}^2$ . This uncertainty is dampened in the dose estimate as a 1 2 result of the assumption that absorption occurs from only the monolayer. This dampening is 3 especially strong for low-exposure subjects. For example, the dose estimates for Subject 4 (who 4 had the lowest dermal exposure) corresponding to the low and high ends of the monolayer load 5 range would be 0.23 and 0.41 pg TEQ/day. Thus, a 37-fold variation in monolayer load resulted 6 in only a 1.8-fold variation in dose. The dampening is less (but still significant) for Subject 9 7 (who had the highest dermal exposures). For this subject, the doses corresponding to the low and 8 high ends of the monolayer load range would be 4.1 and 34.2 pg TEQ/day, respectively. 9 Another source of uncertainty in the dermal absorption estimates concerns the condition

10 of the skin. Some of the artists reported dryness and cracking of skin due to clay activities. 11 These conditions were observed by the dermatologist, but correlation with clay activities could 12 not be confirmed. Wheel operations involve work with wet clay which would hydrate the skin. 13 The abrasive nature of this work could also reduce the thickness of the stratum corneum which is 14 considered the primary barrier to permeation (U.S. EPA, 1992). It is possible that these 15 conditions would allow more dermal permeation than normal intact skin. However, any 16 increased permeation would be limited to the surface areas associated with the damaged skin. 17 Exposure could also occur through the eyes where absorption would likely be greater than intact skin. This would be limited to particles that contact the eye surface which is probably minimal. 18 19

#### 20 9.3. INHALATION UNCERTAINTIES

21 Data from the cascade sampler were used to estimate inhalation exposures. These data 22 were considered to be the most reliable because no samples were below detection limits and the 23 sampler uses a direct measurement method. The cascade, an area sampler, was located as near 24 the subject as possible but normally would not represent an individual's exposure as accurately 25 as a personal air monitor. Unfortunately, the data from the Respicon personal monitor were 26 dominated by nondetects and could not be used. The limited Respicon data that were above 27 detection limits generally indicated higher levels than the cascade, suggesting that personal 28 exposures may have been higher than those detected by the area monitor. Accordingly, use of 29 the cascade data may have resulted in underestimates of inhalation exposures.

30

#### 31 9.4. INGESTION UNCERTAINTIES

32 The only ingestion pathway quantitatively evaluated in this study was direct ingestion of 33 clay deposited from the air onto food items. The measured deposition onto surrogate 34 food/beverage samplers may not match that of actual foods/beverages. Also, other pathways of 35 ingestion may occur. For example, clay could be transferred from hands directly to food.

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- 1 Although this transfer was not observed in this study, it could be a fairly common occurrence
- 2 and has the potential for significant transfers to handheld food items (e.g., sandwiches, chips,
- 3 cookies). Clay ingestion could also occur from wiping the mouth or licking the lips. The
- 4 maximum ingestion levels estimated in this study involved about 2 mg of clay. This appears to
- 5 be low when compared to the 50 mg/day adult soil ingestion rate specified as a default
- 6 assumption in EPA guidance (U.S. EPA, 1997, 1989). This value is for residential scenarios and
- 7 includes both outdoor soils and indoor dusts. While it is logical that dust ingestion alone would
- 8 be less than ingestion of both soil and dust, a residence is likely to be much less dusty than a
- 9 ceramics studio. Ingestion of 69 mg of clay would be required to result in an absorbed dose
- 10 equal to the average dermal dose of 3.37 pg TEQ/d (this assumes the clay has an average
- 11 concentration of 162 pg TEQ/g and 30% of the dioxin is absorbed during ingestion).

1	10. CONCLUSIONS
2	
3	Hypothetical dioxin dose estimates were calculated for each subject assuming that all
4	used a 20% ball clay blend with 162 pg TEQ/g. The single-day total doses across the 10 subjects
5	ranged from 0.49 to 20.81 pg TEQ/d, with an average of 3.45 pg TEQ/d. The dermal dose was
6	the major contributor to total dose, exceeding 78% for all subjects. Ingestion and inhalation
7	contributed similar amounts, generally in the range of 1 to 10% of total dose. Hand and arm
8	exposure accounted for much of the dermal dose for all subjects. The two subjects who wore
9	summer clothing had foot and leg exposures accounting for about 44 to 79% of the dermal dose.
10	Facial exposures were low accounting for less than 3% of total dermal dose.
11	Clay exposure was found to be highly dependent on the type of work being performed.
12	Throwing clay on the wheel resulted in much higher clay exposures than did any other clay
13	activities. This is due to the increased contact with clay while working on the wheel and the wet,
14	sticky consistency of the clay needed for that work. Emptying bags and mixing dried clays also
15	led to high exposures.
16	A Monte Carlo simulation was performed to model how doses could vary in a broad
17	population of artists with exposures outside the hypothetical scenario evaluated in this study.
18	The simulation, using a variety of assumed input distributions, suggests that doses could extend
19	to levels higher or lower than those estimated for the hypothetical scenario. Also, it indicated
20	that clothing, the fraction of ball clay in the blend and dioxin concentration contributed most to
21	variance in total dose. Many of the input distributions used in this simulation were based on very
22	limited data or judgment. Therefore, the simulation results are best interpreted as preliminary
23	indications of how to extrapolate the observations of this study to a broader population, and
24	further study is recommended to confirm these predictions.
25	In the general population, adult daily intakes of CDD/CDFs and dioxin-like
26	polychlorinated biphenyls (PCBs) are estimated to average 43 and 23 pg TEQ, respectively, for a
27	total intake of 66 pg TEQ/day (U.S. EPA, 2003). More than 90% of this intake is derived from
28	food ingestion. These intake values are based on the "administered" dose or the amount taken
29	into the body before absorption. The hypothetical doses presented in this report are on an
30	absorbed dose basis. Thus, the background dose must be converted to an absorbed basis to
31	compare it to the values presented here. U.S. EPA (2003) reports that about 80% of dioxins in
32	foods are absorbed into the body. Applying this factor, the background dose on an absorbed
33	basis is 34.4 and 18.4 pg TEQ/day for CDD/CDFs and dioxin-like PCBs, respectively, for a total
34	intake of 52.8 pg TEQ/day. Comparing these values to the average of the hypothetical doses for
35	the 10 subjects estimated here (3.45 pg TEQ/day) indicates that the ball clay dose is 10% of the
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- 1 background CDD/CDF dose and about 7% of the total CDD/CDF/PCB dose (on a TEQ basis).
- 2 Note that the general population dioxin dose is a long-term average and the hypothetical ball clay
- 3 dioxin dose is an estimate for a single day when exposure occurs. Accordingly, this comparison
- 4 implies that ball clay use is a frequent event, so that the long-term daily average ball clay dose is
- 5 similar to the single-day dose. If ball clay use is infrequent, then the long-term average dose
- 6 from ball clay will be reduced and adjustments would be needed to make a valid comparison to
- 7 the background dioxin dose.

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# Appendix A

Subject Questionnaire Results

# Table A-1. Subject 1

Question	Answer		
Approximately how many hours per week do you work with clay?	50 hours		
Approximately how many weeks per year?	40 weeks		
How long have you been doing clay work with this level of intensity?	1 year		
What type of clay artwork do you do?	Hand building, sculptural work. Largely consists of rolling out slabs and assembling clay parts.		
What types of clothing do you wear while you work?	Short sleeve t-shirt and jeans and closed toe shoes.		
What areas of skin typically are exposed to the clay while you work?	Hands and forearms.		
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Yes. Dryness. No cracking/bleeding. I use lotion 3-4 times through the day.		
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: when rolling slabs - once per hour when assembling clay - 3 or more times per hour Face: 1-2 times per day		
How do you wash your skin after you work with clay?	Water only.		
Do you treat your skin with anything in particular after working with clay?	Yes, Aveeno brand lotion.		

#### Table A-2. Subject 2

Question	Answer
Approximately how many hours per week do you work with clay?	10-15 hours
Approximately how many weeks per year?	15-25 weeks
How long have you been doing clay work with this level of intensity?	24 years
What type of clay artwork do you do?	Mixing clay and maintenance activities associated with the OSU Ceramics area.
What types of clothing do you wear while you work?	Long and short sleeves, long pants, work shoes.
What areas of skin typically are exposed to the clay while you work?	Hands, arms, and face.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Dryness and cracking.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: 2 minutes Face: 5 hours
How do you wash your skin after you work with clay?	Soap and water.
Do you treat your skin with anything in particular after working with clay?	Lotion during winter, but when my hands are very dry a product called Satin Hands is used.

#### Table A-3. Subject 3

Question	Answer
Approximately how many hours per week do you work with clay?	25 hours
Approximately how many weeks per year?	30 weeks
How long have you been doing clay work with this level of intensity?	14 months
What type of clay artwork do you do?	Functional - thrown on wheel Structural - hand built
What types of clothing do you wear while you work?	Jeans with t-shirt and sandals (summer) or long sleeves and closed toe shoes (winter).
What areas of skin typically are exposed to the clay while you work?	Hands, arms, face, neck, and feet.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Dry cracking skin and cuticles on hands, red small-bump rash on backs of hands and inner forearms when using wheel, nasal congestion.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Arms and hands: 3 to 5 minutes Feet, face, and neck: 1-10 hours
How do you wash your skin after you work with clay?	Water only if returning to work, soap and water when finished.
Do you treat your skin with anything in particular after working with clay?	Aveda hand creme, Neutrogena Swiss therapy lotion.

#### Table A-4. Subject 4

Question	Answer
Approximately how many hours per week do you work with clay?	More than 70 hours
Approximately how many weeks per year?	50 weeks
How long have you been doing clay work with this level of intensity?	2 years
What type of clay artwork do you do?	Functional pots, cups, bowls, etc.
What types of clothing do you wear while you work?	Overalls, long/short sleeve shirts and sneakers.
What areas of skin typically are exposed to the clay while you work?	Face, hands, sometimes arms and legs.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Extremely dry with cracking on fingertips.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: 10 minutes Face and body: 10-24 hours
How do you wash your skin after you work with clay?	Water only if returning to work, soap and water when finished.
Do you treat your skin with anything in particular after working with clay?	Heavy cream lotion or bag balm at the end of the day and at intervals throughout the day.

A-5

#### Table A-5. Subject 5

Question	Answer
Approximately how many hours per week do you work with clay?	More than 14 hours
Approximately how many weeks per year?	35 weeks
How long have you been doing clay work with this level of intensity?	6 years
What type of clay artwork do you do?	Hand building objects about 1.5 feet tall.
What types of clothing do you wear while you work?	Short sleeves/pants and shoes.
What areas of skin typically are exposed to the clay while you work?	Hands, lower arms, face.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Yes, dryness, sometimes cracking.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: <5 minutes Arms: 8 hours Face: 0.5-8 hours
How do you wash your skin after you work with clay?	Soap and water.
Do you treat your skin with anything in particular after working with clay?	Lotion.

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#### Table A-6. Subject 6

Question	Answer
Approximately how many hours per week do you work with clay?	30-40 hours
Approximately how many weeks per year?	30-40 weeks
How long have you been doing clay work with this level of intensity?	25 weeks
What type of clay artwork do you do?	Throwing objects using wheel, hand building, and sculptural work.
What types of clothing do you wear while you work?	Short sleeves, pants, shorts, and flip flops shoes.
What areas of skin typically are exposed to the clay while you work?	Arms, hands, feet, face.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Yes, dry skin on feet and hands and nails being unable to grow healthily.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: 30 minutes Legs, feet, and face: 3-5 hours.
How do you wash your skin after you work with clay?	Soap and water.
Do you treat your skin with anything in particular after working with clay?	Lotion.

#### Table A-7. Subject 7

Question	Answer
Approximately how many hours per week do you work with clay?	10 hours
Approximately how many weeks per year?	40 weeks
How long have you been doing clay work with this level of intensity?	4 years
What type of clay artwork do you do?	Clay sculpture. Rolling out slabs, pressing them into molds. Limited work throwing objects using wheel.
What types of clothing do you wear while you work?	Short sleeves and pants (winter/spring/fall) and shorts (summer).
What areas of skin typically are exposed to the clay while you work?	Arms, hands, and face.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Dryness and cracking.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: 1-2 minutes Face and legs 1-2 minutes (powdered clay) or end of day (wet clay).
How do you wash your skin after you work with clay?	Soap and water.
Do you treat your skin with anything in particular after working with clay?	Lotion.

#### Table A-8. Subject 8

Question	Answer
Approximately how many hours per week do you work with clay?	20 hours
Approximately how many weeks per year?	52 weeks
How long have you been doing clay work with this level of intensity?	6 years
What type of clay artwork do you do?	Large clay sculpture. Rolling out slabs, cut and bend them and then press them together.
What types of clothing do you wear while you work?	Pants or shorts, short sleeves or tank tops, sneakers or sandals.
What areas of skin typically are exposed to the clay while you work?	Arms, neck, hands, calves, and shins.
Do you correlate any skin health issues with how much you work with clay? If yes, what?	Dryness and cracking.
In relation to the time you complete working with clay, when do you wash parts of your body that have been exposed to clay?	Hands: 5 minutes Face and legs: 4-24 hours
How do you wash your skin after you work with clay?	Soap and water or just water.
Do you treat your skin with anything in particular after working with clay?	Lotion.

## Appendix B

Pictures of Artisans Prior to Skin Rinse Procedure

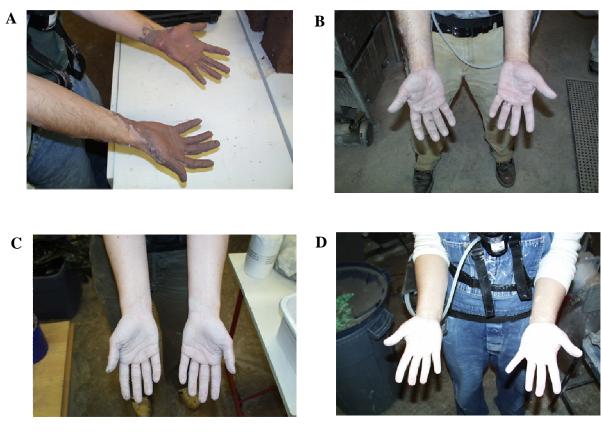


Figure B-1. Subjects 1–4.





Figure B-2. Subjects 5–8.

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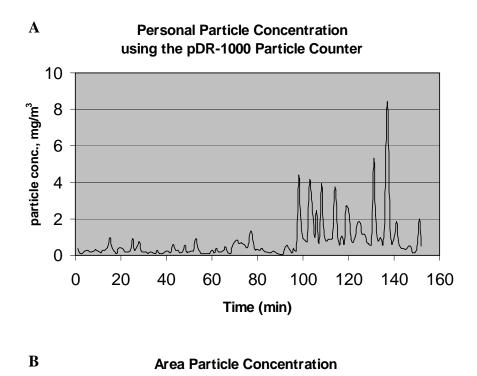
Figure B-3. Subject 9.



Figure B-4. Subject 10.

## Appendix C

Real-time Particle Concentration Data



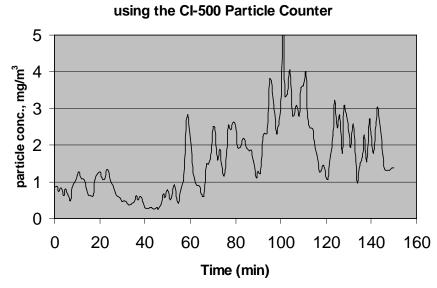


Figure C-1. Subject 1.

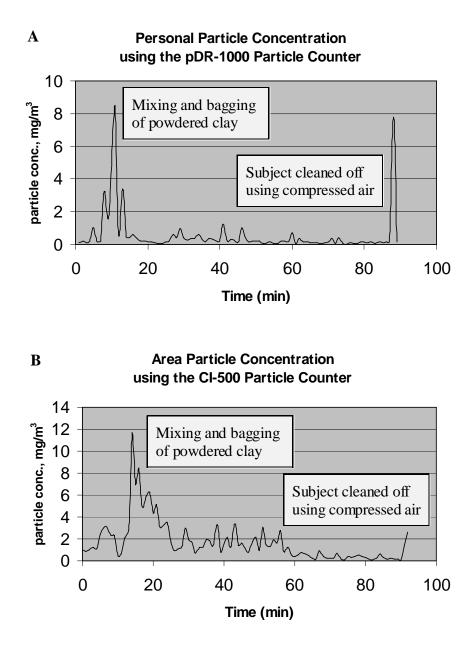
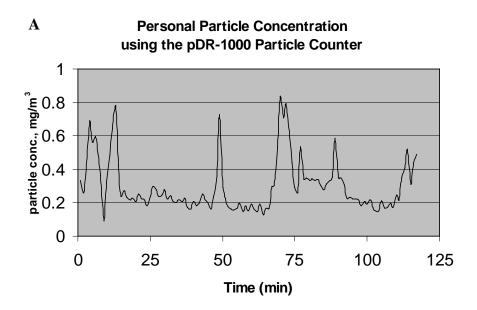
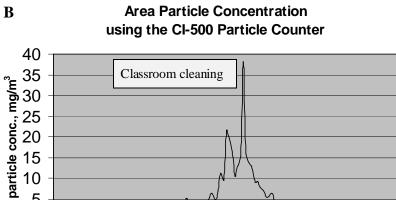


Figure C-2. Subject 2.





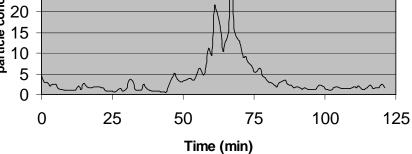


Figure C-3. Subject 3.

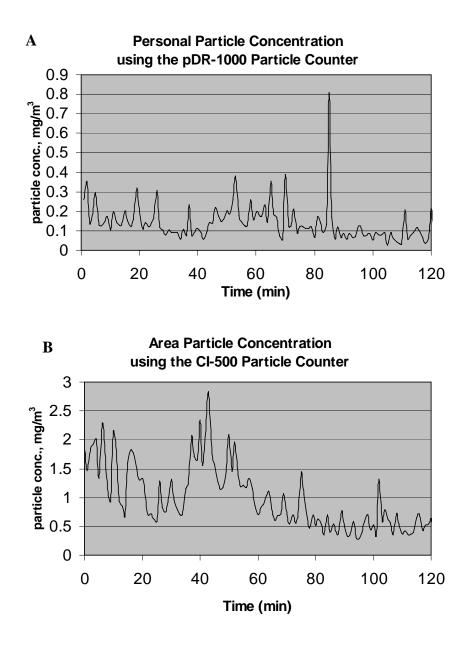


Figure C-4. Subject 4.

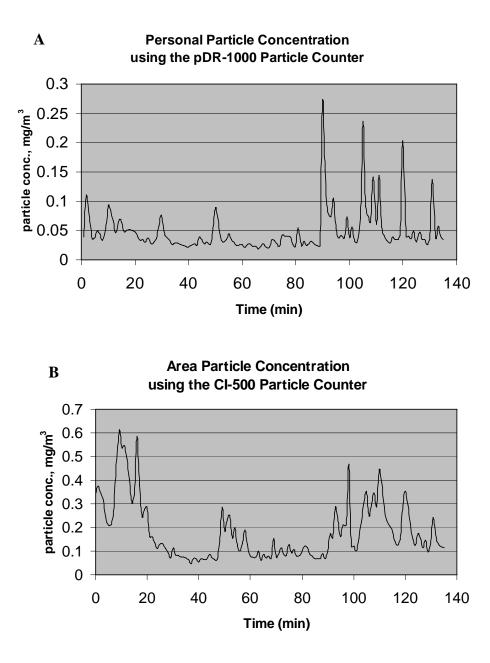


Figure C-5. Subject 5.

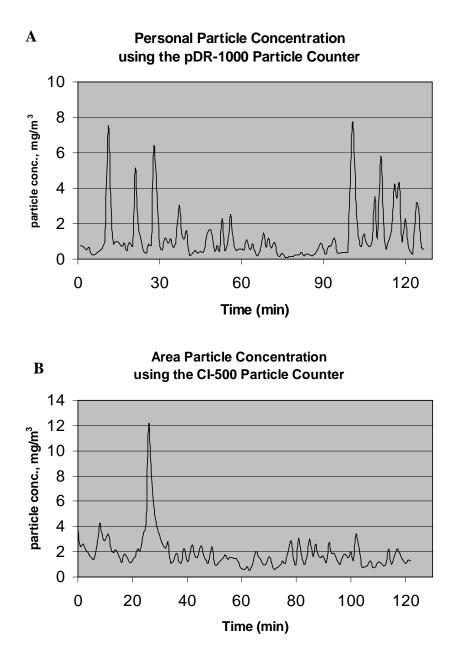


Figure C-6. Subject 6.

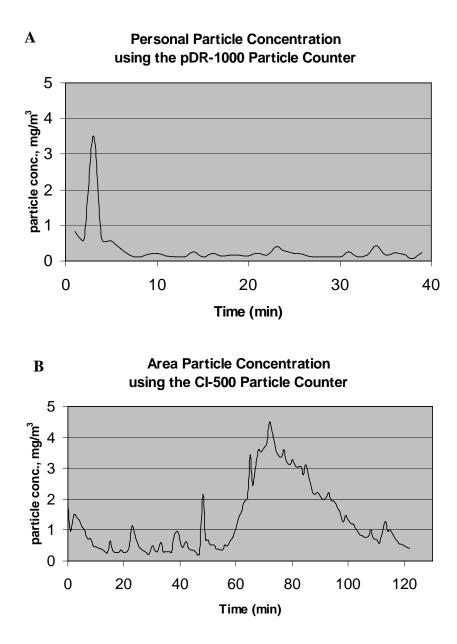


Figure C-7. Subject 7.

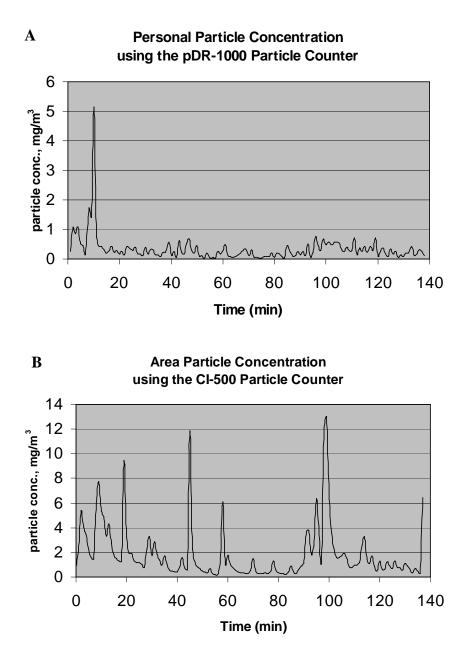
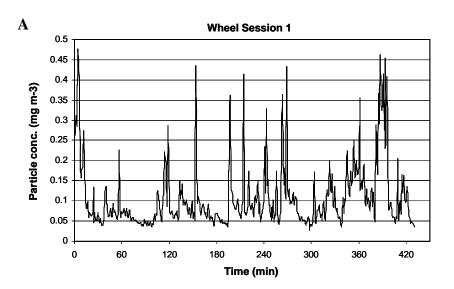


Figure C-8. Subject 8.



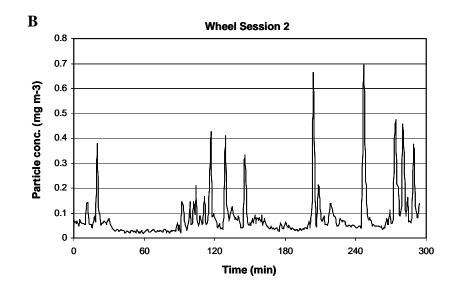


Figure C-9. Subject 9.

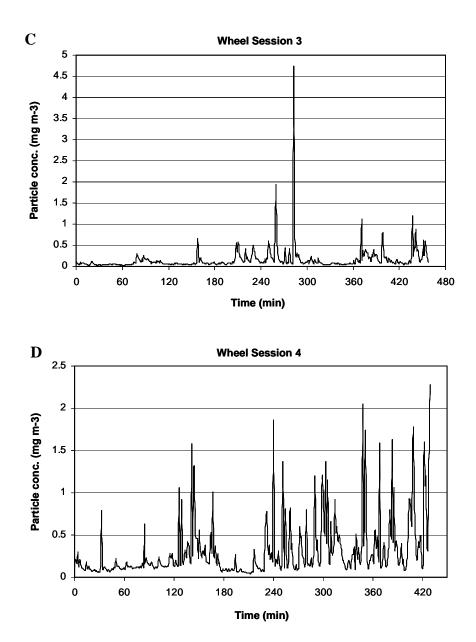


Figure C-9. Subject 9 (continued).

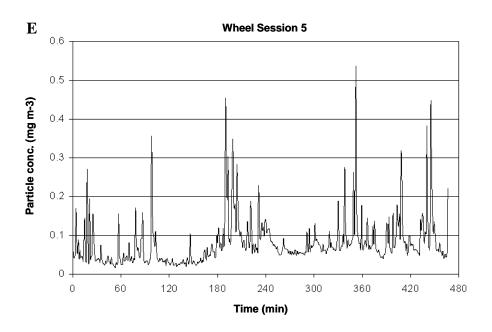


Figure C-9. Subject 9 (continued).

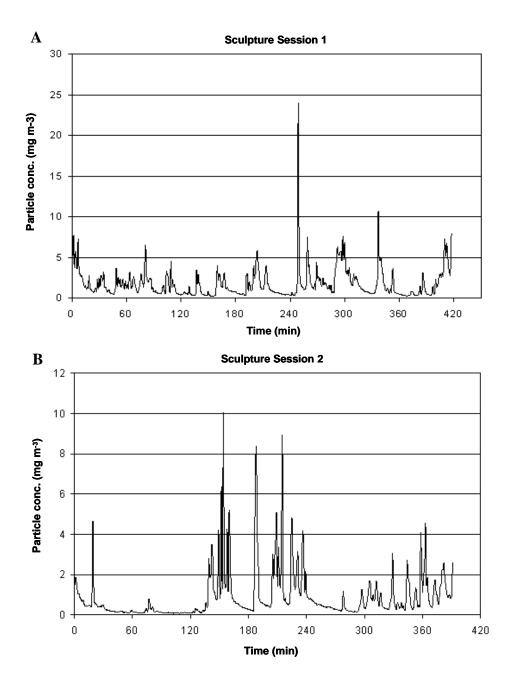


Figure C-10. Subject 10.

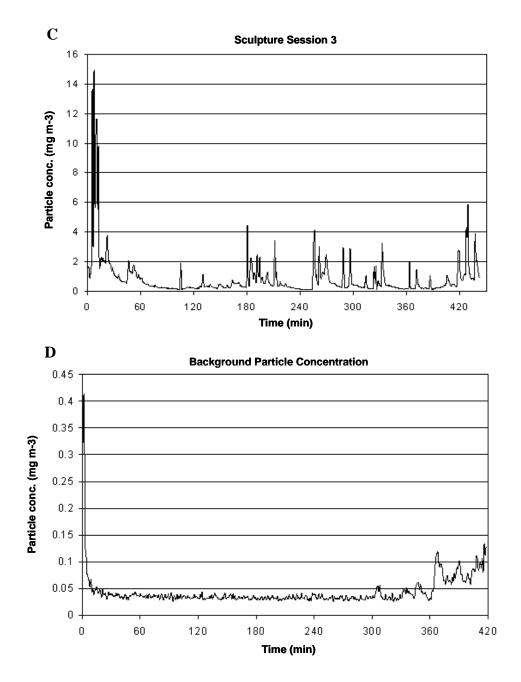


Figure C-10. Subject 10 (continued).

### Appendix D

Respicon, Cascade Impactor, pDR-1000, and Climet CI-500 Data for Each Individual Subject

Aerodynamic Diameter	<4	4–10	10–100	Total
Subject 1	<dl< td=""><td><dl< td=""><td>1.03</td><td>1.90</td></dl<></td></dl<>	<dl< td=""><td>1.03</td><td>1.90</td></dl<>	1.03	1.90
Subject 2	<dl< td=""><td><dl< td=""><td>1.54</td><td>2.42</td></dl<></td></dl<>	<dl< td=""><td>1.54</td><td>2.42</td></dl<>	1.54	2.42
Subject 3	<dl< td=""><td><dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<>	<dl< td=""><td>1.32</td></dl<>	1.32
Subject 4	<dl< td=""><td><dl< td=""><td>1.75</td><td>2.63</td></dl<></td></dl<>	<dl< td=""><td>1.75</td><td>2.63</td></dl<>	1.75	2.63
Subject 5	<dl< td=""><td><dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<>	<dl< td=""><td>1.32</td></dl<>	1.32
Subject 6	1.06	1.25	1.69	4.00
Subject 7	<dl< td=""><td><dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<>	<dl< td=""><td>1.32</td></dl<>	1.32
Subject 8	<dl< td=""><td><dl< td=""><td>1.23</td><td>2.11</td></dl<></td></dl<>	<dl< td=""><td>1.23</td><td>2.11</td></dl<>	1.23	2.11
Background <sup>c</sup>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>1.32</td></dl<></td></dl<>	<dl< td=""><td>1.32</td></dl<>	1.32

Table D-1. Concentration by particle diameter ( $\mu$ m) as measured by the Respicon Air Sampler (mg/m<sup>3</sup>)<sup>a,b</sup>

<sup>a</sup>DL (Detection Limit) =  $0.878 \text{ mg/m}^3$ .

<sup>b</sup> $\frac{1}{2}$  DL was used in place of the  $\frac{1}{2}$  DL results for the purpose of calculating the total concentration.

<sup>c</sup>Based on measurements taken late at night when no students were present in building.

Aerodynamic Diameter	0.5–2	2.0-4.0	4.0-8.0	8.0–16	16–32	>32 µm	Total
Subject 1	<dl< td=""><td>0.02</td><td>0.06</td><td>0.02</td><td>0.06</td><td>0.18</td><td>0.35</td></dl<>	0.02	0.06	0.02	0.06	0.18	0.35
Subject 2	<dl< td=""><td>0.04</td><td>0.03</td><td>0.05</td><td>0.02</td><td>0.31</td><td>0.47</td></dl<>	0.04	0.03	0.05	0.02	0.31	0.47
Subject 3	0.06	0.08	0.19	0.15	0.13	0.39	0.99
Subject 4	<dl< td=""><td><dl< td=""><td>0.03</td><td>0.05</td><td>0.05</td><td>0.22</td><td>0.37</td></dl<></td></dl<>	<dl< td=""><td>0.03</td><td>0.05</td><td>0.05</td><td>0.22</td><td>0.37</td></dl<>	0.03	0.05	0.05	0.22	0.37
Subject 5	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.10</td><td>0.13</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.10</td><td>0.13</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.10</td><td>0.13</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.10</td><td>0.13</td></dl<></td></dl<>	<dl< td=""><td>0.10</td><td>0.13</td></dl<>	0.10	0.13
Subject 6	<dl< td=""><td>0.04</td><td>0.08</td><td>0.14</td><td>0.10</td><td>0.23</td><td>0.61</td></dl<>	0.04	0.08	0.14	0.10	0.23	0.61
Subject 7	0.04	0.05	0.11	0.12	0.06	0.15	0.51
Subject 8	<dl< td=""><td>0.03</td><td>0.07</td><td>0.11</td><td>0.10</td><td>0.31</td><td>0.64</td></dl<>	0.03	0.07	0.11	0.10	0.31	0.64
Background <sup>c</sup>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.017</td><td>0.085</td><td>0.13</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.017</td><td>0.085</td><td>0.13</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.017</td><td>0.085</td><td>0.13</td></dl<></td></dl<>	<dl< td=""><td>0.017</td><td>0.085</td><td>0.13</td></dl<>	0.017	0.085	0.13

Table D-2. Concentration by particle diameter  $(\mu m)$  as measured by the Cascade Impactor Air Sampler  $(mg/m^3)^{a,b}$ 

<sup>a</sup>DL (Detection Limit) =  $0.015 \text{ mg/m}^3$ .

 $^{b}$  DL was used in place of the <DL results for the purpose of calculating the total concentration.

<sup>c</sup>Based on measurements taken late at night when no students were present in building.

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	Mean	Maximum	Minimum
Subject 1	0.75	8.42	0.047
Subject 2	0.57	8.33	0.016
Subject 3	0.30	0.84	0.093
Subject 4	0.14	0.81	0.027
Subject 5	0.049	0.27	0.019
Subject 6	1.22	7.70	0.078
Subject 7	0.32	3.51	0.080
Subject 8	0.34	5.14	0.015

Table D-3. Particle concentration as measured by the pDR-1000 Air Sampler  $(mg/m^3)$ 

Table D-4. Concentration by particle diameter  $(\mu m)$  as measured by the Climet CI-500 Air Sampler  $(mg/m^3)^a$ 

Physical Diameter	0.3–0.5	0.5–1.0	1.0-2.5	2.5-5.0	5.0–10	>10.0	Total
Subject 1	0.001	0.005	0.026	0.222	0.560	1.499	2.313
Subject 2	0.001	0.002	0.016	0.166	0.535	1.747	2.467
Subject 3	0.002	0.009	0.058	0.411	1.214	3.756	5.450
Subject 4	0.002	0.003	0.013	0.124	0.323	0.964	1.429
Subject 5	0.008	0.002	0.003	0.025	0.055	0.167	0.260
Subject 6	0.011	0.006	0.029	0.260	0.679	1.746	2.731
Subject 7	0.005	0.010	0.054	0.377	0.631	0.817	1.895
Subject 8	0.006	0.004	0.021	0.186	0.578	1.878	2.672
Background <sup>b</sup>	0.009	0.005	0.002	0.010	0.010	0.019	0.055

<sup>a</sup>Concentration calculations assume particle density of 2.6 g/cm<sup>3</sup>.

<sup>b</sup>Based on measurements taken late at night when no students were present in building.

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Aerodynamic Diameter	0.5–2	2.0-4.0	4.0-8.0	8.0–16	16–32	>32	Total
Subject 9 Session 1	0.004	<dl< td=""><td>0.004</td><td>0.008</td><td>0.007</td><td>0.024</td><td>0.049</td></dl<>	0.004	0.008	0.007	0.024	0.049
Subject 9 Session 2	<dl< td=""><td><dl< td=""><td>0.005</td><td>0.007</td><td>0.008</td><td>0.024</td><td>0.046</td></dl<></td></dl<>	<dl< td=""><td>0.005</td><td>0.007</td><td>0.008</td><td>0.024</td><td>0.046</td></dl<>	0.005	0.007	0.008	0.024	0.046
Subject 9 Session 3	0.004	0.008	0.012	0.013	0.020	0.044	0.102
Subject 9 Session 4	<dl< td=""><td><dl< td=""><td>0.004</td><td>0.005</td><td>0.009</td><td>0.053</td><td>0.073</td></dl<></td></dl<>	<dl< td=""><td>0.004</td><td>0.005</td><td>0.009</td><td>0.053</td><td>0.073</td></dl<>	0.004	0.005	0.009	0.053	0.073
Subject 9 Session 5	0.007	0.008	0.004	0.026	0.026	0.081	0.152
Subject 10 Session 1 <sup>c</sup>	0.019	0.034	0.075	0.079	0.075	0.198	0.480
Subject 10 Session 2 <sup>c</sup>	0.005	0.015	0.034	0.052	0.040	0.092	0.237
Subject 10 Session 3	0.011	0.018	0.047	0.054	0.032	0.079	0.241
Background <sup>d</sup>	0.004	<dl< td=""><td>0.003</td><td>0.006</td><td>0.004</td><td>0.005</td><td>0.023</td></dl<>	0.003	0.006	0.004	0.005	0.023

Table D-5. Average concentrations by particle diameter ranges (µm) measured by the Cascade Impactor Air Sampler  $(mg/m^3)^{a,b}$ 

<sup>a</sup>DL (Detection Limit) =  $0.0025 \text{ mg/m}^3$ .

 $^{b}$ <sup>b</sup><sup>1/2</sup> DL was used in place of the <DL results for the purpose of calculating the total concentration.

<sup>c</sup>Concentration not adjusted for presence of dog.

<sup>d</sup>Based on measurements taken late at night when no students were present in building.

D-4

Physical Diameter	0.3–0.5	0.5–1.0	1.0-2.5	2.5–5.0	5.0–10	>10.0	Total
Subject 9 Session 1	0.008	0.003	0.005	0.026	0.042	0.070	0.155
Subject 9 Session 2	0.010	0.005	0.003	0.014	0.027	0.058	0.117
Subject 9 Session 3	0.006	0.004	0.005	0.026	0.054	0.124	0.220
Subject 9 Session 4	0.012	0.007	0.011	0.055	0.113	0.240	0.439
Subject 9 Session 5	0.011	0.008	0.004	0.018	0.026	0.048	0.115
Subject 10 Session 1 <sup>b</sup>	0.018	0.015	0.067	0.353	0.746	1.430	2.629
Subject 10 Session 2 <sup>b</sup>	0.003	0.005	0.031	0.172	0.367	0.700	1.278
Subject 10 Session 3	0.006	0.008	0.039	0.181	0.341	0.656	1.231
Background <sup>c</sup>	0.012	0.009	0.003	0.011	0.012	0.016	0.064

Table D-6. Concentration by particle diameter ranges ( $\mu$ m) measured by the Climet CI-500 Air Sampler (mg/m<sup>3</sup>)<sup>a</sup>

<sup>a</sup>Concentration calculations assume particle density of 2.6 g/cm<sup>3</sup>.

<sup>b</sup>Concentration not adjusted for presence of dog.

<sup>c</sup>Based on measurements taken late at night when no students were present in building.

## Appendix E

SEM and EDS Data by Subject



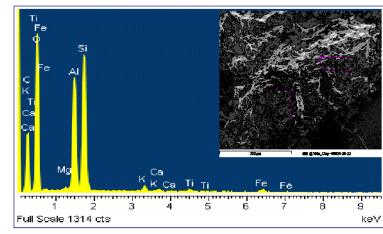


Figure E-1a. Sample of clay used by Subject 1.

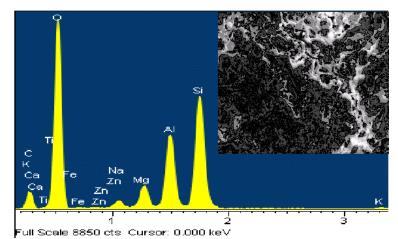
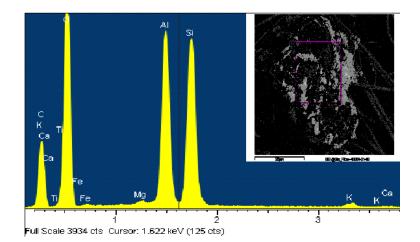
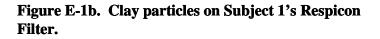
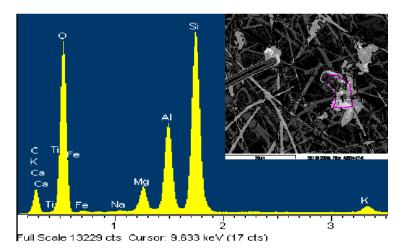


Figure E-2a. Sample of clay used by Subject 2.







# Figure E-2b. Clay particles on Subject 2's Respicon Filter.

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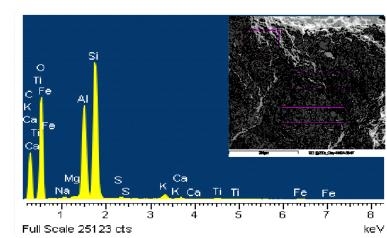


Figure E-3a. Sample of clay used by Subject 3.

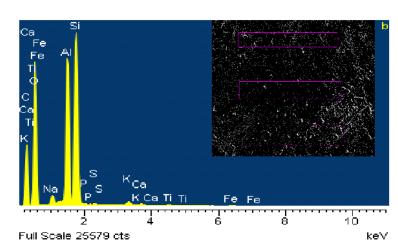


Figure E-4a. Sample of clay used by Subject 4.

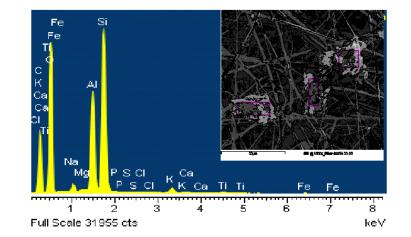


Figure E-3b. Clay particles on Subject 3's Respicon Filter.

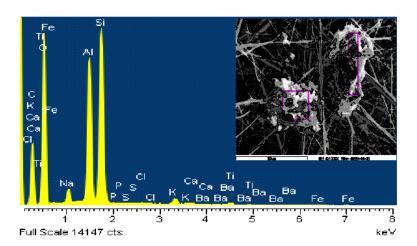


Figure E-4b. Clay particles on Subject 4's Respicon Filter.

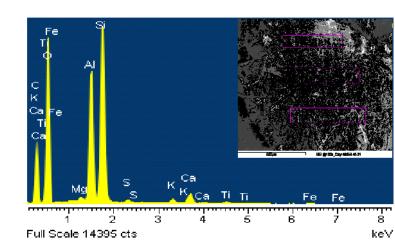


Figure E-5a. Sample of clay used by Subject 5.

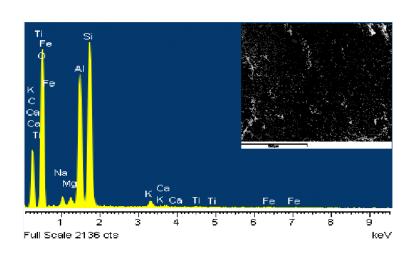


Figure E-6a. Sample of clay used by Subject 6.

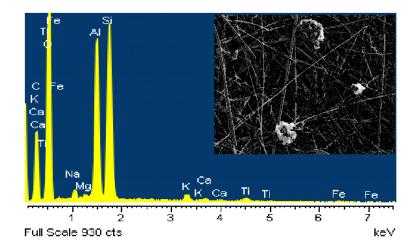


Figure E-5b. Clay particles on Subject 5's Respicon Filter.

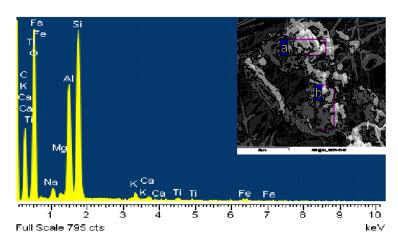


Figure E-6b. Clay particles on Subject 6's Respicon Filter.

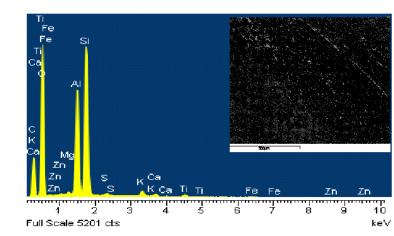


Figure E-7a. Sample of clay used by Subject 7.

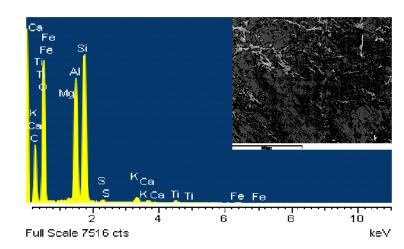


Figure E-8a. Sample of clay used by Subject 8.

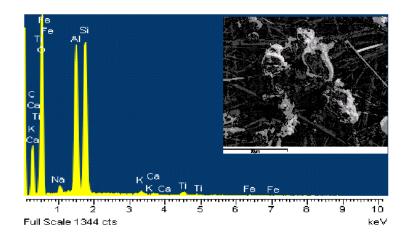


Figure E-7b. Clay particles on Subject 7's Respicon Filter.

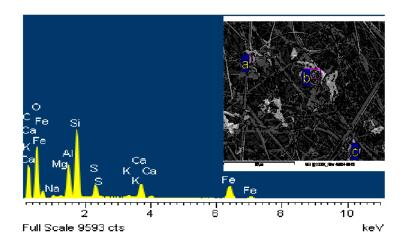


Figure E-8b. Clay particles on Subject 8's Respicon Filter.

9/6/07

### Appendix F

Monte Carlo Simulation Result Graphics

#### Crystal Ball Report - Full

Simulation started on 3/31/2006 at 7:15:34 Simulation stopped on 3/31/2006 at 7:23:41

Run preferences:	
Number of trials run	1,000
Monte Carlo	
Random seed	
Precision control on	
Confidence level	95.00%
Run statistics:	
Total running time (sec)	487.37
Trials/second (average)	2
Random numbers per sec	35
Crystal Ball data:	
Assumptions	17
Correlations	0
Correlated groups	0
Decision variables	0
Forecasts	4

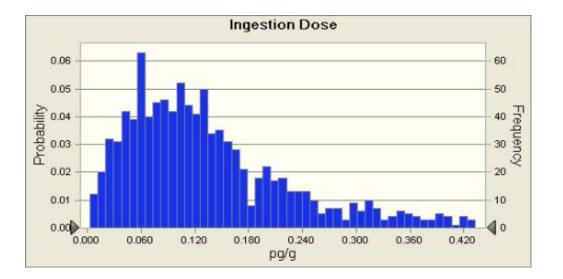
#### Forecasts

#### Worksheet: [VarDp-Dep monte5.xls]Monte

#### **Forecast: Ingestion Dose**

Summary:

Entire range is from 0.003 to 0.730 Base case is 0.058 After 1,000 trials, the std. error of the mean is 0.003



Statistics: Trials Mean Median	Forecast values 1,000 0.141 0.115
Mode	
Standard Deviation	0.104
Variance	0.011
Skewness	1.56
Kurtosis	6.04
Coeff. of Variability	0.74
Minimum	0.003
Maximum	0.730
Range Width	0.727
Mean Std. Error	0.003

#### Forecast: Ingestion Dose (cont'd)

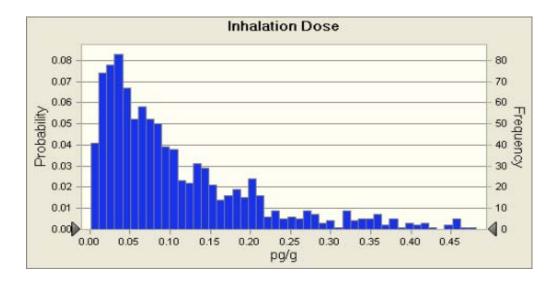
Percentiles:	Forecast values
0%	0.003
10%	0.039
20%	0.059
30%	0.077
40%	0.097
50%	0.115
60%	0.135
70%	0.161
80%	0.207
90%	0.284
100%	0.730

#### **Forecast: Inhalation Dose**

Cell: C83

Summary:

Entire range is from 0.00 to 1.05 Base case is 0.04 After 1,000 trials, the std. error of the mean is 0.00



Statistics:	Forecast values
Trials	1,000
Mean	0.12
Median	0.08
Mode	
Standard Deviation	0.13
Variance	0.02
Skewness	2.51
Kurtosis	11.75
Coeff. of Variability	1.07
Minimum	0.00
Maximum	1.05
Range Width	1.05
Mean Std. Error	0.00

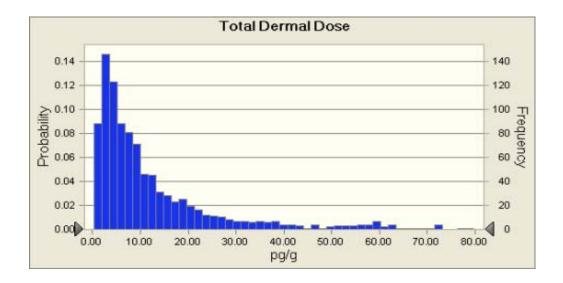
#### Forecast: Inhalation Dose (cont'd)

Percentiles:	Forecast values
0%	0.00
10%	0.02
20%	0.03
30%	0.04
40%	0.06
50%	0.08
60%	0.10
70%	0.14
80%	0.18
90%	0.27
100%	1.05

#### **Forecast: Total Dermal Dose**

Cell: C45

Summary: Entire range is from 0.27 to 217.51 Base case is 10.91 After 1,000 trials, the std. error of the mean is 0.72



Statistics:	Forecast values
Trials	1,000
Mean	15.50
Median	7.92
Mode	
Standard Deviation	22.91
Variance	524.87
Skewness	3.67
Kurtosis	20.69
Coeff. of Variability	1.48
Minimum	0.27
Maximum	217.51
Range Width	217.24
Mean Std. Error	0.72

#### Forecast: Total Dermal Dose (cont'd)

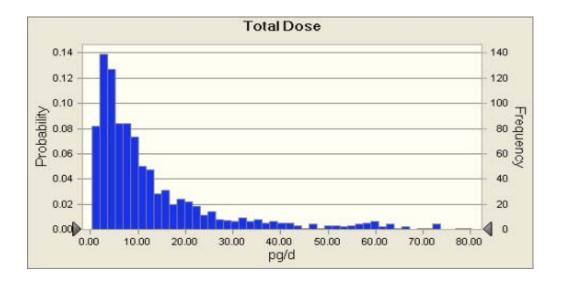
Forecast values
0.27
2.02
3.16
4.29
5.90
7.92
10.08
14.09
20.03
36.15
217.51

#### Forecast: Total Dose

Cell: C86

#### Summary:

Entire range is from 0.28 to 219.14 Base case is 11.01 After 1,000 trials, the std. error of the mean is 0.73



Statistics:	Forecast values
Trials	1,000
Mean	15.76
Median	8.12
Mode	
Standard Deviation	23.01
Variance	529.38
Skewness	3.66
Kurtosis	20.67
Coeff. of Variability	1.46
Minimum	0.28
Maximum	219.14
Range Width	218.86
Mean Std. Error	0.73

#### Forecast: Total Dose (cont'd)

Percentiles:	Forecast values
0%	0.28
10%	2.15
20%	3.32
30%	4.51
40%	6.15
50%	8.12
60%	10.39
70%	14.44
80%	20.58
90%	36.63
100%	219.14

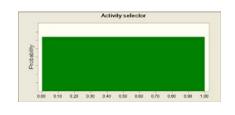
End of Forecasts

#### Assumptions

#### Worksheet: [VarDp-Dep monte5.xls]Monte

#### Assumption: Activity selector

Uniform distribution with parameters:	
Minimum	0.00
Maximum	1.00



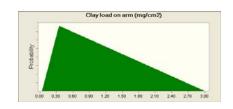
#### **Assumption: Breath Selector**

Uniform distribution with parameters:	
Minimum	0.00
Maximum	1.00

# Breath Selector

#### Assumption: Clay load on arm (mg/cm2)

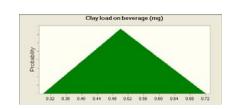
Triangular distribution with parameters:	
Minimum	0.04
Likeliest	0.35
Maximum	3.00
Minimum Likeliest	0.35



#### Assumption: Clay load on beverage (mg)

Triangular distribution with parameters: Minimum

Minimum	0.30
Likeliest	0.50
Maximum	0.72





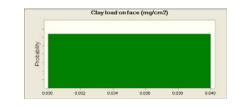
Cell: C51

Cell: C61

#### Assumption: Clay load on face (mg/cm2)

Cell: C40

Uniform distribution with parameters:	
Minimum	0.030
Maximum	0.040

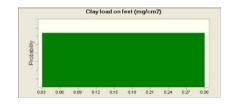


#### Assumption: Clay load on feet (mg/cm2)

Uniform distribution with parameters:	
Minimum	0.03
Maximum	0.30



Cell: C49



#### Assumption: Clay load on food (mg)

Triangular distribution with parameters:	
Minimum	0.30
Likeliest	0.70
Maximum	1.66

#### Assumption: Clay load on hand (mg/cm2)

Triangular distribution with parameters:

Minimum	0.10
Likeliest	3.00
Maximum	10.00

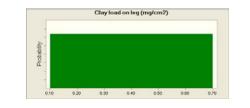
Clay load on food (mg)





#### Assumption: Clay load on leg (mg/cm2)

Uniform distribution with parameters:	
Minimum	0.10
Maximum	0.70



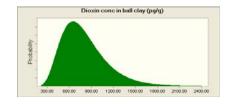
#### Assumption: clothing selector

Uniform distribution with parameters:	
Minimum	0.00
Maximum	1.00



#### Assumption: Dioxin conc in ball clay (pg/g)

Lognormal distribution with parameters:	
Mean	808.00
Std. Dev.	318.00



#### Assumption: Exposure Duration (hr/d)

Triangular distribution with parameters:	
Minimum	1.00
Likeliest	4.00
Maximum	10.00

Exposure Duration (hr/d)



Cell: C9

Cell: C5

Cell: C7

# 100 200 200 400 500 600 700 800 11

#### Assumption: Fraction of ball clay in blend

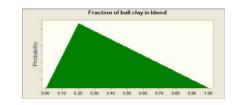
Cell: C6

Cell: C62

Cell: C60

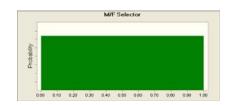
Triangular	distribution	with	parameters:
------------	--------------	------	-------------

Minimum	0.00
Likeliest	0.20
Maximum	1.00



#### Assumption: M/F Selector

Uniform distribution with parameters:	
Minimum	0.00
Maximum	1.00



#### Assumption: MMAD (um)

Triangular distribution with parameters:	
Minimum	13.00
Likeliest	25.00
Maximum	45.00

#### Assumption: Particle Concentration in Air(mg/m3)

Triangular distribution with parameters:

Minimum	0.08
Likeliest	0.44
Maximum	0.99

MMAD (um)



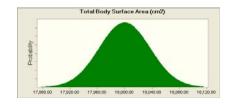


37.40

#### Assumption: Total Body Surface Area (cm2)

Lognormal distribution with parameters:

Mean 18,000.00 Std. Dev.



End of Assumptions

## Appendix G

Evaluation of Clay Dust Inhalation

1 2

#### APPENDIX G. EVALUATION OF CLAY DUST INHALATION

The methodology used to evaluate the dose of clay dust and associated dioxin received via inhalation is discussed in this appendix. The appendix is divided into four sections: clay dust size distribution, particle inhalability, respiratory deposition of clay dust, and delivered dose estimates.

7 8

#### CLAY DUST SIZE DISTRIBUTION

9 As discussed in the main body of this report, the size distribution of clay dust was measured using a Delron cascade impactor and a Climet during regular daily activities in the art 10 11 studio. The Climet optically determines particle concentration for six size bins with the associated physical particle diameter ( $d_p$ ) of 0.3–0.5, 0.5–1, 1–2.5, 2.5–5, 5–10, and >10  $\mu$ m. 12 13 Aerodynamic particle diameter  $(d_{ae})$  can be estimated for the Climet's size bins by assuming that the airborne clay dust has a density of 2.6  $g/cm^3$ , similar to that of bulk clay.<sup>1</sup> Using this 14 15 approach, a clay particle with a  $d_p$  of 10 µm has a  $d_{ae}$  of 16 µm. The Delron cascade impactor fractionates particles directly, based on their  $d_{ae}$ , into the seven ranges of <0.5, 0.5–2, 2–4, 4–8, 16 17 8–16, 16–32, and >32 µm.

18 During normal artisan activities (Subjects 1–8),  $64 \pm 9\%$  (mean  $\pm$  SD) of the aerosol is 19 associated with particles having a  $d_{ae} > 16 \,\mu m$  based on average Climet data. Based on average impactor data,  $63 \pm 13\%$  of the aerosol is associated with a d<sub>ae</sub> > 16 µm (Subjects 1–8). The 20 particle size distributions to which the artisans were exposed was assumed to be log-normally 21 distributed.<sup>2</sup> The cascade impactor data were selected for estimating particle size distributions 22 23 for the following reasons: (1) the impactor measures particle size based on the aerodynamic 24 behavior of particles, whereas the Climet uses light scattering to estimate a physical particle size; 25 (2) the impactor affords a better characterization of the large particles than does the Climet 26 because it contains an additional size bin of  $16-32 \,\mu\text{m}$ ; and (3) particle deposition in the respiratory tract is a function of d<sub>ae</sub>. Thus, uncertainty in estimates of respiratory deposition is 27 28 reduced by the direct measurement of d<sub>ae</sub> by the impactor. The clay dust size distribution was 29 not estimated for runs where two or more of the impactor stages were below the nondetect level. 30 When engaged in normal artisan activities, the mass median aerodynamic diameter 31 (MMAD) of clay dust to which artisans were exposed ranged from 13 to 45  $\mu$ m. Table G-1

<sup>2</sup>For more information about particle sizing and the log-normal distribution, the reader is referred to Hinds (1999).

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 $<sup>{}^{1}</sup>d_{ae} = d_{p} \{ (clay density * Cc(d_{p}) )/(H_{2}O density * Cc(d_{ae}) ) \}^{0.5}, where: Cc(d_{p}) and Cc(d_{ae}) are the Cunningham slip correction factor for the physical and aerodynamic particle size, respectively. For more information, the reader is referred to ICRP (1994), page 239.$ 

- 1 provides a characterization of clay dust exposures for each subject. Figure G-1 illustrates a log-
- 2 probability plot of a typical (i.e., near the average MMAD) clay dust particle size distribution
- 3 and a background sample from the studio. The prevalence of fewer large particles in the
- 4 background aerosol can be explained easily, based on particle-settling velocities. The settling
- 5 velocities for the d<sub>ae</sub> of 1-, 10-, and 20- $\mu$ m particles are 3.5 × 10<sup>-3</sup>, 0.3, and 1.2 cm/s,
- 6 respectively. Due to their rapidly settling velocities, large particles ( $d_{ae} > 10 \,\mu$ m) are maintained
- 7 in the air only by active generation or resuspension from surfaces. The substantive presence of
- 8 large particles (52% of mass associated with a  $d_{ae} > 10 \,\mu$ m) in the background sample is
- 9 suggestive of particle resuspension due to movement (e.g., walking and setting up sampling
- 10 equipment in the studio).

	Size distr	Total concentration		
Subject	MMAD (µm)	$(mg/m^3)$		
1	26.9	3.9	0.35	
2	44.6	4.8	0.47	
3	18.5	4.3	0.99	
4	n.a.	n.a.	0.37	
5	n.a.	n.a.	0.13	
6	20.2	3.0	0.61	
7	13.0	3.6	0.51	
8	26.7	3.3	0.64	
$Mean \pm SD$	$25.0 \pm 11$	$3.8\pm0.7$	$0.51\pm0.25$	

 Table G-1. Clay dust size distribution and concentration during normal activities

<sup>a</sup>The aerosol size distribution is described in terms of the mass median aerodynamic diameter (MMAD) and geometric standard deviation ( $\sigma_g$ ). n.a. = not available

11 Data were also available for two subjects during specific activities (i.e., when sculpting 12 and using a pottery wheel) (see Table G-2). During pottery wheel operations, an average 13 MMAD of 33  $\mu$ m with a geometric standard deviation ( $\sigma_g$ ) of 5.4 was observed. A dog was 14 present during two of the sculpting runs. The MMAD with the dog present was 21  $\mu$ m versus 15 only 16  $\mu$ m without the dog. The shift toward larger particles when the dog was present appears 16 to be consistent with particle resuspension due to the dog's movement around the studio.

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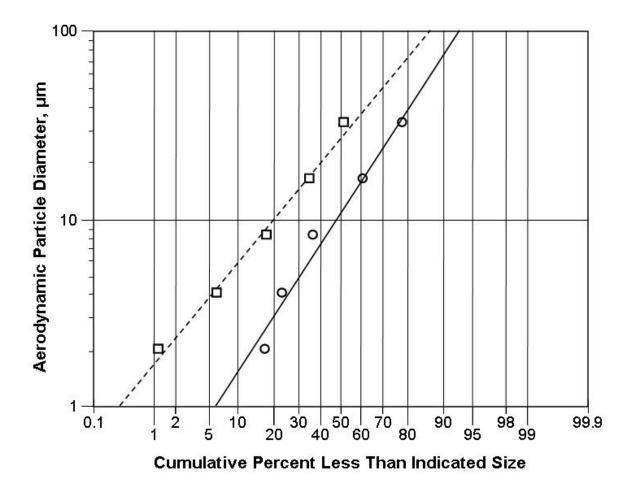


Figure G-1. Clay dust particle size distribution during normal artisan activities from analysis of cascade impactor data. Illustrated are the data for Subject 8 () and a background sample when work was not being done in the studio ( $\circ$ ). The dashed and solid lines illustrate the log-normal distribution for these respective data. The mass median aerodynamic diameter (MMAD) of clay dust was 27 µm ( $\sigma_g = 3.3$ ) for Subject 8, whereas the background sample had an MMAD of 11 µm ( $\sigma_g = 4.6$ ).

#### 1 PARTICLE INHALABILITY

For a given particle size, inhalability is the ratio of the particle concentration that enters the respiratory tract through the nose or mouth to the concentration of these particles in the ambient air. Inhalability depends mainly on particle size (i.e.,  $d_{ae}$ ), route of breathing, wind speed, and a person's orientation with respect to wind direction. Wind speeds in the art studio were assumed to be 0.3 m/s or less (Baldwin and Maynard, 1998). The artisans were presumed to move about the studio such that their orientation was random with respect to wind direction.

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		Size distr	Total	
Subject		MMAD µm	σ <sub>g</sub>	concentration (mg/m <sup>3</sup> )
Subject 9	Run 1	33.7	6.2	0.049
(Pottery wheel)	Run 2	n.a.	n.a.	0.046
	Run 3	24.8	4.3	0.102
	Run 4	n.a.	n.a.	0.073
	Run 5	39.3	5.6	0.152
М	$ean \pm SD$	$32.6\pm7.3$	$5.4\pm0.9$	$0.085\pm0.044$
Subject 10 <sup>b</sup>	Run 1	21.2	3.9	0.48
(Sculpting work)	Run 2	20.4	3.2	0.24
	Run 3	16.0	3.5	0.24

Table G-2. Clay dust size distribution and concentration during specific activities

<sup>a</sup>The aerosol size distribution is described in terms of the mass median aerodynamic diameter (MMAD) and geometric standard deviation ( $\sigma_g$ ).

<sup>b</sup>A dog was present during Runs 1 and 2 but not during Run 3. Therefore, these three runs were not averaged as was done in the case of the pottery wheel work.

n.a. = not available

1 The clay dust aerosol present under normal activities in the art studio was observed to 2 have an average MMAD of 25  $\mu$ m and  $\sigma_g$  of 3.8. Hence, 50% (on average, by mass) of the airborne clay dust is composed of particles having a  $d_{ae}$  of  $\geq 25 \ \mu m$ , a size that is generally 3 4 considered to be unable to penetrate the thorax (ACGIH, 2004). These large particles 5  $(d_{ae} > 25 \,\mu m)$ , if inhaled, will deposit almost completely and exclusively in the extrathoracic (ET) airways. Thus, determining inhalability is key to estimating the delivered dose of these large 6 7 particles. For smaller particles, inhalability still describes the fraction of airborne particles that 8 may enter the respiratory tract and thereby the availability of these particles for deposition in the 9 lung.

Only limited data are available on the inhalability of particles from calm air (wind speeds of 0.3 m/s and less). Inhalability from calm air depends on the route of breathing. Logistic functions describing particle inhalability during nasal [P(I<sub>N</sub>)] and oral [P(I<sub>O</sub>)] breathing are given by Ménache et al. (1995) and Brown (2005):

14

$$P(I_N) = 1 - \frac{1}{1 + \exp(10.32 - 3.114\ln(d_{ae}))}$$
(G-1)

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$$P(I_{O}) = \frac{1.44}{1 + 0.44 \exp(0.0195d_{ae})}$$
(G-2)

1

Note that these equations depend only on aerodynamic particle diameter, dae. Given by Eq G-1, 2  $P(I_N)$  begins a rapid decline from 0.95 at  $d_{ae} = 11 \mu m$ , to 0.5 at  $d_{ae} = 27.5 \mu m$ , and 0.1 at 3 4  $d_{ae} = 56 \mu m$ . Equation G-2 predicts a slow decline in P(I<sub>0</sub>) from 0.95 at  $d_{ae} = 8 \mu m$ , to 0.5 at 5  $d_{ae} = 74 \ \mu m$ , and 0.1 at  $d_{ae} = 175 \ \mu m$ . 6 Figure G-2 illustrates particle inhalability predicted by Eqs G-1 and G-2 (shown by solid 7 lines) along with relevant experimental data. Based on high wind speeds (1-8 m/s), the 8 American Conference of Governmental Industrial Hygienists (ACGIH) inhalability criterion is 9 also illustrated (shown by dashed lines) for comparative purposes. Equation G-1 for  $P(I_N)$ describes the experimental nasal inhalability data well with an  $r^2$  of 0.86 (model sum of squares 10 divided by the total corrected sum of squares). A negative  $r^2$  is obtained for the fit of the 11 ACGIH (2004) criterion to these data.<sup>3</sup> Equation G-2 describes the experimental oral 12 inhalability data with an  $r^2$  of 0.69, whereas the ACGIH criterion fit with an  $r^2$  of 0.32. 13 14 15 **RESPIRATORY DEPOSITION OF CLAY DUST** 16 Inhaled particles may be either exhaled or deposited in the ET, tracheobronchial (TB), or 17 pulmonary (PU) airways. The deposition of particles in the respiratory tract depends primarily 18 on inhaled particle size (i.e., d<sub>ae</sub>), route of breathing (through the nose or mouth), tidal volume 19  $(V_T)$ , and breathing frequency (f). Reference respiratory values for males and females were 20 adopted from the International Commission on Radiological Protection (ICRP, 1994). In 21 addition to breathing patterns (Table G-3) necessary for deposition calculations, males and 22 females were assumed to have a functional residual capacity of 3,300 mL and 2,680 mL, 23 respectively. The majority (70%) of the subjects were female; only Subjects 1, 2, and 5 were 24 male. 25 Particle deposition in the respiratory tract was predicted using the publicly available

26 Multiple Path Particle Dosimetry (MPPD) model.<sup>4</sup> The MPPD model was developed by the

27 CIIT

<sup>4</sup> The MPPD program is available on request from the CIIT Centers for Health Research (<asgharian@ciit.org>).

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<sup>&</sup>lt;sup>3</sup>An  $r^2$  is calculated as the model sum of squares (MSS) divided by the total corrected sum of squares (TSS). The MSS equals the TSS minus the residual sum of squares (RSS). In typical linear regressions, when a model is fitted to a data set, the resulting  $r^2$  must be non-negative because the least square fitting procedure assures RSS  $\leq$  TSS. When  $r^2$  is computed on excluded data, i.e., data not used to fit the model, the RSS can exceed the TSS. In this case,  $r^2$  (which is not the square of r) can be negative, indicating that the mean of the data is a better predictor than the model.

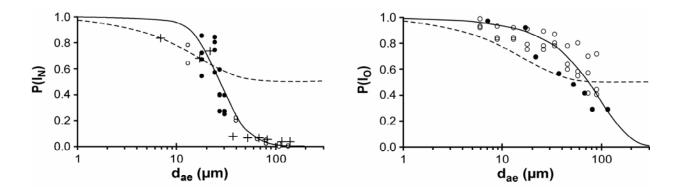


Figure G-2. Particle inhalability from calm air for nasal  $[P(I_N)]$  and oral  $[P(I_O)]$  breathing as a function of aerodynamic particle diameter  $(d_{ae})$ . Left panel [— Equation G-1, • Breysse and Swift (1990), + Hinds et al. (1998),  $\circ$  Hsu and Swift (1999), - - ACGIH (2004)]. Right panel [— Equation G-2,  $\circ$  Aitken et al. (1999), • Kennedy and Hinds (2002), - - ACGIH (2004)].

Table G-3. Breathing patterns used in particle deposition calculations<sup>a</sup>

Activity		Males	Females
Sitting	$V_{\rm T} (\rm mL) \\ f(\rm min^{-1})$	750 12	464 14
Light exercise	$V_{\rm T} ({\rm mL}) \\ f({\rm min}^{-1})$	1,250 20	992 21

Source: ICRP (1994), Table 8.

1 2

Centers for Health Research (CIIT), United States, in collaboration with the National Institute of Public Health and the Environment (RIVM), the Netherlands, and the Ministry of Housing, Spatial Planning and the Environment, the Netherlands. The MPPD model may be used to predict the deposition in the human respiratory tract for particles between 0.01 and 20  $\mu$ m in diameter. In the lung, the model considers deposition by the mechanisms of impaction, sedimentation, and diffusion. Additional model details are available elsewhere (DeWinter-Sorkina and Cassee, 2002). For the size of the clay dust, only impaction and sedimentation are of concern.

3 Using the MPPD model, deposition was predicted for the ET, TB, and PU regions of the

4 respiratory tract. Particle deposition was estimated individually for oral and nasal breathing.

5 During oral breathing, deposition in the TB airways did not always reach zero by a  $d_{ae}$  of 20  $\mu$ m

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1 (the upper limit for the MPPD model). For  $d_{ae} > 20 \ \mu m$ , deposition in the TB airways was

- 2 estimated by a best fit polynomial (3rd or 4th degree) determined using CurveExpert 1.3 (112B
- 3 Crossgate St., Starkville, MS 39759). This polynomial function was fitted to TB deposition
- 4 fractions for  $d_{ae}$  from 10 to 20  $\mu$ m. The predicted ET deposition during oral breathing for a  $d_{ae}$
- $5 > 20 \,\mu\text{m}$  was taken as one minus the TB deposition fraction for oral breathing. For nasal
- 6 breathing, these additional steps were unnecessary because TB deposition was well under 1% at
- 7 a  $d_{ae}$  of 20  $\mu$ m.

8 External to the MPPD model, all of the predicted deposition fractions were corrected for 9 particle inhalability using Eqs G-1 and G-2. The current version of MPPD model offers an 10 inhalability correction for nasal breathing only. For a given d<sub>ae</sub>, an inhalability corrected 11 deposition fraction is the product of the uncorrected deposition fraction and the predicted 12 inhalability for that d<sub>ae</sub>. Unless otherwise specified, all mention of particle deposition fractions

13 in the main body of this report and subsequently in this appendix refer explicitly to inhalability

14 corrected deposition fractions.

15 The deposition fraction  $(DF_r)$  of an aerosol in a region of the respiratory tract is the 16 integral of the deposition fractions across all particle sizes in the aerosol:

17

$$DF_{r}(MMAD, \sigma_{g}) = \int_{0}^{\infty} DF_{r}(d_{i})\rho(d_{i})\delta d_{i}$$
 (G-3)

18

19 where:

20  $DF_r(d_i)$  = the deposition fraction in region, r, of particles having an aerodynamic 21 diameter of  $d_i$ 22  $\rho(d_i)$  = the mass fraction associated with the interval  $\delta d_i$ 

23

The total deposition fraction for the respiratory tract is the sum of  $DF_r$  for the ET, TB, and PU regions. Equation G-3 can be approximated by summing the particle deposition fractions at known intervals or percentiles of the particle size distribution. Here, the interval of 1% was used and the approximation is:

28

$$DF_{r}(MMAD, \sigma_{g}) \approx \frac{1}{100} \sum_{P=0.01}^{0.99} DF_{r}(d_{i})$$
 (G-4)

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1	where:
2	$DF_r(d_i)$ = the deposition fraction in region, r, of particles having an aerodynamic diameter
3	$d_i$ (the particle size associated with a given percentile, P, of the size
4 5	distribution).
6	For a log-normal distribution, d <sub>i</sub> is given by:
7	
	$d_i = MMAD \sigma_g^{z(P)} $ (G-5)
8	where:
9	z(P) = the normal standard deviate for a given probability
10	
11	Table G-4 provides the predicted regional deposition fractions for the clay dust in the
12	respiratory tract of each subject for oral and nasal breathing at two activity levels. These
13	deposition fraction estimates were based on each subject's measured aerosol exposure size
14	distribution (see Tables G-1 and G-2). Subjects 4 and 5 lacked aerosol size distribution data and
15	were assumed exposed to an aerosol with an MMAD of 25 $\mu$ m and $\sigma_g$ of 3.8, this being the
16	average for artisans during normal activities (see Table G-1). The deposition fraction estimates
17	for Subject 10 were based on Run 3, when the dog was not present in the studio.
18	
19	DELIVERED DOSE ESTIMATES
20	The rate of particle deposition in a region of the respiratory tract may be expressed as:
21	
	• $D_r(t) = C(t) (t)V_T(t)DF_r(t)$ (G-6)
22	
23	where:
24	$\dot{D}_r$ = the rate of deposition per unit time in region r
25	C = the exposure concentration
26 27	f = breathing frequency
27	$V_T$ = tidal volume DF <sub>r</sub> = the deposition fraction in region r
<u>2</u> 9	
30	Note that all of the variables in Eq G-6 may vary with time. The dose to a respiratory region is
31	determined by integrating Eq G-6 over the exposure duration.

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			Sitt	ing					Light e	xercise	2	
	Nasa	ıl breat	hing	Oral breathing		Nasal breathing			Oral breathing			
Subject	ЕТ	ТВ	PU	ЕТ	ТВ	PU	ЕТ	ТВ	PU	ЕТ	ТВ	PU
1	0.441	0.015	0.022	0.473	0.082	0.058	0.473	0.006	0.011	0.516	0.060	0.052
2	0.336	0.011	0.016	0.412	0.059	0.042	0.360	0.004	0.008	0.442	0.044	0.037
3	0.472	0.028	0.033	0.431	0.104	0.067	0.531	0.010	0.020	0.486	0.074	0.075
4	0.447	0.021	0.022	0.471	0.091	0.050	0.487	0.007	0.013	0.521	0.064	0.056
5	0.458	0.016	0.023	0.479	0.086	0.061	0.492	0.006	0.011	0.523	0.063	0.054
6	0.526	0.023	0.022	0.521	0.108	0.053	0.566	0.007	0.012	0.581	0.075	0.059
7	0.549	0.035	0.041	0.432	0.128	0.085	0.622	0.013	0.025	0.498	0.090	0.095
8	0.451	0.018	0.017	0.507	0.087	0.041	0.483	0.005	0.010	0.557	0.061	0.046
9	0.368	0.020	0.023	0.396	0.077	0.047	0.410	0.007	0.014	0.437	0.054	0.053
10	0.533	0.030	0.033	0.462	0.118	0.072	0.593	0.010	0.020	0.525	0.083	0.081

# Table G-4. Regional deposition fractions (corrected for inhalability) for claydust in the respiratory tract

ET = extrathoracic; PU = pulmonary; TB = tracheobronchial

3

4

5

By assuming that aerosol characteristics and an individual's activity levels are fairly

6 constant over discrete periods of time, the dose to a respiratory region may be approximated by:

$$D_{r} = 0.06 \sum_{j=1}^{n} (V_{T} f)_{j} (CT)_{j} [F_{m} DF_{m,r} = F_{N} DF_{N,r}]_{j}$$
(G-7)

#### 7 where:

8	$D_r$ = the dose (µg) to region r of the respiratory tract
9	$V_T$ and $f$ = tidal volume (mL) and breathing frequency (min <sup>-1</sup> ) for a specified activity j
10	C and T = exposure concentration $(mg/m^3)$ and duration (hr) during activity j
11	$F_m$ and $F_N$ = the fraction of a breath entering the respiratory tract through the mouth and
12	nose, respectively, during activity j
13	$DF_{m,r}$ and $DF_{N,r}$ = the deposition fraction for oral and nasal breathing, respectively, in
14	region r of the respiratory tract while performing activity j
15	Constant $0.06 = a$ unit conversion parameter
16	

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1 As expressed, an "activity" in Eq G-7 could be associated with changes in exposure

2 concentration, the particle size distribution, and/or an individual's exertion level. For simplicity,

- 3 only two exertion levels (sitting and light exercise) and a single particle size distribution (see
- 4 Tables G-1 and G-2) were considered for each subject.

5 The fraction of flow through the mouth (F<sub>m</sub> in Eq G-7) increases with activity level and 6 varies between individuals. For the two activity levels considered here, most people (87%) will 7 breathe through their nose (Niinimaa et al., 1981). Hence, for these people,  $F_m = 0$  and  $F_N = 1$  in 8 Eq G-7. However, 13% of people will be oronasal breathers even at rest, i.e., they will breathe 9 simultaneously through the nose and mouth (Niinimaa et al., 1981). This latter group is commonly referred to in the literature as "mouth breathers" (e.g., ICRP, 1994). Derived from 10 11 Niinimaa et al. (1981), the fraction of air respired through the mouth  $(F_m)$  is well described by a 12 modified exponential function in the form of: 13

$$F_{\rm m} = \alpha \exp\left(\frac{\gamma}{{\bf v}_{\rm e}}\right) \tag{G-8}$$

14where:15
$$\hat{V}_e = \text{minute ventilation}$$
16 $\alpha = 0.748 \text{ and } \gamma = -7.09 (r^2 = 0.997) \text{ in mouth breathers for  $10\dot{V}_e 80 \text{ L/min}$  and17 $35.3\dot{V}_e 80 \text{ L/min}, \alpha = 0.744, \text{ and } \gamma = -18.3 (r^2 = 0.998) \text{ in normal augmenters}$ 181919For  $\dot{V}_e < 35.3 \text{ L/min}$ , normal augmenters breathe entirely through the nose, i.e.,  $F_m = 0$ .  $F_N$  is one20minus  $F_m$  regardless of the activity.21Table G-5 gives the estimated clay dust doses to regions of the respiratory tract for each23subject during nasal and oronasal breathing. Estimates are for a 4-hour exposure assuming that24the exposed individual spent 50% of his or her time sitting and 50% engaged in light exercise.25For oronasal breathing in Table G-5, there is a small positive bias in ET doses and a26calculating ET and TB doses shifts the pattern of deposition toward the head relative to the real-27life pattern of deposition. This shift occurs due to deposition being calculated at a higher airflow28rate through the nose and mouth than actually occurs during oronasal breathing. The deposition29calculations presumed that all inhaled airflow was through the nose or mouth. In reality, inhaled30air is partitioned between the nose and the mouth, and the actual flows (for sitting and light31exercise) are roughly half of that used in the deposition calculations. For breathing by a single$ 

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1 route (nasal or oral), changing activity from sitting to light exercise approximately triples flow 2 rates but only slightly increases ET deposition and modestly decreases TB deposition (see Table G-4). The effect of using Eq G-7 for calculating doses during oronasal breathing should 3 4 similarly affect the pattern of deposition. Ultimately, particles deposited in the ET and TB 5 regions will typically be cleared to the throat and swallowed within 24 to 48 hours 6 postdeposition (ICRP, 1994). Hence, the exact site of deposition (i.e., ET versus TB) is of little 7 significance because both regions effectively contribute to ingested doses. 8 Table G-6 provides estimates of the dioxin absorption in each subject for nasal and 9 oronasal breathing. Particles deposited in the ET and TB regions clear rapidly (within 1–2 days) 10 to the throat and are swallowed. The absorption of dioxin from particles deposited within the ET 11 and TB regions was treated as if the particles had been ingested. Dose estimates for oronasal 12 breathing are slightly more conservative from a safety or risk perspective than presuming nasal 13 breathing. However, nasal breathing may be considered as representative of the majority of the 14 population (87%). Oronasal breathing is thought to represent 13% of healthy individuals 15 (Niinimaa et al., 1981). In contrast to healthy subjects, Chadha et al. (1987) found that the 16 majority (11 of 12) of patients with asthma or allergic rhinitis breathe oronasally even at rest. 17 On average across all the subjects, dioxin doses are about 1.2 times greater for oronasal than for 18 nasal breathing.

19

	N	asal breath	ing	Or	onasal breat	thing
Subject	ЕТ	ТВ	PU	ЕТ	ТВ	PU
1	664	12	20	693	53	48
2	678	11	19	757	52	47
3	1,677	47	75	1,612	143	154
4	580	13	19	598	45	41
5	256	4.6	7.7	264	21	19
6	1,114	22	29	1,126	85	70
7	1,011	30	49	917	90	100
8	997	18	24	1,067	72	57
9	110	2.9	4.5	114	8.8	9.2
10	455	12	18	431	39	39
Mean	754	17	27	758	61	58
SD	460	13	21	445	39	42

Table G-5. Regional doses (µg) of clay dust in the respiratory tract<sup>a</sup>

<sup>a</sup> Doses calculated by Eq G-7 as described in the text.

ET = extrathoracic; PU = pulmonary; TB = tracheobronchial

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	Na	sal breathi	ng	Oron	nasal breath	ing
Subject	ET and TB <sup>b</sup>	PU <sup>c</sup>	Total	ET and TB <sup>b</sup>	PU <sup>c</sup>	Total
1	0.033	0.003	0.035	0.036	0.006	0.043
2	0.034	0.003	0.036	0.039	0.006	0.045
3	0.084	0.010	0.094	0.085	0.020	0.105
4	0.029	0.002	0.031	0.031	0.005	0.037
5	0.013	0.001	0.014	0.014	0.002	0.016
6	0.055	0.004	0.059	0.059	0.009	0.068
7	0.051	0.006	0.057	0.049	0.013	0.062
8	0.049	0.003	0.052	0.055	0.007	0.063
9	0.005	0.001	0.006	0.006	0.001	0.007
10	0.023	0.002	0.025	0.023	0.005	0.028
Mean	0.038	0.004	0.041	0.040	0.007	0.047
SD	0.023	0.003	0.026	0.023	0.006	0.029

Table G-6.	Estimates of	dioxin	absorption <sup>a</sup>	(pg TEQ)
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<sup>a</sup> Dioxin concentration was assumed to be 162 pg toxic equivalent (TEQ) per gram clay. <sup>b</sup> Absorption fraction of 0.3 assumed, extrathoracic (ET) and tracheobronchial (TB) rapidly clear into the gastrointestinal tract. <sup>c</sup> Absorption fraction of 0.8 assumed, due to slow clearance from pulmonary (PU) region.

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### Appendix H

Skin Rinsing Data

Subject	Rinse 1	Rinse 2	Rinse 3
1	0.321	NA <sup>a</sup>	0.773
2	2.957	2.804	0.083
3	0.558	0.427	0.333
4	0.139	0.126	0.18
5	2.908	1.919	3.042
6	9.893	12.522	10.319
7	0.158	0.149	0.313
8	0.443	1.018	2.618

Table H-1. Weight of clay rinsed from skin of each subject during each individual skin rinse (g)

<sup>a</sup>Sample lost during analysis.

Subject	<b>Right Hand</b>	Left Hand	Arms	Legs	Feet	Face
Subject 9	9,750	11,243	398.55	509.80	214.40	16.70
Wheel	1,874	2,352	790.25	596.25	144.00	0.00
	4,059	4,270	388.60	1,276.70	267.20	4.35
	1,536	2,845	5,005.35	958.50	220.65	9.60
	1,367	3,426	8,630.60	273.95	2,991.50	524.60
Subject 10	70	14	33.50	8.40	17.40	0.00
Sculpture	83	65	58.50	42.85	42.65	9.80
	74	98	131.80	9.20	14.10	25.70

Table H-2. Residual clay (mg)

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# Appendix I

Alternative Method for Estimating Dermal Absorption

1 2 3

#### APPENDIX I. ALTERNATIVE METHOD FOR ESTIMATING DERMAL ABSORPTION

This document uses the fraction absorbed approach to estimate dermal absorption, which is the method recommended in current U.S. Environmental Protection Agency guidance (U.S. EPA, 2004, 1992). This method does not accurately represent the mechanisms of dermal absorption and presents difficulties in extrapolating experimental results to actual exposure conditions. The discussion below presents an alternative approach using a more mechanistic model. This method is based on work by Dr. Annette Bunge, as published in Bunge and Parks (1998).

11

#### 12 BASIC MODEL

where:

Bunge and Parks (1998) present three approaches for estimating dermal dose from soil, depending on whether absorption is small, large, or based on slow soil-release kinetics (i.e., desorption from soil is slow relative to dermal permeation). The slow-release kinetics approach was selected as the best one to use because the high lipophilicity of dioxin, presence of organic carbon in the clay, and small particles associated with clay all suggest that dioxin will be tightly bound to the particles and slowly released. On this basis, the absorbed dermal dose (pg) is estimated as follows:

$$AbsDose = C_{soil,0}M_{soil} \left[ 1 - \exp\left(-k_{soil}\rho_{soil}f_{area}A_{\exp}t_{\exp}/M_{soil}\right) \right]$$
(I-1)

20	
21	$C_{soil,0} = concentration of dioxin in soil at = 0 (pg/mg)$
22	$M_{soil}$ = mass of soil on exposed skin (mg)
23	$k_{soil}$ = rate constant for first-order soil release kinetics (cm/s)
24	$\rho_{soil} = soil bulk density (mg/cm^3)$
25	$f_{area}$ = fraction of exposed area in contact with soil
26	$A_{exp} = exposed skin area (cm2)$
27	$t_{exp} = exposure time (hr)$
28	
29	The rate constant and soil density terms can be combined into one term representing the
30	transfer rate from soil (k) with units of mg $cm^{-2} hr^{-1}$ . If the amount of dioxin absorbed is less
31	than about 10% of the original amount on the skin (i.e., $C_{soil,0} \times M_{soil}$ ), then Eq I-1 simplifies to:

$$AbsDose = k f_{area} A_{exp} t_{exp} C_{soil,0}$$
(I-2)

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#### 1 ESTIMATING k

2 As discussed above, Eq I-2 is based on the assumption of slow soil-release kinetics. 3 Assuming that desorption from soil is slow relative to dermal permeation, the rate of dermal 4 permeation can be used to estimate the rate of desorption from soil. This approach is used here. 5 As discussed in Section 5, this report derives the dermal absorption properties of dioxin 6 from Roy et al. (1990), who measured dermal absorption of tetrachlorodibenzo-p-dioxin (TCDD) in soil with an organic carbon content of 0.45% and applied at supermonolayer coverage 7 (monolayer estimated as  $1.3 \text{ mg/cm}^2$  and amount applied was  $6 \text{ mg/cm}^2$ ). The saturation limit 8 9 for TCDD in this soil was estimated as follows:

$$C_{sat} = F_{oc} K_{oc} S_w \tag{I-3}$$

10	where:
11	$C_{sat}$ = saturation limit for TCDD in soil (mg/kg)
12	$F_{oc}$ = fraction organic carbon in soil = 0.0045
13	$K_{oc}$ = organic carbon-to-water partition coefficient = 10 <sup>7</sup> L/kg (U.S. EPA, 2003)
14	$S_w$ = solubility of TCDD in water = 2 × 10 <sup>-5</sup> mg/L (U.S. EPA, 2003)
15	
16	On this basis, the soil used by Roy et al. would have a saturation limit for TCDD of 0.8 mg/kg.
17	Roy et al. used soils with TCDD concentration of 1 mg/kg (1 ppm). Thus, the testing was

- 18 conducted at levels slightly above the saturation limit, which should yield maximum flux rates
- 19 through the skin.

20 The 24-hour average flux rate from Roy et al. was calculated as follows:

$$J = AbsDose/(A_{exp} t_{exp})$$
(I-4)

where:

J = flux through the skin (ng cm<sup>-2</sup> hr<sup>-1</sup>) AbsDose = 0.048 ng (includes amount in skin)  $A_{exp} = 1.77 \text{ cm}^{2}$   $t_{exp} = 24 \text{ hr}$ 

This yields a flux estimate of 0.0011 ng cm<sup>-2</sup> hr<sup>-1</sup>. Now, an absorption rate constant ( $k_a$ ) can be calculated as follows:

$$ka = J_{SM} / C_{sat} \tag{I-5}$$

29 where:

30

 $J_{SM}$  = maximum flux for supermonolayer coverage = 0.0011 ng cm<sup>-2</sup> hr<sup>-1</sup>

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1 2	$C_{sat} = 0.8 \text{ mg/kg} = 0.8 \text{ ng/mg}$
3	On this basis, $k_a$ is estimated to be 0.0014 mg cm <sup>-2</sup> hr <sup>-1</sup> and assumed equal to k.
4	
5	ESTIMATING THE ABSORBED DOSE
6	Finally, the absorbed dose can be calculated using Eq I-2. As an example, the parameter
7	values for Subject 2 were used:
8	
9	$C_{soil,0} = 162 \text{ pg/g} = 0.162 \text{ pg/mg}$ $A_{exp} = 970 \text{ cm}^2$
10	
11	$t_{exp} = 4 hr$
12	$f_{area} = 1.0$ (actual load exceeded monolayer)
13	
14	This yields an absorbed dose of 0.88 pg. The absorbed dose calculation presented in Section 7
15	included an adjustment to reflect the observed difference between rat in vivo testing and rat in
16	vitro testing. These tests indicated that the absorbed dose in vivo was about twice as high as the
17	absorbed dose in vitro. Applying that factor to the dose estimate derived above yields an
18	absorbed dose of 1.8 pg. This is very similar to the value reported in Table 9 (1.65 pg) based on
19	the fraction absorbed approach. Note that the amount of dioxin in the monolayer can be
20	estimated as 97 pg (0.162 pg/mg $\times$ 0.62 mg/cm <sup>2</sup> $\times$ 970 cm <sup>2</sup> ). This means that the absorbed dose
21	is less than 10% of the applied dose and Eq I-2 is valid to use.

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