

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233410144>

Selective Soil Particle Adherence to Hands: Implications for Understanding Oral Exposure to Soil Contaminants

ARTICLE in ENVIRONMENTAL SCIENCE & TECHNOLOGY · NOVEMBER 2012

Impact Factor: 5.33 · DOI: 10.1021/es302473q · Source: PubMed

CITATIONS

15

READS

53

2 AUTHORS:



[Michael V. Ruby](#)

Integral Consulting, Inc.

39 PUBLICATIONS 2,904 CITATIONS

[SEE PROFILE](#)



[Yvette Lowney](#)

Exponent

25 PUBLICATIONS 356 CITATIONS

[SEE PROFILE](#)

Selective Soil Particle Adherence to Hands: Implications for Understanding Oral Exposure to Soil Contaminants

Michael V. Ruby*,† and Yvette W. Lowney‡

†Integral Consulting Inc., 285 Century Place, Suite 190, Louisville, Colorado 80027, United States

‡Exponent, 4141 Arapahoe Avenue, Suite 101, Boulder, Colorado 80303, United States

ABSTRACT: Over the last 30 years, there has been extensive research designed to quantify the extent of oral bioavailability and bioaccessibility of organic and inorganic contaminants in soil. One aspect of this research is the soil particle size selected to represent environmental exposures, which may affect study results and comparability across studies. Different research groups have studied soil particle sizes ranging from $<45\text{ }\mu\text{m}$ to $<2000\text{ }\mu\text{m}$. This article reviews the historical and technical considerations that pertain to the selection of an appropriate particle size fraction for evaluating the relative oral bioavailability of chemicals from soil, which include (1) how the resultant data will be used in human health risk assessment, (2) soil fractions historically used in oral bioavailability studies, (3) studies of soil adherence to human hands, (4) the distribution of contaminants in soils as a function of particle size, and (5) the effect of differential bioavailability as a function of soil particle size and geochemical matrix. These factors are first discussed from a general perspective, applicable to all contaminants in soil, and then more specifically for polycyclic aromatic hydrocarbons (PAHs) in soil. Based on this review, a specific soil particle size of $<150\text{ }\mu\text{m}$ is recommended for future studies on the oral bioavailability and bioaccessibility of PAHs in soil.



INTRODUCTION

One of the assumptions incorporated into studies to characterize human exposures to contaminants in soil is the notion that the nature of the matrix studied is representative of the material to which humans are actually exposed. One aspect of this assumption is the particle size fraction of the soil that is used in studies of the oral bioavailability and bioaccessibility of chemicals in soils (use of the terms "oral bioavailability" and "bioaccessibility" herein are consistent with those in use by U.S. EPA).¹ Historically, a wide variety of soil particle sizes has been used by different research groups (ranging from <45 to $<2000\text{ }\mu\text{m}$) thereby making it difficult to directly compare reported results across studies. This article reviews factors that affect decisions regarding the particle size that best represents oral exposures to humans, including studies of soil adherence on hands and distribution of contaminants in soils as a function of particle size, the historical context regarding selection of soil particle sizes, and considerations of how the resultant data will be used in risk assessment. These factors are discussed from a general perspective, one that applies to all contaminants in soil, and then specifically with respect to oral exposures to polycyclic aromatic hydrocarbons (PAHs) in soil. It is not the intent herein to address the amount of soil being ingested, but rather the size of the soil particles ingested. The reader is referred to USEPA² for a thorough discussion of soil mass ingested by children and adults.

APPLICATIONS TO RISK ASSESSMENT

Under the current regulatory paradigm developed by the U.S. Environmental Protection Agency (U.S. EPA), contaminant remediation standards or goals that are developed for direct contact with soil are based on the assumption that incidental ingestion of soil provides the primary pathway for human exposure to soil contaminants.³ The general understanding is that this incidental ingestion is largely the result of hand-to-mouth contact (or hand-to-food contact and subsequent ingestion of that food) after loading of soil onto the hands during normal daily activities (including play, for young children). Although other mechanisms exist that could contribute to soil ingestion, such as ingestion of soil particulates adhering to vegetables or inhalation of soil particulates, followed by ingestion of particulates after mucociliary clearance, the available information suggests that these are minimal contributors to ingestion exposures. Because soil ingestion by adults is lower than that for children,² ingestion of soil particulates on vegetables and ingestion of particulates subsequent to inhalation and mucociliary clearance do not appear to be significant

Received: June 19, 2012

Revised: November 1, 2012

Accepted: November 1, 2012

Published: November 14, 2012

contributors given that adult consumption of vegetables, and inhalation volumes for air, are higher than those for children.² In addition, mechanistic modeling to evaluate the contribution to soil ingestion from mouthing behavior yields soil exposure estimates that are similar to values from soil ingestion tracer studies (68 vs 100 mg/day), with about 90% assumed to be contributed from hand-to-mouth contact.²

This pathway of incidental ingestion is distinct from the soil ingestion that might be incurred by a child who exhibits pica behavior for soil. In the instance of pica, larger masses of bulk soils may be ingested, and the risks in these instances may include shorter-term toxicity.⁴ The focus of this paper is to better understand the nature of the particles contributing to long-term exposure to soil, associated with loading onto hands and subsequent, inadvertent, ingestion.

Under the conventional paradigm for human health risk assessment outlined by the National Academy of Sciences,⁵ risks from exposure to contaminants in soil are estimated by combining information regarding the potential toxicity of the chemical(s) of interest together with information regarding human exposure to those chemicals. Exposure from contaminated soil is calculated according to the following formula:

$$\text{Exposure}_{\text{ingestion}} = \frac{C_s \times \text{IR}_s \times \text{RBA}}{\text{BW}}$$

where

- C_s = concentration of contaminant in soil ($\mu\text{g/g}$)
- IR_s = soil ingestion rate (g/day)
- RBA = relative bioavailability adjustment (unitless)
- BW = body weight (kg)

Thus, ingestion exposures are expressed in terms of mass (units of micrograms of chemical per kilogram of body weight per day). As a result, it is the mass of the chemical that defines the level of exposure and hence the associated potential for toxicity, or "risk". Therefore, in refining our understanding of exposures to chemicals in soils from incidental ingestion, the ultimate goal remains to understand what controls the mass of the chemical ingested. This distinction is important for two reasons. First, although small particles (e.g., clay and silt size) are generally more abundant on hands than larger particles (e.g., fine sand), the mass of soil adhering may reside in the larger particles. If those larger particles contain a significant mass of contaminant, then they may contribute to exposure (i.e., mass of contaminant ingested). Second, most studies of contaminant enrichment in soil report the enrichment as a function of concentration when it is actually enrichment as a function of mass that is important for selecting a soil particle size for characterizing human exposures.

In the context of assessing exposures to contaminants in environmental media, U.S. EPA provides guidance for how to select inputs to exposure assessments. Risk Assessment Guidance for Superfund⁶ states that "some intake variables may not be at their individual maximum values, but when in combination with other variables will result in estimates of the Reasonable Maximum Exposure (RME)." Thus, some intake factors will be set at high-end values, while some are estimates of mean values, such that the overall estimate of intake represents an RME. Review of U.S. EPA's Exposure Factors Handbook² confirms that recommendations for inputs to exposure calculations can vary from mean to high-end values; however, it does not specifically discuss soil particle sizes ingested. In light of this approach to characterizing exposures, we have selected to present the particle size cutoffs that would account for 50% and

90% of the mass adhering to hands (termed the 50th and 90th percentile values herein) for each of the studies for which these values are reported or can be calculated. The selection of the most appropriate value for characterizing exposure is discussed below.

HISTORICAL PERSPECTIVE

The earliest published studies on the oral bioavailability of contaminants in soil were conducted for dioxins/furans in the mid-1980s. Two studies performed at the National Institute of Environmental Health Sciences, by McConnell et al.⁷ and Lucier et al.,⁸ used the $<250\text{ }\mu\text{m}$ (60 mesh sieve) soil fraction to investigate oral bioavailability of soils from the Times Beach and Minker Stout, Missouri, sites. During the same time period, Bonaccorsi et al.⁹ and Shu et al.¹⁰ used $30\text{--}74\text{ }\mu\text{m}$ and $<420\text{ }\mu\text{m}$ soil size fractions, respectively, for studies of dioxin bioavailability from soil at Seveso, Italy, and Times Beach, Missouri. None of these authors provide rationales for why they chose a particular size fraction for their studies.

Subsequently, in the 1990s, several research groups began conducting studies on PAH bioavailability from soils. These studies generally used finer particle sizes—Goon et al. (crushed to $<100\text{ }\mu\text{m}$),¹¹ Rozett et al. (studied a range of particle sizes with the smallest being $<150\text{ }\mu\text{m}$ and the largest being $<850\text{ }\mu\text{m}$),¹² and Weyand et al. ($<150\text{ }\mu\text{m}$)¹³—although sometimes larger soil size fractions were used (e.g., Koganti et al., $<1000\text{ }\mu\text{m}$).¹⁴ Once again, these authors did not provide any rationale for the particle sizes selected to represent oral exposures.

In the early 1990s, U.S. EPA began developing a swine model for the assessment of soil lead bioavailability. The earliest version of this model used a $<149\text{ }\mu\text{m}$ (100 mesh sieve) particle size.¹⁵ However, this particle size was increased to $<250\text{ }\mu\text{m}$ in the final version of U.S. EPA's swine model.¹⁶ The reason for the change from <149 to $<250\text{ }\mu\text{m}$ is not documented. U.S. EPA has also developed a swine model for determination of relative arsenic bioavailability from soil, which uses a $<250\text{ }\mu\text{m}$ soil fraction.¹⁷ U.S. EPA's selection and use of the $<250\text{ }\mu\text{m}$ soil fraction most likely influenced later research groups, which generally have used the $<250\text{ }\mu\text{m}$ particle size for oral bioavailability research models (Maddaloni et al., lead in humans;¹⁸ Roberts et al., arsenic in primates;^{19,20} Budinsky et al., dioxins/furans in rats and swine;²¹ Finley et al., dioxins/furans in rats²²). Recently, James et al. developed a swine model for PAH bioavailability from soil using a $<45\text{ }\mu\text{m}$ soil fraction.²³ The selection of this particle size was based on the research of Siciliano et al.²⁴ (discussed below) and was selected as a soil fraction that would be enriched in clay and silt size particles because "it is commonly thought that metallic toxicant concentrations will be higher in the clay fraction and organic toxicant concentrations higher in the silt fraction."

The $<250\text{ }\mu\text{m}$ soil fraction has also been used in environmental health studies for lead and arsenic that have been conducted at mining sites around the western U.S. (Anaconda, Montana;²⁵ Butte, Montana;²⁶ Midvale, Utah²⁷) and in U.S. EPA's Urban Soil Lead Abatement Demonstration Project (also known as the "Tri-City Lead Study") conducted in the late 1980s to evaluate the effect of lead-contaminated soil removal on lead in children's blood.^{28,29} It is also the basis upon which U.S. EPA's Integrated Exposure Uptake Biokinetic (IEUBK) model, for estimating blood lead concentrations in children, is validated because the environmental health lead studies used for that purpose relied on soil samples sieved to $<250\text{ }\mu\text{m}$.³⁰ Recommendations for conducting bioavailability studies to support blood lead modeling with the IEUBK specify that it is "critical to sieve soil

Table 1. Summary of Soil Adherence Studies

study	year	data reporting method	study type and conditions	particle size cutoff accounting for 50% of adhering mass	particle size cutoff accounting for 90% of adhering mass
Duggan et al. ³³	1985	number of particles adhering in each size range	field	NM ^a	NM
Duggan and Inskip ³⁴	1985	mass of soil adhering for each size fraction	laboratory	57 μm	130 μm
Que Hee et al. ³⁵	1985	mass of house dust adhering for each size fraction	laboratory	NA ^b	NA
Driver et al. ³⁸	1989	mass of soil adhering for each size fraction	laboratory	NR ^c	NR
Sheppard and Evenden ³⁹	1994	enrichment ratios of the mass of specific size fractions adhering	laboratory	NR	NR
Kissel et al. ⁴⁰	1996	mass of soil adhering for each size fraction	laboratory: dry soil Laboratory: Wet soil	62 μm 150 μm	210 μm 350 μm
Choate et al. ⁴¹	2006	mass of soil adhering for each size fraction	laboratory: low moisture soil laboratory: medium moisture soil laboratory: high moisture soil	33 μm 44 μm 80 μm	110 μm 120 μm 220 μm
Yamamoto et al. ⁴²	2006	mass of soil adhering for each size bin	field	67 μm ^d	134 μm ^d
Siciliano et al. ²⁴	2009	mass of soil adhering in each size fraction	field laboratory: agricultural soils laboratory: brownfield soils	40 μm 40 μm 125 μm	130 μm 370 μm 760 μm
Bergstrom et al. ⁴³	2011	estimated mass adhering for each size fraction	laboratory	NR	NR

^aNM = No mass-based estimate of soil adherence, 90% of particles were <10 μm . ^bNA = Not applicable (study used house dust not soil). ^cNR = Not reported or not calculable from data presented. ^dAverage value for the population of children (three of nine) with the largest soil particles adhering.

samples to <250 to more closely represent the size of soil particles that would be expected to adhere to children's hands".³¹ Finally, U.S. EPA's Superfund Lead-Contaminated Residential Sites Handbook specifies analysis of the <250 μm size fraction for evaluation of childhood exposures to lead in residential soils.³²

The selection of the <250 μm soil size fraction for assessment of human exposure to metals (and metalloids) in soil appears to have emerged from the environmental health studies described above. At that time (late 1980s), there were few data available to consider when selecting a particle size cutoff (see Table 1 for list and dates of studies). Given the data published in the last 15 years (discussed below), it appears that the <250 μm soil size fraction may not be the optimum soil fraction for assessing human exposures due to direct contact with soil.

■ SOIL PARTICLE SIZES ADHERING TO HUMAN HANDS

A number of studies on the size of particles that adhere to human hands have been conducted (summarized in Table 1). Some of the primary distinctions between these studies are (1) whether they studied adherence under field conditions or in the laboratory, (2) the methods by which the hand was exposed to soil (press, contact by inversion of soil container over hand, crumbling of soil in hand, or rubbing soil into digits), (3) the methods by which soil was removed from the hand (wash, wipe, or abrasion), (4) the particle size measurement method (optical microscopy, mass in different sieved fractions, or particle size analyzer), (5) whether they studied the effects of moisture content of the soil or the hand (a variable controlling particle size adhesion), and (6) whether they reported the results as the distribution of the number of individual particles or the distribution of soil mass adhering as a function of particle size. Only one study, Duggan et al., reported results based on the

former measure, and their results are clearly anomalous when compared to all of the other studies (discussed below).³³

Studies that have measured soil particle sizes adhering to hands are reviewed below and are broken out as those studies that report the number of particles adhering as a function of particle size versus those that report the mass adhering as a function of particle size because of the importance of this distinction.

Studies Reporting the Number of Particles Adhering to Hands as a Function of Size. Duggan et al. studied soil particle sizes naturally adhering to 20 children's hands following play activities.³³ The authors used a hand wipe method followed by particle sizing by optical microscopy (50 particles sized per wipe). They observed a mean particle diameter of 4.5 μm and a maximum particle diameter of 100 μm . This study has been cited widely as the basis for selecting particle size fractions to which humans are exposed through hand-to-mouth activity. While it has the advantage of having studied children in their natural environment, it has the limitation of having reported only the number of particles in each size class adhering to the children's hands, and not the soil particle sizes that contributed most greatly to the mass of material adhering.

Studies Reporting the Mass of Soil Adhering to Hands as a Function of Size. Duggan and Inskip report on a small study (one subject and four soil samples) in which 20 mg of prefractionated soil (fractions were 0–53, 53–100, 100–150, and 150–500 μm) were rubbed into the thumb and forefingers, removed by gentle abrasion, and then weighed.³⁴ Under these conditions, the authors observed 48, 28, 16, and 8% of the mass in the 0–53, 53–100, 100–150, and 150–500 μm fractions adhered, respectively (data normalized to adherence for the total mass from all four fractions). Based on these data, the 50th and 90th percentile values are 57 and 130 μm , respectively (Table 1, Figure 1). The authors state that "if the hand-mouth route is the

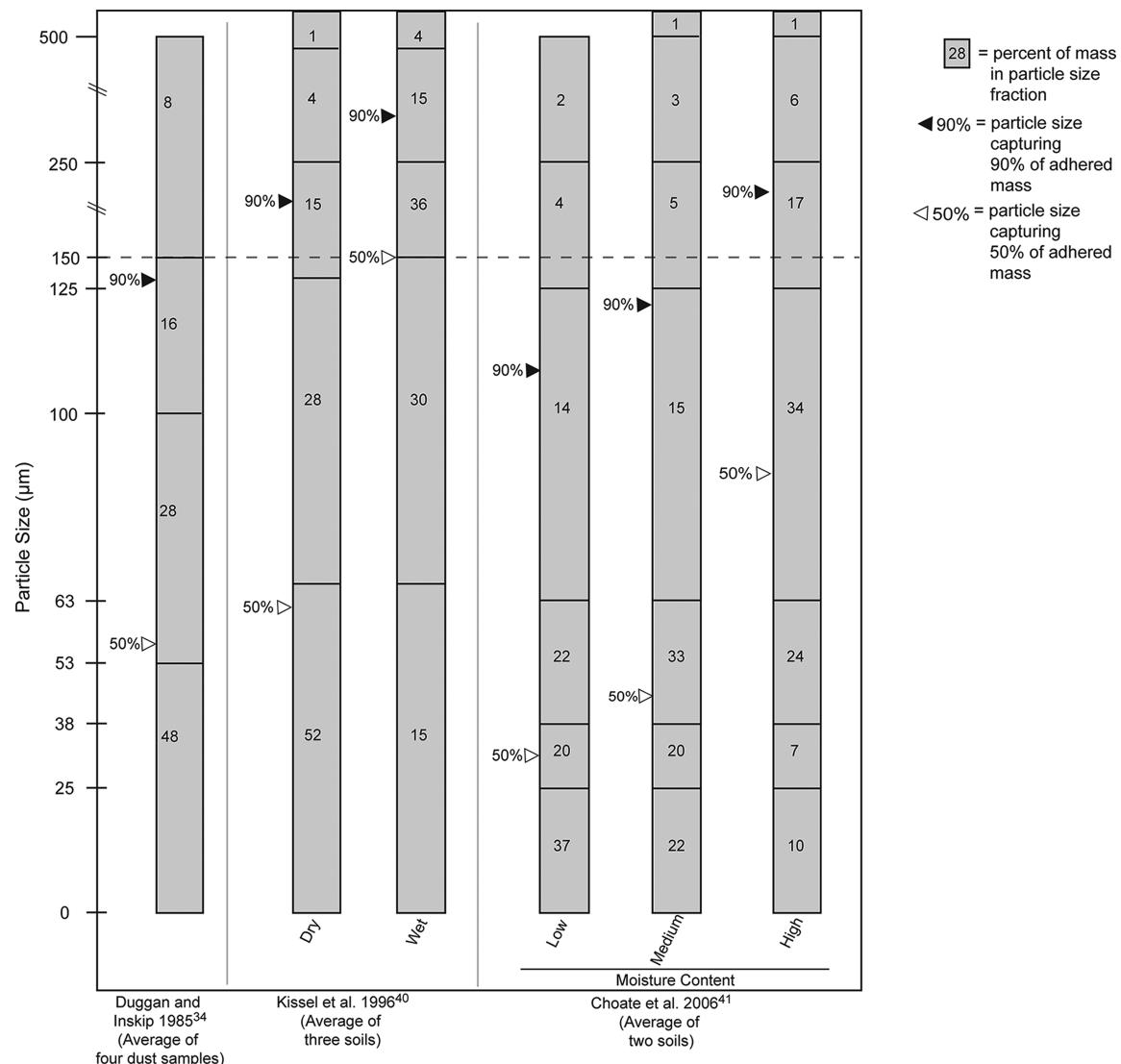


Figure 1. Summary of studies presenting mass of soil adhering to hands as a function of particle size and soil moisture content. Black arrow (►) indicates particle size capturing 90% of adhering mass, white arrow (▷) indicates particle size capturing 50% of adhering mass.

important one for children, then there would be some merit in analyzing only those particles of diameter less than, say, 200 μm.” The rationale for the selection of a 200 μm particle size is not discussed in the publication, but it would capture about 95% of the mass adhering to hands.

Que Hee et al. conducted a study that involved only a single volunteer and a single house dust sample.³⁵ The house dust was prefractionated into fractions of <44, 44–149, 149–177, 177–246, 246–392, and 392–833 μm. The hand of a “small adult” was placed lightly over a dish containing 5 g of each individual soil fraction. The hand and dish were inverted and then reinverted. The mass adhering was calculated by difference in weight of dust in the containers pre- and posthand contact. These authors report that for all materials in the <246 μm fractions an equal mass adhered to the palm of the volunteer. This result stands in contrast to all of the other studies reported herein, which have all shown that smaller particle sizes preferentially adhere to hands for dry soils. The use of house dust, as opposed to soil, may be the cause of this discrepancy. House dust is composed of a large amount of organic material (e.g., insect parts, food particles, exfoliated skin cells, hair, and small organisms^{36,37}) relative to soil. If this organic material occurred in the size fractions <246

μm in this study, it could have altered the adherence characteristics of the different size fractions. As a result, this study is not considered to be comparable to soil adherence studies.

Driver et al. conducted a study that involved the adherence of 11 soils fractionated into 3 particle sizes (<150 μm, <250 μm, and bulk) to the hand of a single volunteer (soils were a combination of both top soil and subsurface soil).³⁸ Using hand press trials (each test in triplicate), these authors measured the mass of material adhering to one subject’s hand from each size fraction of material for each soil. The mass adhering was calculated by difference from the weight of the soil container pre- and postloading, and results were reported as the mass adhering per square centimeter of skin surface. The mass of soil adhering was greatest for the <150 μm fraction (average of 1.40 mg/cm²), followed by the <250 μm fraction (0.95 mg/cm²), and then bulk soil (0.58 mg/cm²). Due to the manner in which the study was performed, the data could not be used to calculate the relative distribution of mass adhering from each size fraction. Across the 11 soils tested, there was more than 2-fold variability in the masses adhering for the <150 μm and the <250 μm fractions.

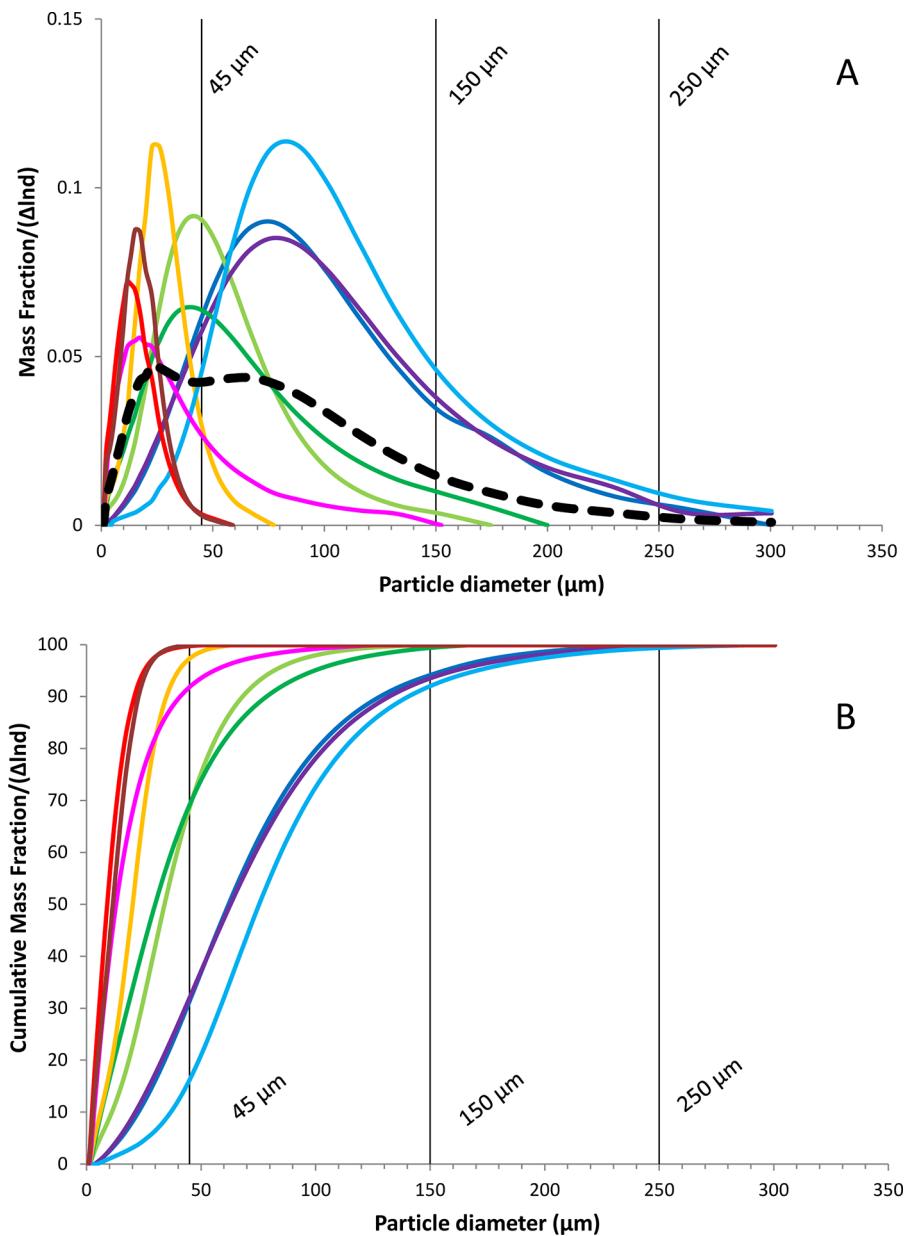


Figure 2. Mass fraction of soil adhering to children's hands as a function of particle size (data from Yamamoto et al.).⁴² Panel A presents distributions for individual children (colored lines) and the average distribution for all nine children (solid dashed line). Panel B presents the cumulative mass fraction adhering as a function of particle size.

Sheppard and Evenden conducted hand press trials for 11 different soils, selected to represent a range of soil types, followed by washing to remove the soil.³⁹ Particle sizes were measured in solution using a particle size analyzer and the particle mass in each size class (the mass fraction) was calculated based on the assumptions that all particles were spherical and had the same density (2.54 g/cm^3). These authors found that particles less than about $50 \mu\text{m}$ preferentially adhered to hands relative to particles in the $50\text{--}100 \mu\text{m}$ size range. The authors did not report the mean or maximum size adhering: the particle size analyzer had a measurement limit of $100 \mu\text{m}$, so the entire range of adhering particles was most likely not measured. These authors also studied the soil material not removed by the washing procedure and concluded that there was strong adhesion of clay particles ($<2 \mu\text{m}$), which are similar in size to skin surface roughness characteristics. This has implications for hand-to-

mouth transfer of soil and suggests that some portion of the clay fraction that adheres to hands may not be ingested due to difficulty of removal once it has adhered to skin.

Both Kissel et al. and Choate et al. studied the effect of soil moisture content on particle size adherence to hands and found that increased soil moisture could substantially increase the adhering particle sizes.^{40,41} Kissel et al. studied two soil moisture contents (1–6% and 14–19%) and used hand press trials with three soils, followed by washing and sieving. This work indicated that for dry soils (<6% moisture content), the bulk of adhering soil mass (about 80%) was in the sub- $135 \mu\text{m}$ size fraction (Figure 1; data interpolated from Figure 1 of Kissel et al.).⁴⁰ However, for wet soils (14–19% moisture content), the $<135 \mu\text{m}$ size fraction accounted for only about 45% of the mass adhered, and the $>135 \mu\text{m}$ fraction became the dominant contributor to mass adhered (55%). Choate et al. observed

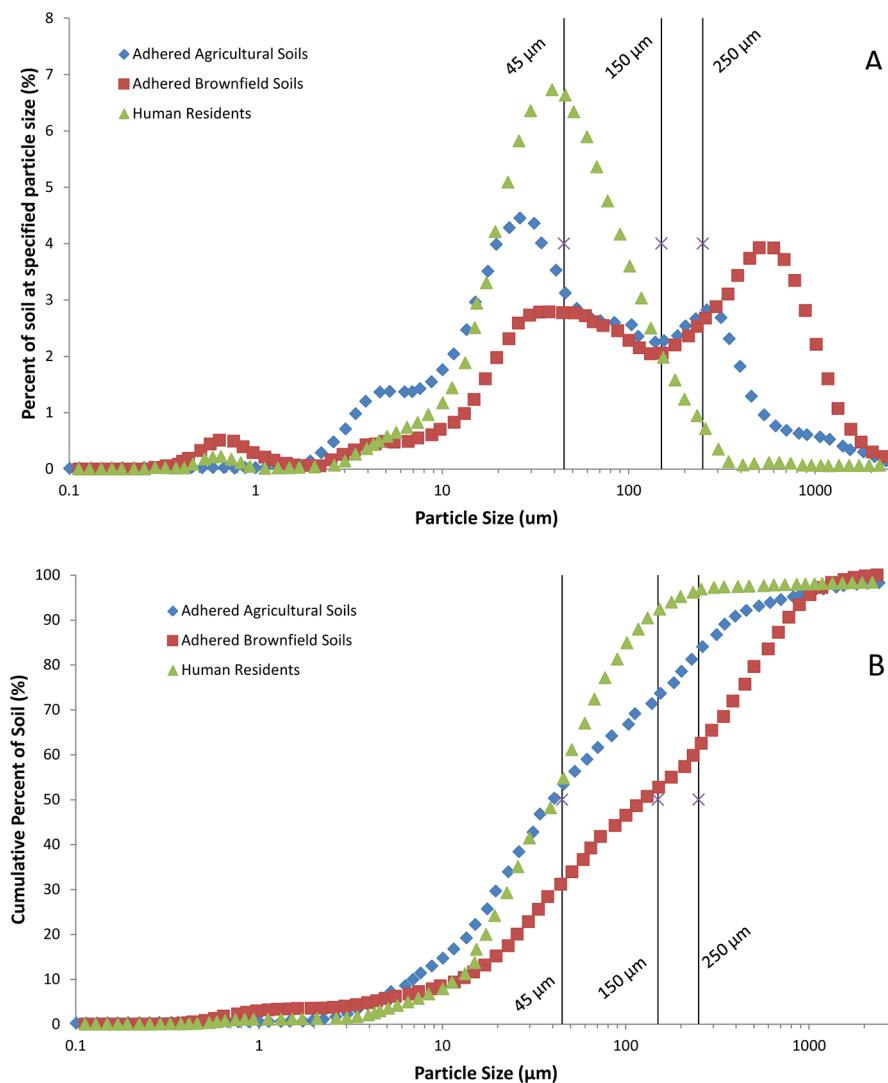


Figure 3. Soil mass adhering to hands as a function of particle size (data from Siciliano et al.).⁴⁶ Panel A presents the distributions for the three soil/exposure conditions studied and panel B presents the cumulative distributions for those three studies.

similar results when studying the effect of three soil moisture contents—low (1–2%), medium (3–4%), and high (9–10%)—on adherence of two soils that were contacted by volunteer's palms (the hand was placed over an open-ended container of soil and the container was inverted 10 times), washed with deionized water, and then wet sieved. These authors report that for dry and moderately moist soils, 75–80% of the adhering mass was in the <63 μm size fraction (Figure 1; data interpolated from Figures 1 and 2 of Choate et al.).⁴¹ However, for the moist soil (9–10% water content), the 63–125 and 125–250 μm fractions constituted (on average) 34 and 17%, respectively, of the adhering mass.

Yamamoto et al. studied the distribution of particle sizes on the hands of young children ($n = 9$; average of 4 years of age) following play activities at a nursery school.⁴² This is the first published study to evaluate adhering particle size distribution, as a function of soil mass adhered, under real-life conditions. Children's hands were washed and the particles were analyzed with a particle size analyzer. Results were converted to mass of material adhering for each of 46 particle size bins based on the assumption that all particles were spherical and had equivalent density (2.54 g/cm³). Figure 8 of Yamamoto et al. is reproduced here as Figure 2a (figures in this paper were generated from the

raw data provided by Dr. Yamamoto; the y -axis nomenclature [mass fraction/ $\Delta \ln d$] stands for the mass fraction per particle size bin; the bins sizes were designed so that taking their natural log resulted in equivalent bin sizes), and Figure 2b provides a cumulative distribution of mass fraction for each of the nine children.

Yamamoto et al. found a 6-fold difference in the mode particle size adhering to the hands of different children, consistent with previous studies that have shown large variability among individuals or study populations. The mode diameter (i.e., the value that occurs most frequently in a distribution) was used to characterize the central tendency of the distributions and varied from approximately 15 to 90 μm for different children (Figure 2a) (this is essentially the particle size at which the maximum mass of material is adhering). The maximum size particles observed were in the 100–300 μm range. In addition, increasing hand moisture was associated with an increased mass of soil adhered to hands and a slight increase in mean particle size.

This is a particularly useful study because it provides data on individual study participants. Of the children studied, 30% of the population (3 of 9 children) had considerably larger particles adhering to their hands than the other children (Figure 2a). If these larger particles, in the range of 50–150 μm, contain

significant contaminant mass, then they will contribute to exposure and it is important that they be included in the size fraction that is used for characterizing oral exposures (as described below, the 50–150 μm fraction does contain an appreciable mass of the PAHs in soil). For this reason, the 50th and 90th percentile values were calculated for the three children with the largest particles adhering (Figure 2a). This results in 50th and 90th percentile values of 67 and 134 μm , respectively (Table 1). This approach to interpreting the data is consistent with guidance for conducting risk assessment, discussed above, as it captures a high percentile of mass adhered for all individuals, and ensures that meaningful data from a complex data set is not overlooked.

Siciliano et al. conducted a laboratory study of soil adherence to human hands for 13 agricultural soils and 17 soils from a brownfield site.²⁴ In this study, volunteers crumbled a handful of soil, excess soil was lightly brushed off, the hand was washed with a dilute nitric acid solution, and particle sizes were determined with a particle size analyzer. For these two types of soils, the mean particle sizes adhering were reported as 34 and 105 μm , for agricultural soils and brownfield soils, respectively. When hand-washing trials were conducted in the field on 19 residents of Iqaluit, Canada (age range of 4 to 62 years with a median age of 23 years), the mean particle size adhering was 36 μm . Figure 2 from Siciliano et al. is reproduced herein as Figure 3a (data reproduced by digitizing the original figure) and are also presented as cumulative percent of soil mass adhering (Figure 3b). The bimodal distribution in Figure 3a for the agricultural soils and brownfield soils suggests a large degree of variability between the different soils tested (curves are aggregation of data for 13 and 17 different soils, respectively). For applications to risk assessment, preference is given to the data collected in the field, which resulted in 50th and 90th percentile values of 40 and 130 μm , respectively (Table 1). Less weight is given to the laboratory derived values, which generally produced larger soil particles adhering to hands (the agricultural and brownfield soils had 90th percentile values of 370 and 760 μm , respectively; Table 1). Siciliano et al. recommend, based on these data, that soils should be sieved to <45 μm for evaluating human exposures to contaminants in soil. In reviewing the study data, we find that selection of the <45 μm value would exclude nearly 50% of the mass adhered to the hands of residents. This is not consistent with our goal to identify the particle size fraction that captures the bulk of the soils contributing to ingestion exposures, while excluding, to the extent possible, those particle sizes that are not relevant for exposure.

The most recent paper to evaluate the particle sizes of soils adhering to hands, Bergstrom et al., conducted a laboratory study on the hand adherence of particulates from nine geologic media derived from mining, smelting, and quarrying activities.⁴³ The mining and smelting samples were primarily collected from the banks and sand bars/beaches of rivers that had received mining and smelting wastes and thus likely contained tailings and slag, while the quarried materials were described as “gravel products”. As a result, these materials were distinctly different from typical soil and consisted primarily of very fine to very coarse sand. Each sample was sieved to four different size fractions (<63, 63–150, 150–250, and 250–2000 μm), and the mass of material and metals concentrations were determined for each fraction. Six volunteers actively handled each unfractionated medium under wet and dry conditions (wet conditions ranged from 3.5% to 14.7% moisture content, depending on the water holding capacity of the media, and dry conditions were <0.25% moisture

content). Subjects’ hands were washed with deionized water and the collected material was dried and analyzed for metals concentrations. Adhering particle sizes were not directly measured. Rather, proportions of adhering particle size fractions were estimated using a maximum likelihood estimation (MLE) technique. Fractions of adhering mass attributed to each size fraction were allowed to vary to minimize a function representing the difference between predicted and observed concentrations of metals in adhering media. Based on the MLE analysis, the authors report that greater than 60% of the adhered mass was <63 μm in the dry media (7 of 9 samples). In the trials with wet media, the <63 μm fraction was estimated to account for less than 25% of the adhered material (8 of 9 samples), and the largest particle size category (>150 μm) dominated the mass adhered for 7 of the 9 media tested. These results suggest that, particularly for the wet media, larger particles are preferentially adhering relative to the studies on soils discussed above. This may be due to the unique character of the materials tested and the fact they consisted primarily of relatively coarse materials.

The studies discussed above are summarized in Table 1, in terms of the type of study, the data reporting method, and the particle size cutoff that would account for 50% or 90% of the adhering mass. This last metric either could not be determined, or was not reported, for a number of the studies for various reasons, including (1) the authors did not report their results on the basis of mass adhering,³³ (2) the authors studied house dust, not soil,³⁵ (3) the authors did not fractionate their soils into sufficiently fine fractions to support this calculation,³⁸ and (4) the manner in which data were reported would not support this calculation.³⁹ The 50th and 90th percentile values are also not presented for Bergstrom et al. because the size of adhering particles was inferred from modeling and not directly measured, and because the authors caution that the media tested “are not conventional soils”.⁴³

DISTRIBUTION OF CONTAMINANTS IN SOIL AS A FUNCTION OF PARTICLE SIZE

If a contaminant is not evenly distributed across soil particle sizes, then preferential ingestion of a specific particle size fraction may either increase or decrease the mass of contaminant ingested for a given mass of soil ingested. For example, if a chemical is enriched in the fine fraction of soils and this fraction is preferentially ingested, then the mass of chemical ingested will increase relative to what would have been ingested if the chemical were evenly distributed in soil. There is an extensive body of literature regarding the enrichment of both organic and inorganic compounds in soils and a thorough review of this topic is beyond the scope of this paper. In general, the concentration of both organic and inorganic compounds is enriched in the fine fraction of soils,^{24,43–46} although site-specific exceptions occur. Unfortunately, most authors report only enrichment as a function of concentration, when reporting distributions in terms of both concentration and calculated mass would be more useful for overall evaluation of oral exposures. The distributions of organic and inorganic compounds in soil are dependent on the source of the contamination (e.g., size of contaminant particles released to soil) and the redistribution of the organic chemicals or inorganic elements into different sorption domains or mineral phases during weathering in the soil environment. The literature addressing this issue for PAHs is discussed in detail below.

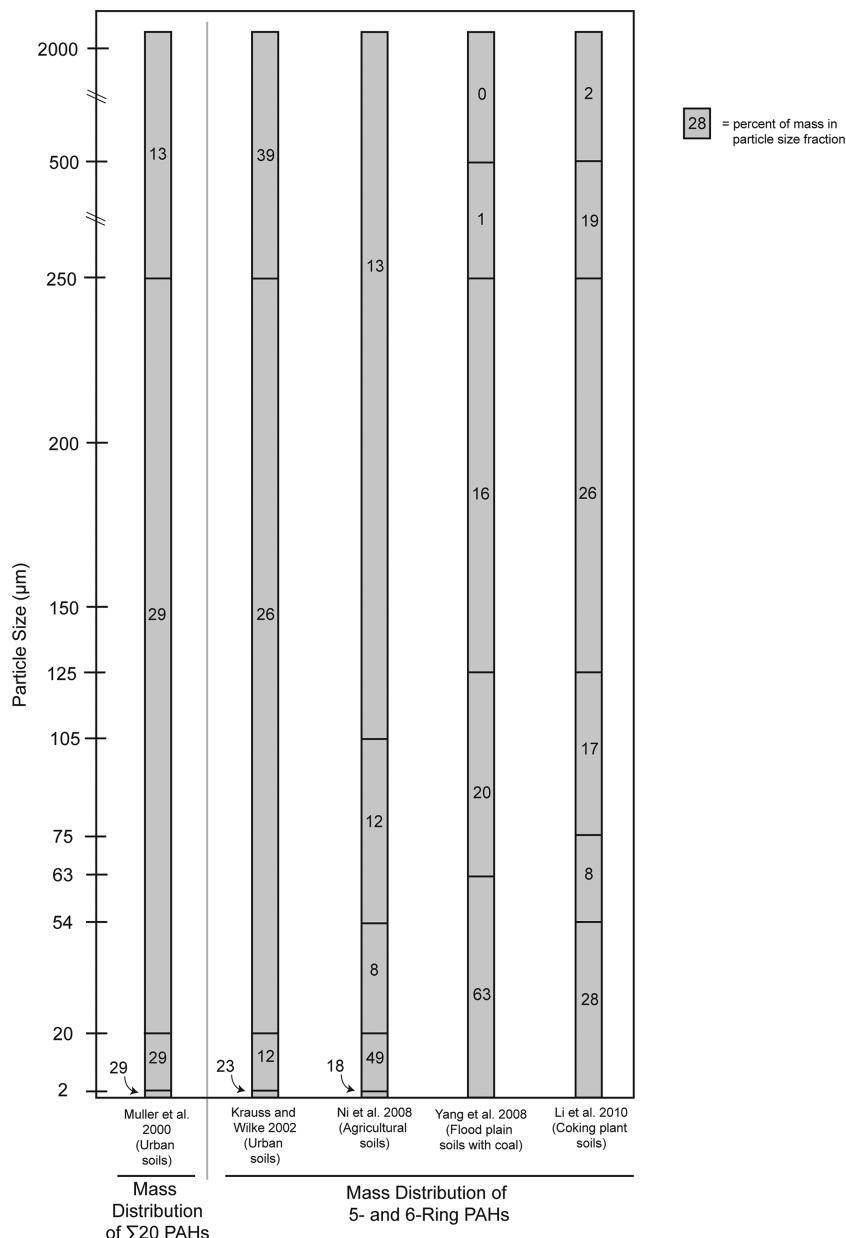


Figure 4. Distribution of the mass of PAHs in different soil particle size fractions, based on reanalysis of data from the five studies indicated.

■ DIFFERENTIAL BIOAVAILABILITY AS A FUNCTION OF PARTICLE SIZE AND GEOCHEMICAL MATRIX

Both the size and the chemical composition of an ingested particle can affect the oral bioavailability of organic and inorganic chemicals. This issue is reviewed in detail for inorganic chemicals in Ruby et al.⁴⁷ Basically, mineral forms that are more stable under acidic conditions (e.g., the stomach) yield lower oral bioavailability, and smaller particles yield greater bioavailability because dissolution occurs faster and more extensively during passage through the gastrointestinal tract. The morphology of the mineral phases, particularly the rinding or encapsulation of primary mineral phases by secondary alteration phases, will also impact the oral bioavailability of inorganic elements.⁴⁷

For hydrophobic organic chemicals (HOCs), there are fewer data on the factors that control oral bioavailability than there are for inorganic elements. It appears that the form in which the HOC enters a soil (e.g., matrix effects), the structure of the matrix particles (e.g., porosity), and the organic carbon–water

partition coefficient (K_{oc}) values of the different organic carbon phases in the soil (e.g., natural organic matter, kerogen, and black carbon forms such as soot and char) will determine the tendency of a soil to sequester HOCs.^{48,49} Studies indicate that differences of up to 2 orders of magnitude exist between the K_{oc} values of natural organic matter and black carbon forms in soil.⁴⁸ Based on this, we postulate that the extent and type of black carbon in soils will control the oral bioavailability of HOCs to humans. There is only one published study on the effects of black carbon on the oral bioavailability of an HOC in soil or sediment. Saghir et al. evaluated the ability of lampblack soot to reduce the oral bioavailability of hexachlorobenzene in soil when dosed orally to rats;⁵⁰ other studies that attempt to address this have only looked at total organic carbon as a variable effecting oral bioavailability. However, studies using ecological receptors (e.g., earthworms, benthic invertebrates) have demonstrated decreased HOC uptake from soils and sediments containing elevated levels of black carbon, coal, coke, kerogen, and biochar.^{48,51,52} The

differential oral bioavailability of PAHs as a function of particle size and geochemical matrix is discussed below.

■ CONSIDERATIONS SPECIFIC TO PAHS

The following analysis is specific to the selection of a particle size for oral bioavailability and bioaccessibility studies for PAHs in soils.

Consistent with the body of research on other contaminants, a variety of particle sizes has been used for oral bioavailability studies of PAHs in soils, ranging from $<100\text{ }\mu\text{m}$ to $<1000\text{ }\mu\text{m}$.^{14,53} A review of the literature regarding PAH bioaccessibility (i.e., *in vitro* testing) over the last 10 years (17 publications) reveals a pattern that is similar to that observed for oral bioavailability studies. Although $<250\text{ }\mu\text{m}$ was the size fraction most commonly used (seven publications), bioaccessibility data for four other particle size fractions have also been reported ($<2\text{ mm}$, $<1\text{ mm}$, $125\text{--}250\text{ }\mu\text{m}$, and $<45\text{ }\mu\text{m}$).^{46,54,56}

Distribution of PAHs among Soil Particle Size Fractions.

To accurately characterize oral exposures to PAHs in soils, it is important to understand how PAHs are distributed among the different particle size fractions. For example, if PAHs are present only in the finest particles, then exposure will occur only from ingestion of those fine particles. However, if PAHs are evenly distributed across all particle sizes that are ingested, then any of those particles will constitute an exposure.

A number of publications have evaluated the distribution of PAHs in soils as a function of particle size.^{45,46,57–61} Of these seven studies, only five report the data required to establish the distribution of PAHs as a function of mass (rather than just as a function of concentration) in surficial soils and are, therefore, the focus of our review. There are a similar number of publications that evaluate PAH distribution as a function of particle size in sediments. These papers are also not reviewed here because of the distinct nature of soils versus sediments.

A study by Muller et al. evaluated the distribution of PAHs as a function of soil particle size fraction in 10 urban surface soils from Bangkok, Thailand.⁵⁹ Each sample was separated into 4 size fractions: <2 , $2\text{--}20$, $20\text{--}250$, and $250\text{--}2000\text{ }\mu\text{m}$, and each fraction was analyzed for 20 PAHs ranging in size from 2 to 6 rings. Geometric mean concentrations of total PAHs, across all 10 samples, decreased in the following order: $2\text{--}20\text{ }\mu\text{m}$ (219 mg/kg) $> <2\text{ }\mu\text{m}$ (201 mg/kg) $> 20\text{--}250$ (139 mg/kg) $> 250\text{--}2000\text{ }\mu\text{m}$ (51 mg/kg). However, when these results are converted to a mass distribution, by correcting for the mass of soil in each size fraction of each sample, the geometric mean mass of total PAHs is found to be evenly distributed across the three smallest size fractions, with a distribution of $<2\text{ }\mu\text{m}$ (29% of total mass) = $2\text{--}20\text{ }\mu\text{m}$ (29%) = $20\text{--}250$ (29%) $> 250\text{--}2000\text{ }\mu\text{m}$ (13%) (Figure 4). For these soils, expressing PAH distribution on a mass basis shifts the distribution to a larger particle size fraction, relative to the distribution based on PAH concentrations. These authors did not report the concentrations of individual PAHs in different particle size fractions, so the mass distribution of carcinogenic (five- and six-ring) PAHs cannot be determined for this study.

Krauss and Wilcke studied the distribution of PAHs in 11 urban top soils from in and around the city of Bayreuth, Germany, and reported on the same 4 particle size fractions (<2 , $2\text{--}20$, $20\text{--}250$, and $250\text{--}2000\text{ }\mu\text{m}$) and for the same 20 PAHs as Muller et al.⁴⁵ The study samples represented a diversity of soil types and land uses, including a forested area, road-side, garden, alluvial grassland, agricultural soils, a landfill, and a former gasworks site. The authors report the concentrations of five- and six-ring PAHs, relative to the sum of all 20 PAHs (as a percent).

Using these data (interpolated from Figure 1a of the article) and the average distribution of soil mass in the different size fractions, the mass-distributions of five- and six-ring PAHs were calculated. On a concentration basis, the five- and six-ring PAHs were distributed relatively evenly across the four size fractions (range of 3.8–5.1 mg/kg). As result, the mass-based distribution was primarily influenced by soil texture (i.e., the distribution of mass in the different soil fractions) and yielded a result of $250\text{--}2000\text{ }\mu\text{m}$ (39% of total mass) $> 20\text{--}250\text{ }\mu\text{m}$ (26%) $> <2\text{ }\mu\text{m}$ (23%) $> 2\text{--}20\text{ }\mu\text{m}$ (12%) (Figure 4).

Ni et al. studied the distribution of PAHs as a function of soil size fractions for nine agricultural soils from Zhejiang province, China.⁶⁰ Each soil was separated into 5 size fractions: <2 , $2\text{--}20$, $20\text{--}54$, $54\text{--}105$, and $105\text{--}2000\text{ }\mu\text{m}$, and each fraction analyzed for the 16 U.S. EPA priority pollutant PAHs. The authors report the percent of soil mass in each particle size fraction for each soil, and also the average percent of five- and six-ring PAHs in each size fraction. From these data, the mass distribution of five- and six-ring PAHs was calculated for each of the five particle size fractions. These results indicate that the mass of five- and six-ring PAHs are predominantly in the clay ($<2\text{ }\mu\text{m}$) and fine silt ($2\text{--}20\text{ }\mu\text{m}$) fractions of these soils (total of 67% of mass; Figure 4). This outcome is influenced by both the soil texture and the concentrations in the different soil size fractions, because both of these variables span a wide range in these samples.

Yang et al. evaluated the distribution of PAHs in 16 river floodplain soils from the Mosel river in Germany that were known to be impacted by coal and coal-derived particles from coal mining and coking operations.⁶¹ Each soil was fractionated into 5 fractions: <63 , $63\text{--}125$, $125\text{--}250$, $250\text{--}500$, and $500\text{--}2000\text{ }\mu\text{m}$, and each fraction was analyzed for 19 PAHs ranging in size from 2 to 6 rings. When the geometric mean percent of five- and six-ring PAHs was calculated (data interpolated from Figure 4 of the article), as a function of total PAHs in each fraction, and was corrected by the mass of material in each size fraction, the mass distribution of five- and six-ring PAHs is $<63\text{ }\mu\text{m}$ (63%) $> 63\text{--}125\text{ }\mu\text{m}$ (20%) $> 125\text{--}250\text{ }\mu\text{m}$ (16%) $> 250\text{--}500\text{ }\mu\text{m}$ (1%) $> 500\text{--}2000\text{ }\mu\text{m}$ (0%) (Figure 4). It should be noted that the floodplain soils evaluated in this study were fine grained materials (59% of mass was $<63\text{ }\mu\text{m}$), and that, as with the Ni et al. study, the mass distribution of five- and six-ring PAHs was partially controlled by the soil texture. The authors noted a strong positive correlation between total PAH concentrations and black carbon (e.g., coal, $r^2 = 0.98$, $p < 0.005$) and concluded that the distribution of PAHs in these soils is largely controlled by the particle size distribution of coal and coal-derived particles, which are both the primary PAH sources to these soils and the geosorbents that will sorb any PAHs in the soils most strongly.

Li et al. reports on a study that evaluated the distribution of PAHs in 15 samples from a former coke oven plant in Beijing, China.⁵⁸ Each soil was separated into 6 size fractions (<50 , $50\text{--}75$, $75\text{--}125$, $125\text{--}250$, $250\text{--}500$, and $500\text{--}2000\text{ }\mu\text{m}$), and the concentrations of the 16 U.S. EPA priority pollutant PAHs were determined in each fraction. The results indicated (data interpolated from Figure 2 of article) that the geometric mean concentrations of the five- to six-ring PAHs were distributed relatively evenly across the $<50\text{ }\mu\text{m}$ and the $125\text{--}2000\text{ }\mu\text{m}$ size particles, with considerably lower concentrations in the $50\text{--}125\text{ }\mu\text{m}$ particles. When these data are corrected for the mass of soil in each size fraction, the mass-distribution of PAHs becomes $<50\text{ }\mu\text{m}$ (28%) $> 125\text{--}250\text{ }\mu\text{m}$ (26%) $> 250\text{--}500\text{ }\mu\text{m}$ (19%) $> 75\text{--}125\text{ }\mu\text{m}$ (17%) $> 50\text{--}75\text{ }\mu\text{m}$ (8%) $> 500\text{--}2000\text{ }\mu\text{m}$ (2%) (Figure 4).

4). As in the Yang et al. publication,⁶¹ the mass distribution of carcinogenic PAHs is controlled by the particle size distribution of the PAH source materials (coal tar and coal tar pitch in this case). The results also indicate that total PAH concentration in soils was strongly correlated with black carbon content ($r^2 = 0.92$) and less strongly with total organic carbon content ($r^2 = 0.73$).

Several trends emerge from the five studies reviewed above, despite varying particle size cutoffs used and the different data reporting approaches. Whether the data are reported for total PAHs, or for carcinogenic PAHs, particles up to 250 μm contain an appreciable mass of PAHs (Figure 4). Thus, particles up to 250 μm in size can contribute to oral exposures. In all of these studies, the soil texture is an important determinant of overall PAH mass distribution, because in most cases the concentrations of PAHs are relatively evenly distributed across the different size fractions. It is also clear that for sites with solid PAH source materials, the particle size of that source material will dictate the particles that contain the carcinogenic PAHs. Therefore, it is not necessarily correct to assume that PAHs will always be heavily enriched in the clay and silt fraction of soils.

Oral Bioavailability of PAHs from Soil as a Function of Particle Size. There is only one published study that addresses the effect of soil particle size on the oral bioavailability of PAHs from soil. Rozett et al. (published as an abstract only) studied the oral bioavailability of pyrene and genotoxic PAHs from one contaminated soil from a manufactured gas plant site.¹² The soil was fractionated into seven different particle size fractions ranging from <150 to <1000 μm , blended with different batches of rodent diet, and dosed to mice. The absorption of pyrene was quantified based on the urinary excretion of pyrene metabolites, and the absorption of genotoxic PAHs by the presence of DNA adducts in lung and forestomach tissue. The <150 μm soil size fraction produced the greatest excretion of pyrene metabolites and formation of adducts, relative to the coarse size fractions. As a result, the authors concluded that oral bioavailability of PAHs from soil is enhanced in the finest particle size fraction that they studied.

There is also only one published study of the solubility of PAHs in soil in a bench-scale “bioaccessibility test” from multiple soil particle size fractions. Siciliano et al.⁴⁶ evaluated two different soil particle sizes (<45 and <4000 μm) and found that the fraction of total PAHs extracted in this test was greater for the <4000 μm size fraction than for the <45 μm size fraction; however, this study evaluated only one particle size that is relevant to oral exposures, because a <4000 μm size fraction (particles up to fine gravel) is not expected to contribute to long-term incidental soil ingestion. From this data set, it is not possible to conclude whether the larger PAHs (five- and six-ring compounds that are the PAHs associated with carcinogenic activity) will consistently have higher or lower bioavailability in the fine fraction of soils relative to the coarser fractions of relevance.

Selection of a Soil Particle Size Fraction for PAH Bioavailability and Bioaccessibility Studies. The goal of this analysis is to identify the soil particle size fraction that best represents oral exposures due to hand-to-mouth transfer of particulate material, and then to select a particle size cutoff that provides the best representation of incidental oral exposures, for use in *in vivo* and *in vitro* experimental work. Because the fractionation occurring due to hand adherence of soil versus sieving creates different particle size distributions, it is not possible to select a sieve size that will produce a distribution

identical to hand-adhered particles for all soils. For example, for a clay loam soil, in which the soil mass is contained primarily in particles <50 μm , sieving with a 250 μm sieve would result in a particle size distribution similar to that which adheres to hands (there are not very many large particles to adhere to hands or to be sieved out). In contrast, sieving a sandy soil, in which the soil mass is contained primarily in larger particles (50–2000 μm) with a 250 μm sieve would result in a sample in which large particles are over-represented relative to what would adhere to hands (many large particles that would not adhere to hands pass through the sieve and are included in the sample).

Given that a number of studies on soil adherence to hands have recently emerged in the literature and that they report a range of results, a weight-of-evidence approach was taken for selecting a particle size fraction that would best represent soil exposure due to incidental ingestion. Because it is unknown (i.e., existing information is contradictory) whether PAH bioavailability will be greater from large or small particles (as discussed above), and also because the data indicate that significant mass of five- and six-ring PAHs may be present in soil particles up to 250 μm , it seems unwise to exclude a significant proportion of soil particles that would potentially be ingested. For these reasons, and to be consistent with risk assessment guidance for selecting high-end versus mean values for exposure parameters, we have selected the 90th percentile values for characterizing the mass of soils adhering to hands and contributing to ingestion exposures. In addition, we have given preference to the two studies that assess exposures by residents or children to soil under conditions of natural contact.^{24,42}

Based on these considerations, a size cutoff of 150 μm was selected as one that would include the bulk of particles adhering to hands while not overemphasizing large particulate material that would not be ingested. The 150 μm particle size captures 92% of the mass of soil adhering in both the Yamamoto et al. (Figure 2, population of children with the largest particles adhering)⁴² and in field trials reported by Siciliano et al. (Figure 3).²⁴ It also captures between 80% and 95% of the hand-adhered material in the Duggan and Inskip, Kissel et al., and Choate et al. studies (with the exception of the Kissel et al. wet soil for which a 150 μm particle size cutoff would capture only 45% of the hand adhered material) (Figure 1).^{34,40,41} The 150 μm cutoff would exclude about 30% and 50% of the mass reported by Siciliano for the agricultural and brownfield soil studies, respectively; however, in comparison to data from individuals studied in the field, those studies appear to have anomalously large particles adhering to hands. As a result, the 150 μm particle size cutoff would capture the bulk of the soil mass observed to be on the hands of children and adults, including both small and large particles, but does so without creating a sieving-induced bias toward larger particles than would generally adhere to hands.

■ FUTURE RESEARCH

For the purposes of assessing incidental oral exposures of children and adults to carcinogenic PAHs in soil, a definitive study of target soil particle sizes of relevance has yet to be conducted. Such a study would utilize both field and laboratory components (adherence to two- to three-year old children’s and adult hands in both settings) to understand the effect of age-dependent characteristics (physical and behavioral), and field versus laboratory studies, and to further assess differences in intersubject variability. The distribution of PAHs as a function of particle size in these soils would be determined, and reported on both a concentration and mass basis for individual PAHs in

different soil particle size fractions. Because published data on the distribution of PAHs in soil are limited, it would be useful to develop these data for a variety of soils that contain PAHs from different sources (e.g., soot from diesel exhaust, char from pyrolysis, coal tar and coal tar pitch from manufactured gas plant sites or coking facilities, and nonaqueous phase liquids such as diesel or fuel oil) and a range of soil textures.

The results reported by Sheppard and Evenden suggest that some fraction of the clay size material (<2 µm) that adheres to a hand is not ingested because it remains adhered to hands following hand-mouthing behavior in children.³⁹ Because the one study conducted to date reports a hand-to-mouth transfer efficiency of only 11 to 22%, depending on mouthing type activity (thumb sucking, finger mouthing, or palm licking),⁶² it is unclear whether the strong adherence of clay particles to hands is creating a particle size fractionation during hand-to-mouth transfer. A study of particle size fractionation during hand-to-mouth transfer would be a valuable addition to the understanding of the soil particle sizes contributing to incidental soil ingestion because no such study currently exists.

Although it may be tempting to further characterize the bioavailability of chemicals from different particle size fractions, the utility of such data would be limited: they may allow for a better understanding of the bioavailability data that have been reported to date, but such a retrospective evaluation likely has little merit given the other differences and limitations of the existing database on bioavailability. Moving forward, it does not matter what the bioavailability is from different particle sizes if the fraction used in the bioavailability study is the fraction that is being ingested. Therefore, future research would be best focused on determining the particle size range contributing to oral exposures. Based on the information presented above, a reasonable estimate of the upper range of the soil particle size that contributes to soil ingestion is 150 µm.

AUTHOR INFORMATION

Corresponding Author

*Phone: (720) 465-3314, ext. 14; fax: (303) 404-2945; e-mail: mruby@integral-corp.com.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was conducted in response to issues that arose while designing a study of the oral bioavailability of PAHs from soil on behalf of the Strategic Environmental Research and Development Program. The authors thank Dr. Naomichi Yamamoto for sharing his data on soil adherence to children's hands and the four anonymous reviewers whose comments and suggestions resulted in significant improvements to the manuscript.

REFERENCES

- (1) USEPA. *Guidance for Evaluating the Oral Bioavailability of Metals in Soils for Use in Human Health Risk Assessment*; OSWER 9285.7-80; U.S. Environmental Protection Agency: Washington, DC, 2007.
- (2) USEPA. *Exposure Factors Handbook*; EPA/600/R-090/052F; U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment: Washington, DC, 2011.
- (3) USEPA. *Mid-Atlantic Risk Assessment Regional Screening Table*. http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/index.htm (accessed Oct 18, 2012).

(4) Tsuji, J. S.; Benson, R.; Schoof, R. A.; Hook, G. C. Health effect levels for risk assessment of childhood exposure to arsenic. *Regul. Toxicol. Pharmacol.* **2004**, *39*, 99–110.

(5) NRC. *Risk Assessment in the Federal Government: Managing the Process*; Working papers; National Academy of Sciences, National Research Council, Committee on the Institutional Means for Assessment of Risks to Public Health, 1983.

(6) USEPA. *Risk Assessment Guidance for Superfund: Vol. 1 - Human Health Evaluation Manual (Part A)*; Interim Final; EPA/S40/1-89/002; U.S. Environmental Protection Agency, Office of Emergency and Remedial Response: Washington, DC, 1989.

(7) McConnell, E. E.; Lucier, G. W.; Rumbaugh, R. C.; Albro, P. W.; Harvan, D. J.; Hass, J. R.; Harris, M. W. Dioxin in soil: Bioavailability after ingestion by rats and guinea pigs. *Science* **1984**, *223*, 1077–1079.

(8) Lucier, G. W.; Rumbaugh, R. C.; McCoy, Z.; Hass, R.; Harvan, D.; Albro, P. Ingestion of soil contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) alters hepatic enzyme activities in rats. *Fundam. Appl. Toxicol.* **1986**, *6*, 364–371.

(9) Bonaccorsi, A.; di Domencio, A.; Fanelli, R.; Merli, F.; Motta, R.; Vanzati, R.; Zapponi, G. A. The influence of soil particle adsorption on 2,3,7,8-tetrachlorodibenzo-p-dioxin biological update in the rabbit. *Arch. Toxicol.* **1984**, No. Suppl 7, 431–434.

(10) Shu, H. P.; Teitelbaum, P.; Webb, A. S.; Marple, L.; Brunck, B.; Del Rossi, D.; Murray, F. J.; Paustenbach, D. Bioavailability of soil-bound TCDD: Dermal bioavailability in the rat. *Fundam. Appl. Toxicol.* **1988**, *10*, 335–343.

(11) Goon, D.; Hatoum, N. S.; Klan, M. J.; Jernigan, J. D.; Farmer, R. G. Oral bioavailability of "aged" soil-adsorbed benzo[a]pyrene (BaP) in rats. *Toxicologist* **1991**, *10*, 218.

(12) Rozett, K.; Singh, R.; Roy, T.; Neal, W.; Weyand, E. H. Bioavailability of chemical components of soil contaminated with manufactured gas plant residue. *Fundam. Appl. Toxicol.* **1996**, *30* (1), 324.

(13) Weyand, E. H.; Rozett, K.; Koganti, A.; Singh, R. Effect of soil on the genotoxicity of manufactured gas plant residue. *The Toxicologist* **1996**, *30* (1 (Part 2)), 321.

(14) Koganti, A.; Spina, D. A.; Rozett, K.; Ma, B.-L.; Weyand, E. H. Studies on the applicability of biomarkers in estimating the systemic bioavailability of polynuclear aromatic hydrocarbons from manufactured gas plant tar-contaminated soils. *Environ. Sci. Technol.* **1998**, *32* (20), 3104–3112.

(15) LaVelle, J. M.; Poppenga, R. H.; Thacker, B. J.; Giesy, J. P.; Weis, C.; Othoudt, R.; Vandervoort, C. Bioavailability of lead in mining wastes: An oral intubation study in young swine. *Chem. Speciation Bioavailability* **1991**, *3* (3/4), 105–148.

(16) USEPA. *Estimation of Relative Bioavailability of Lead in Soil and Soil-Like Materials Using in Vivo and in Vitro Methods*; OSWER 9285.7-77; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC, 2007.

(17) USEPA. *Estimation of Relative Bioavailability of Arsenic in Soil and Soil-Like Materials by in Vivo and in Vitro Methods*; USEPA Review Draft; U.S. Environmental Protection Agency, Region 8: Denver, CO, 2005.

(18) Maddaloni, M.; Lolacono, N.; Manton, W.; Blum, C.; Drexler, J.; Graziano, J. Bioavailability of soilborne lead in adults, by stable isotope dilution. *Environ. Health Perspect.* **1998**, *106* (Suppl 6), 1589–1594.

(19) Roberts, S. M.; Weimer, W. R.; Vinson, J. R. T.; Munson, J. W.; Bergeron, R. J. Measurement of arsenic bioavailability in soil using a primate model. *Toxicol. Sci.* **2002**, *67*, 303–310.

(20) Roberts, S. M.; Munson, J. W.; Lowney, Y. W.; Ruby, M. V. Relative oral bioavailability of arsenic from contaminated soils measured in the Cynomolgus monkey. *Toxicol. Sci.* **2007**, *95* (1), 281–288.

(21) Budinsky, R. A.; Rowlands, J. C.; Casteel, S.; Fent, G.; Cushing, C. A.; Newsted, J. L.; Giesy, J. P.; Ruby, M. V.; Aylward, L. L. A pilot study of oral bioavailability of dioxins and furans from contaminated soils: impact of differential hepatic enzyme activity and species differences. *Chemosphere* **2008**, *70*, 1774–1786.

(22) Finley, B.; Fehling, K.; Warmerdam, J.; Morinello, E. J. Oral bioavailability of polychlorinated dibenz-p-dioxins/dibenzofurans in industrial soil. *Hum. Ecol. Risk Assess.* **2009**, *15* (6), 1146–1167.

- (23) James, K.; Peters, R. E.; Laird, B. D.; Ma, W. K.; Wickstrom, M.; Stephenson, G. L.; Siciliano, S. D. Human exposure assessment: A case study of 8 PAH contaminated soils using in vitro digestors and the juvenile swine model. *Environ. Sci. Technol.* **2011**, *45*, 4586–4593.
- (24) Siciliano, S. D.; James, K.; Zhang, G.; Schafer, A. N.; Peak, D. Adhesion and enrichment of metals on human hands from contaminated soil at an arctic urban brownfield. *Environ. Sci. Technol.* **2009**, *43* (16), 6385–6390.
- (25) Hwang, Y.-H.; Bornschein, R. L.; Grote, J.; Menrath, W.; Roda, S. Environmental arsenic exposure of children around a former copper smelter site. *Environ. Res.* **1997**, *72*, 72–81.
- (26) BSB DOH. *The Butte-Silver Bow County Environmental Health Lead Study: Final Report*; Butte-Silver Bow County Department of Health: Butte, MT, 1992.
- (27) Bornschein, R.; Clark, S.; Pan, W.; Succop, P. Midvale Community Lead Study. *Chem. Speciation Bioavailability* **1991**, *3* (3/4), 149–162.
- (28) Aschengrau, A.; Beiser, A.; Bellinger, D.; Copenhafer, D.; Weitzman, M. The impact of soil lead abatement on urban children's blood lead levels: Phase II results from the Boston lead-in-soil demonstration project. *Environ. Res.* **1994**, *67*, 125–148.
- (29) Van Leeuwen, P.; Bornschein, R.; Clark, S. *Cincinnati Lead Soil Demonstration Project*; Hazardous Materials Conference; Hazardous Materials Institute: Greenbelt, MD, 1992.
- (30) USEPA. *Short Sheet: TRW Recommendations for Sampling and Analysis of Soil at Lead (Pb) Sites*; EPA 540-F-00-010, OSWER 9285.7-38; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC, 2000.
- (31) USEPA. *Short Sheet: IEUBK Model Soil/Dust Ingestion Rates*; EPA 540-F-00-007, OSWER 9285.7-33; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC, 1999.
- (32) USEPA. *Superfund Lead-Contaminated Residential Sites Handbook; Final*; OSWER 9285.7-50; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Lead Sites Workgroup: Washington, DC, 2003.
- (33) Duggan, M. J.; Inskip, M. J.; Rundle, S. A.; Moorcraft, J. S. Lead in playground dust and on the hands of schoolchildren. *Sci. Total Environ.* **1985**, *44*, 65–79.
- (34) Duggan, M. J.; Inskip, M. J. Childhood exposure to lead in surface dust and soil: A community health problem. *Public Health Rev.* **1985**, *13*, 1–54.
- (35) Que Hee, S. S.; Peace, B.; Clark, C. S.; Boyle, J. R.; Bornschein, R. L.; Hammond, P. B. Evolution of efficient methods to sample lead sources, such as house dust and hand dust, in the homes of children. *Environ. Res.* **1985**, *38*, 77–95.
- (36) Hunt, A.; Johnson, D. L.; Watt, J. M.; Thornton, I. Characterizing the sources of particulate lead in house dust by automated scanning electron microscopy. *Environ. Sci. Technol.* **1992**, *26* (8), 1513–1523.
- (37) Kniest, F. M. Settled house-dust and its aerosols, their importance for allergic patients. *J. Aerosol Sci.* **1991**, *22*, S827–S830.
- (38) Driver, J. H.; Konz, J. J.; Whitmyre, G. K. Soil adherence to human skin. *Bull. Environ. Contam. Toxicol.* **1989**, *43*, 814–820.
- (39) Sheppard, S. C.; Evenden, W. G. Ecosystem processes: Contaminant enrichment and properties of soil adhering to skin. *J. Environ. Qual.* **1994**, *23*, 604–613.
- (40) Kissel, J. C.; Richter, K. Y.; Fenske, R. A. Factors affecting soil adherence to skin in hand-press trials. *Bull. Environ. Contam. Toxicol.* **1996**, *S6* (5), 722–728.
- (41) Choate, L. M.; Ranville, J. F.; Bunge, A. L.; Macalady, D. L. Dermally adhered soil: 1. Amount and particle-size distribution. *Integr. Environ. Assess. Manage.* **2006**, *2* (4), 375–384.
- (42) Yamamoto, N.; Takahashi, Y.; Yoshinaga, J.; Tanaka, A.; Shibata, Y. Size distributions of soil particles adhered to children's hands. *Arch. Environ. Contam. Toxicol.* **2006**, *51*, 157–163.
- (43) Bergstrom, C.; Shirai, J.; Kissel, J. Particle size distributions, size concentration relationships, and adherence to hands of selected geologic media derived from mining, smelting, and quarrying activities. *Sci. Total Environ.* **2011**, *409* (20), 4247–4256.
- (44) Acosta, J. A.; Cano, A. F.; Arocena, J. M.; Martinez-Martinez, S. Distribution of metals in soil particle size fractions and its implications to risk assessment of playgrounds in Murcie City (Spain). *Geoderma* **2008**, *149* (1–2), 101–109.
- (45) Krauss, M.; Wilcke, W. Sorption strength of persistent organic pollutants in particle-size fractions of urban soils. *Soil Sci. Soc. Am. J.* **2002**, *66*, 430–437.
- (46) Siciliano, S. D.; Laird, B. D.; Lemeieux, C. L. Polycyclic aromatic hydrocarbons are enriched but bioaccessibility reduced in brownfield soils adhered to human hands. *Chemosphere* **2010**, *80*, 1101–1108.
- (47) Ruby, M. V.; Schoof, R.; Brattin, W.; Goldade, M.; Post, G.; Harnois, M.; Mosby, D. E.; Casteel, S. W.; Berti, W.; Carpenter, M.; Edwards, D.; Cragin, D.; Chappell, W. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ. Sci. Technol.* **1999**, *33* (21), 3697–3705.
- (48) Cornelissen, G.; Gustafsson, Ö.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; Van Noort, P. C. M. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **2005**, *39* (18), 6881–6895.
- (49) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Weber, W. J., Jr.; Westall, J. C. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **1997**, *31* (12), 3341–3347.
- (50) Saghir, S. A.; Bartels, M. J.; Budinsky, R. A., Jr.; Harris, E. E.; Clark, A. J.; Staley, J. L.; Chai, Y.; Davis, J. W. Effect of organic carbon content, clay type, and aging on the oral bioavailability of hexachlorobenzene in rats. *Environ. Toxicol. Chem.* **2007**, *26* (11), 2420–2429.
- (51) Ghosh, U.; Luthy, R. G.; Cornelissen, G.; Werner, D.; Menzie, C. A. In-situ sorbent amendments: A new direction in contaminated sediment management. *Environ. Sci. Technol.* **2011**, *45*, 1163–1168.
- (52) Gomez-Eyles, J. L.; Sizmur, T.; Collins, C. D.; Hodson, M. E. Effects of biochar and the earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements. *Environ. Pollut.* **2011**, *159* (2), 616–622.
- (53) Magee, B.; Anderson, P.; Burmaster, D. Absorption adjustment factor (AAF) distributions for polycyclic aromatic hydrocarbons (PAHs). *Hum. Ecol. Risk Assess.* **1996**, *2* (4), 841–873.
- (54) Sips, A. J. A. M.; Bruij, M. A.; Dobbe, C. J. G.; Van de Kamp, E.; Oomen, A. G.; Pereboom, D. P. K. H.; Rompelberg, C. J. M.; Zeilmaker, M. J. *Bioaccessibility of Contaminants from Ingested Soil in Humans: Method Development and Research on the Bioaccessibility of Lead and Benzo[a]pyrene*; Report 711701012/2001; RIVM, National Institute of Public Health and the Environment: Bilthoven, The Netherlands, 2001.
- (55) Holman, H.-Y. N.; Goth-Goldstein, R.; Aston, D.; Yun, M.; Kengsoona, J. Evaluation of gastrointestinal solubilization of petroleum hydrocarbon residues in soil using an in vitro physiologically based model. *Environ. Sci. Technol.* **2002**, *36* (6), 1281–1286.
- (56) Minhas, J. K.; Vasiluk, L.; Pinto, L. J.; Gobas, F. A. P. C.; Moore, M. M. Mobilization of chrysene from soil in a model digestive system. *Environ. Toxicol. Chem.* **2006**, *25* (7), 1729–1737.
- (57) Guggenberger, G.; Pichler, M.; Hartmann, R.; Zech, W. Polycyclic aromatic hydrocarbons in different forest soils: Mineral horizons. *Z. Pflanzenernahr. Bodenkd.* **1996**, *159*, 565–573.
- (58) Li, H.; Chen, J.; Wu, W.; Piao, X. Distribution of polycyclic aromatic hydrocarbons in different size fractions of soil from a coke oven plant and its relationship to organic carbon content. *J. Hazard. Mater.* **2010**, *176*, 729–734.
- (59) Müller, S.; Wilcke, W.; Kanchanakool, N.; Zech, W. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in particle-size separates of urban soils in Bangkok. *Thailand Soil Sci.* **2000**, *165* (5), 412–419.
- (60) Ni, J. Z.; Luo, Y. M.; Wei, R.; Li, X. H. Distribution of polycyclic aromatic hydrocarbons in particle-size separates and density fractions of typical agricultural soils in the Yangtze River Delta, east China. *Eur. J. Soil Sci.* **2008**, *59*, 1020–1026.
- (61) Yang, Y.; Ligouis, B.; Pies, C.; Grathwohl, P.; Hofmann, T. Occurrence of coal and coal-derived particle-bound polycyclic aromatic

hydrocarbons (PAHs) in a river floodplain soil. *Environ. Pollut.* **2008**, *151*, 121–129.

(62) Kissell, J. C.; Shirai, J. H.; Richter, K. Y.; Fenske, R. A. Empirical investigation of hand-to-mouth transfer of soil. *Bull. Environ. Contam. Toxicol.* **1998**, *60*, 379–386.