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## Effects of Soil and Aging on the Dermal Bioavailability of Hydrocarbons and Metals in Soil

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# EFFECTS OF SOIL MATRIX AND AGING ON THE DERMAL BIOAVAILABILITY OF HYDROCARBONS AND METALS IN THE SOIL: DERMAL BIOAVAILABILITY OF SOIL CONTAMINANTS

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## ABSTRACT

The potential health risk from exposure to chemically contaminated soil can be assessed from bioavailability studies. The aims of this research were: (a) to determine the dermal bioavailability of contaminants in soil for representatives of hydrocarbon classes of chemicals, namely, volatiles (toluene) and polycyclic aromatic hydrocarbons [benzo(a)pyrene] as well as for heavy metals (arsenic, mercury, and nickel, respectively, as arsenic acid, mercuric chloride, and nickel chloride); and (b) to examine the effects of soil matrix and chemical sequestration in soil with time (“aging”) on their bioavailability. In vitro flow-through diffusion cell studies were performed utilizing dermatomed male pig skin and radioactive chemicals to measure dermal penetration. The volatility of toluene reduced the amount of the chemical available for dermal penetration. With soil contact, the penetration of toluene was 16-fold to 21-fold less than toluene without soil. Benzo(a)pyrene penetration was decreased faster in soil with a higher clay content than one with more organic carbon. The soil matrix as well as aging in soil lowered the dermal penetration of the metal compounds by 95-98%. This study provided evidence that the bioavailability from dermal exposure to the chemicals examined can be significantly reduced by soil matrix and aging in soil.

Keywords: soil contaminants, dermal exposure, bioavailability effects

## 1. INTRODUCTION

The potential health risk from exposure to chemically contaminated soil is related to the amount of chemical that desorbs from soil and which is subsequently absorbed by the

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body, i.e. bioavailability. Soil properties such as organic carbon content, clay content, particle size, and pH affect chemical sorption and desorption processes, and thus may have significant impacts on the bioavailability of chemicals from soils (NEPI, 2000a; Pu et al., 2004). Another major determinant of bioavailability is chemical aging in soil (Alexander, 2000). Chemical aging in soil is the movement of chemicals from the surface of soil particles into less accessible sites with time (Linz and Nakles, 1997; Reid et al., 2000). The mechanisms for chemical aging are not fully understood, however, it has been proposed that hydrophobic chemicals can partition into the solid phase of soil organic matter as well as become entrapped within soil nanopores where they may be retained and become less accessible (Steinberg et al., 1987; Brusseau et al., 1991; Pignatello and Xing, 1996).

Most of the emphasis on chemical aging has been on organic chemicals in soil (Steinberg et al., 1987; Scribner et al., 1992; Hatzinger and Alexander, 1995; Kelsey et al., 1997; Roy and Singh, 2001; Abdel-Rahman et al., 2006). However, metals also age in soil (Lock and Janssen, 2003; Turpeinen et al., 2003). The interaction of metals with soil is more complex than organic chemicals with soil. Metals may be associated with many components of soil in various ways (ion exchange, adsorption, precipitation, complexation) or be present in the structure of minerals (Balasoiu et al., 2001). The mechanism for the aging of metals in soil may be different than for organic compounds (Alexander, 2000). Proposed mechanisms include penetration into the mineral lattice of soil and diffusion through intraparticle pores (Yin et al., 1997). Intraparticle diffusion may lead to the sequestration of metals within microporous solids, such as hydrous iron, aluminum, and manganese oxides, and some types of organic matter (Axe and Trivedi, 2002).

Compared to other routes of exposure to soil contaminants (oral, inhalation), the dermal route may not always be the most important route, but it can contribute significantly to total exposure. Because human skin comprises more than 10% of total body mass and 1.8 m<sup>2</sup> of body surface (Roberts and Walters, 1998; USEPA, 2001), it has the potential to absorb significant quantities of chemicals into the body during daily activities. A chemical that cannot penetrate skin may be limited to local toxic effects on the skin but if it readily penetrates skin and enters the circulation, it may have systemic effects. Therefore, it is necessary to know the capacity of a chemical for dermal absorption in order to assess its overall potential risk (Mattie et al., 1994).

The studies reported in this paper were conducted to assess the dermal bioavailability of contaminants in soil for representatives of hydrocarbon classes of chemicals, namely, volatiles (toluene) and polycyclic aromatic hydrocarbons [benzo(a)pyrene] as well as for heavy metals (arsenic, mercury, and nickel, respectively, as arsenic acid, mercuric chloride, and nickel chloride). Toluene is a very common contaminant of soil in the vicinity of hazardous waste sites. The chemical has been identified in 84% of the soil samples collected from National Priorities List (NPL) hazardous waste sites where it was detected in environmental media (ATSDR, 2000a,b). Toluene is not usually found in high concentrations in surface soils due to loss through volatilization, but it remains in subsurface soils (NEPI, 2000a). Dermal contact with toluene can remove protective epidermal lipids from skin. The defatting action of the chemical alters the barrier properties of skin (Boman and Maibach, 2000) and can cause irritation and cell damage (Shibata et al., 1994; USEPA, 1983).

PAHs are ubiquitous contaminants of soil and are derived from the incomplete combustion of organic materials (ATSDR, 1995; Loehr and Webster, 1997). New Jersey has the most sites with PAH contamination. Soil concentrations of benzo(a)pyrene (BaP) in NPL sites in the state range between 1.1 and 8,100 mg/kg (ATSDR, 1995; ATSDR, 1999a). BaP has been classified as a probable carcinogen in humans. Dermal exposure to BaP can cause skin irritation with rash and/or burning sensations. Repeated exposure can produce skin changes such as thickening and darkening (NJDHSS, 1998).

Natural levels of arsenic in soil usually range from 1 to 40 mg/kg, although much higher levels may be found in mining areas, at waste sites, near high geological deposits of arsenic-rich minerals, or from pesticide applications (ATSDR, 2000c). In soil, arsenic can occur as arsenates ( $\text{AsO}_4^{3-}$ ) or arsenites ( $\text{AsO}_2^-$ ), with trivalent arsenites being more toxic than the pentavalent arsenates. At high redox potential and acidic pH, the arsenate species predominates in soil. However, at low redox potential and alkaline pH, the arsenite species is more significant (Masscheleyn et al., 1991; Peters et al., 1996; Balasoiu et al., 2001). Direct dermal contact with inorganic arsenicals may cause skin irritation and contact dermatitis. Usually the effects are erythema and swelling which may progress to papules, vesicles, or necrotic lesions in extreme cases (Holmqvist, 1951; ATSDR, 2000c).

Most of the mercury in soil is generally present as the divalent species. Compounds such as  $\text{HgCl}_2$  and  $\text{Hg}(\text{OH})_2$  as well as inorganic Hg (II) compounds complexed with organic anions can be formed in soil (Andersson, 1979). Levels of Hg (II) as high as 123,000 mg/kg have been detected in heavily contaminated sites such as Berry's Creek in New Jersey (Lipsky et al., 1981; Yin et al., 1997). However, from 0.2 to 19,500 mg/kg of mercury (species not specified) have also been found in urban NPL sites in New Jersey (ATSDR, 1999b). Contact with skin of all species of mercury can result in systemic toxicity (Hostynek et al., 1998). The predominant skin reaction to mercury is erythematous and pruritic skin rashes (ATSDR, 1999b).

Analytical methods for nickel usually do not distinguish the form of nickel in soil. Therefore, the total amount of nickel is reported but the nature of the nickel compounds is often not known. Nickel or nickel compounds have been detected in soils near NPL sites at concentrations ranging from 2 to 10,522  $\mu\text{g}/\text{kg}$ . Soil concentrations of nickel up to 9,000 mg/kg have also been found near industries that extract nickel from ore (ATSDR, 2005). Allergic contact dermatitis is the most common adverse health effect of nickel in humans. Approximately 10-20% of the population is sensitive to nickel and once an individual is sensitized, even minimal contact with the metal may cause a reaction in some sensitive individuals (ATSDR, 2005).

The relative contribution of the soil matrix and chemical aging in soil on the dermal bioavailability of the representative chemicals were determined so that the impact of the results on health risk could be evaluated. Bioavailability was assessed by measuring dermal penetration. Specifically: (a) the dermal penetration of each of the chemicals aged in soil was compared to the respective pure chemicals (without soil) and to the chemicals added freshly to soil; (b) the effects of soil composition (percent sand, clay, organic matter) on dermal penetration were examined.

## 2. MATERIALS AND METHODS

### 2.1 Chemicals

[Ring-U-14C] toluene, with a specific activity of 16.4 mCi/mmol and radiochemical purity of 95%, was purchased from Amersham Corp., Arlington Heights, IL. Prior to use, the radioisotope was diluted with non-radioactive toluene (HPLC grade, Aldrich Chemical Co., Milwaukee, WI). Benzo(a)pyrene, generally labeled with tritium [3H(G)], having a specific activity of 50 Ci/mmol and radiochemical purity of 99%, was obtained from American Radiolabeled Chemicals, Inc., St. Louis, MO. Arsenic in the form of arsenic acid ( $H_3AsO_4$ ) (Sigma/Aldrich Chemical Co., St. Louis, MO) was used as a carrier and labeled with arsenic-73 (Los Alamos National Laboratory, Los Alamos, NM). Mercury-203 as mercuric chloride (3.1 mCi/mg specific activity, radiochemical purity > 99%) was a product of Amersham Pharmacia Biotech, Inc., Piscataway, NJ. Nickel-63 as nickel chloride (12.6 mCi/mg specific activity, 99.9% radiochemical purity) was obtained from New England Nuclear Life Science Products, Boston, MA.

### 2.2 Soils

Studies were conducted on two different soils that are representative of soil types widely distributed in the United States (USDA, 1972; 1977). The Atsion soil consists of 90% sand, 8% silt, 2% clay, 4.4% organic matter; has a pH of 4.2; and was collected from the Cohansey sand formation near Chatsworth in south central New Jersey. The Keyport soil contains 50% sand, 28% silt, 22% clay, 1.6% organic matter; has a pH of 5; and was collected from the Woodbury formation near Moorestown in southwestern New Jersey. Soil particle size distribution was as follows: Atsion soil = 50-100  $\mu m$  (22.2%), 100-250  $\mu m$  (76.3%), > 250  $\mu m$  (1.5%); Keyport soil = 50-100  $\mu m$  (17%), 100-250  $\mu m$  (65.3%), 250-500  $\mu m$  (13.6%), > 500  $\mu m$  (4.1%). Soil analyses were performed by the Soil Testing Laboratory at Rutgers Cooperative Extension Resource Center, Rutgers University, New Brunswick, NJ. Organic matter content was measured by a modified Walkley and Black (1934) dichromate oxidation method.

### 2.3 Chemical Aging in Soil

Individual chemicals were added to each of the soils that were previously autoclaved and hydrated to 11% (w/w) with sterile distilled-deionized water. This is the maximum amount of water that could be used to lightly moisten the soils without there being an excess of water when each chemical was added to the soils. Toluene was added to soil at a concentration of 72 mg chemical/g soil (sum of labeled and unlabeled toluene). The final concentration of 3H-BaP tracer (400 ng/g soil) together with unlabeled BaP was 1.67 mg/g soil. For the metal compounds, there were 83, 5.4, and 2.4  $\mu g/g$  soil, respectively, for arsenic acid, mercuric chloride, and nickel chloride. After each chemical was mixed thoroughly with the soils to ensure uniform distribution of chemical, treated soils were added to Teflon-sealed vials and aged in the dark at room temperature for three months.

## 2.4 Animal Model

Whole pig skin was obtained from the costo-abdominal areas of euthanized (40-60 lb) male Yorkshire pigs (Cook College Farm, Rutgers University, New Brunswick, NJ). The pig has been widely accepted as an animal model for studying human percutaneous absorption of a large variety of chemicals under various experimental conditions (Bartek et al., 1972; Reifenrath and Hawkins, 1986) because of the well documented histological (Monteiro-Riviere and Stromberg, 1985), physiological, biochemical, and pharmacological similarities between pig skin and human skin (Qiao and Riviere, 2000). Skin was transported to the laboratory in ice-cold HEPES buffered (25 mM) Hank's balanced salt solution (HHBSS), pH 7.4, containing gentamycin sulfate (50 mg/l) (Collier et al., 1989) after which it was immediately prepared for diffusion cells according to Bronaugh and Stewart (1985).

## 2.5 In Vitro Dermal Penetration Studies

Excised skin was cut to a thickness of 200  $\mu\text{m}$  with a dermatome (Padgett Electro-Dermatome Model B, Padgett Instruments Inc., Kansas City, MO) and circular pieces were mounted into Teflon flow-through diffusion cells (Crown Bio Scientific, Inc., Somerville, NJ). The exposed skin surface area (0.64  $\text{cm}^2$ ) was maintained at a temperature of 32°C. The dermal side of each skin sample was perfused with HHBSS containing 10% fetal bovine serum (Sigma/Aldrich) at a flow rate of 3 ml/h and aerated continuously with oxygen (Collier et al., 1989). Each chemical was applied separately to the stratum corneum surface of the skin either alone in 5  $\mu\text{l}$  of vehicle (acetone for BaP, ethanol for the metals), immediately after the addition of 30 mg of soil, or after aging in 30 mg of each of the two soils. The chemical doses/ $\text{cm}^2$  of skin surface area were: BaP (78  $\mu\text{g}$ ), arsenic acid (3.9  $\mu\text{g}$ ), mercuric chloride (253 ng), and nickel chloride (112.5 ng). After skin was treated and diffusion cells were capped, charcoal tubes (SKC Inc., Eighty-Four, PA) attached to the upper chambers of the diffusion cells, trapped any toluene volatilizing from the skin surface. Volatilization of toluene that occurred during soil treatment, during the aging process, and skin treatment, decreased the amount of the toluene dose that was available for dermal penetration. Toluene losses were detected by measuring radioactivity in glacial acetic extracts of charcoal as well as non-aged and aged chemical in soil. Volatilization losses of the toluene dose were very high and varied between the treatment groups (90% for pure toluene, 64–66% for freshly spiked soils, and 94–95% for aged soils). The maximum amount of toluene that was available for dermal penetration in each treatment was the fraction of the initial dose that remained after volatilization. Therefore, the available toluene doses were 337  $\mu\text{g}/\text{cm}^2$  of skin for pure toluene; 1210 and 1159  $\mu\text{g}/\text{cm}^2$ , respectively, in freshly spiked Atsion and Keyport soils; and 180 and 218  $\mu\text{g}/\text{cm}^2$ , respectively, for toluene in aged soils.

Receptor fluid (perfusate) was collected in scintillation vials containing 10 ml of Formula-989 liquid scintillation cocktail (Packard Instruments Co., Inc., Meriden, CT) up to 16 h postdosing. After 16 h of exposure to chemical alone or in soil, loosely adsorbed chemical was washed from the surface of the skin with soap and water (once with 1 ml of a 1% aqueous soap solution and twice with 1 ml of distilled-deionized water). Skin samples were completely solubilized in Solvable (Packard) for 8 h at 50°C to determine the amount of radioactivity remaining in skin. Radioactivity in all samples was counted

by liquid scintillation spectrometry (LS 7500, Beckman Instruments, Inc., Fullerton, CA). Sample quench was corrected by using the H-ratio method.

## 2.6 Statistical Analysis

All data were reported as the mean + standard error of the mean (SEM). Statistical differences between treatment groups were determined by one-way analysis of variance (ANOVA) with Scheffe's test except for differences between the soils which were determined by Student's independent t-test. The level of significance was  $p < 0.05$ .

## 3. RESULTS

The dermal penetrations of the chemicals are reported in Tables 1 and 2 as total penetrations. Total penetration represents the sum of chemical penetrating into receptor fluid and the amount in skin that potentially can penetrate into receptor fluid with time (Chu et al., 1996). Percent total penetration equals: (the amount of the initial dose that penetrated skin divided by the amount of the initial dose applied to skin) X 100 for all chemicals except for toluene. For toluene, the percent total penetration equals: (the amount of the available dose that penetrated skin divided by the amount of the available dose applied to skin) X 100. Tables 1 and 2 show that contact with either Atsion or Keyport soils for a short time (16 h) significantly decreased the total penetration of each chemical versus their pure counterparts.

Table 1. Effects of Time in Atsion Soil on the Dermal Penetration of Hydrocarbon or Heavy Metal Compounds

Chemicals	Pure	Freshly Spiked	Aged
Toluene	92.8 ± 4.5 <sup>a</sup>	5.9 ± 0.8 <sup>b</sup>	3.9 ± 0.5 <sup>b</sup>
Benzo(a)pyrene	76.0 ± 3.2	8.5 ± 0.9 <sup>b</sup>	3.7 ± 0.5 <sup>b</sup>
Arsenic	44.6 ± 2.8	10.0 ± 1.6 <sup>b</sup>	1.5 ± 0.3 <sup>b,c</sup>
Mercury	66.3 ± 4.2	37.8 ± 3.6 <sup>b</sup>	3.3 ± 0.9 <sup>b,c</sup>
Nickel	57.9 ± 2.2	11.5 ± 1.0 <sup>b</sup>	2.8 ± 0.3 <sup>b,c</sup>

<sup>a</sup>Percent total penetration (mean ± SEM) = (amount of available dose that penetrated skin divided by amount of available dose applied to skin) X 100 for toluene. For the other chemicals, available dose is replaced by initial dose. For each chemical, n = 8-14 replicates per treatment from three pigs.

<sup>b</sup>Significantly different from pure chemical ( $p < 0.05$ , ANOVA)

<sup>c</sup>Significantly different from chemical in freshly spiked Atsion soil ( $p < 0.05$ , ANOVA)

Although the available dose of toluene in the freshly spiked soils was higher than for pure toluene, the total penetration of non-aged toluene in Atsion and Keyport soils was only 5.9% and 4.5%, respectively. Three months aging in the soils further reduced the total penetration of each chemical compared to chemical in freshly spiked soil, however, the difference was only significant for the three metals. In spite of the fact that the dose was lower for toluene aged in the two soils than in the freshly spiked soils, aging did not significantly reduce the total penetration of toluene relative to the total penetration of toluene in the freshly spiked soils.

*Table 2. Effects of Time in Keyport Soil on the Dermal Penetration of Hydrocarbon or Heavy Metal Compounds*

Chemicals	Pure	Freshly Spiked	Aged
Toluene	92.8 ± 4.5 <sup>a</sup>	4.5 ± 0.6 <sup>b</sup>	2.6 ± 0.4 <sup>b</sup>
Benzo(a)pyrene	76.0 ± 3.2	3.5 ± 0.5 <sup>b</sup>	1.8 ± 0.2 <sup>b</sup>
Arsenic	44.6 ± 2.8	6.0 ± 0.8 <sup>b</sup>	0.8 ± 0.1 <sup>b,c</sup>
Mercury	66.3 ± 4.2	39.8 ± 4.2 <sup>b</sup>	2.5 ± 0.2 <sup>b,c</sup>
Nickel	57.9 ± 2.2	12.4 ± 2.0 <sup>b</sup>	1.8 ± 0.5 <sup>b,c</sup>

<sup>a</sup>Percent total penetration (mean ± SEM) = (amount of available dose that penetrated skin divided by amount of available dose applied to skin) X 100 for toluene. For the other chemicals, available dose is replaced by initial dose. For each chemical, n = 8-14 replicates per treatment from three pigs.

<sup>b</sup>Significantly different from pure chemical (p < 0.05, ANOVA)

<sup>c</sup>Significantly different from chemical in freshly spiked Keyport soil (p < 0.05, ANOVA)

Although the individual data for the receptor fluid and skin are not presented in the tables, it should be noted that very small quantities of each chemical (< 0.5% of the initial/available dose) penetrated into the receptor fluid for all BaP and metal treatments as well as for toluene aged in both soils. For pure toluene, 11.1% of the available dose was detected in the receptor fluid. This amount decreased significantly to 2.8% and 2%, respectively, in the freshly spiked Atsion and Keyport soils. From 92% to greater than 99% of the total penetration of the chemicals was due to the amount of chemical found in skin except for the following treatments: pure toluene (88%), toluene in freshly spiked Atsion (52%) and Keyport (56%) soils, and arsenic aged in Keyport soil (75%). The remainder of the initial/available dose that did not penetrate skin for each treatment was found in the skin wash (data not shown). From 7–57% of the initial/available dose was detected in the skin wash for the pure chemicals. As less soil-sorbed chemical penetrated skin than pure chemical, quantities of chemical in the skin wash increased to 59–99% of the initial/available dose.

When comparisons of the total penetration were made between the soils for each chemical (Table 3), it was determined that total penetration was significantly lower in the Keyport than in the Atsion soil for freshly spiked BaP and arsenic as well as for aged BaP, arsenic, and nickel.

*Table 3. Impact of Soil Type on the Dermal Penetration of Hydrocarbon or Heavy Metal Compounds*

Chemicals	Fresh Atsion	Fresh Keyport	Aged Atsion	Aged Keyport
Toluene	5.9 ± 0.8 <sup>a</sup>	4.5 ± 0.6	3.9 ± 0.5	2.6 ± 0.4
Benzo(a)pyrene	8.5 ± 0.9	3.5 ± 0.5 <sup>b</sup>	3.7 ± 0.5	1.8 ± 0.2 <sup>c</sup>
Arsenic	10.0 ± 1.6	6.0 ± 0.8 <sup>b</sup>	1.5 ± 0.3	0.8 ± 0.1 <sup>c</sup>
Mercury	37.8 ± 3.6	39.8 ± 4.2	3.3 ± 0.9	2.5 ± 0.2
Nickel	11.5 ± 1.0	12.4 ± 2.0	2.8 ± 0.3	1.8 ± 0.5 <sup>c</sup>

<sup>a</sup>Percent total penetration (mean ± SEM) = (amount of available dose that penetrated skin divided by amount of available dose applied to skin) X 100 for toluene. For the other chemicals, available dose is replaced by initial dose. For each chemical, n = 8-14 replicates per treatment from three pigs

<sup>b</sup>Significantly different from chemical in freshly spiked Atsion soil (p < 0.05, Student's independent t-test)

<sup>c</sup>Significantly different from chemical aged in Atsion soil (p < 0.05, Student's independent t-test)

#### 4. DISCUSSION

Both soils were equally effective in decreasing the dermal penetration of toluene regardless of the time that the chemical was in the soils. Batch equilibrium experiments performed by Tell and Uchrin (1991) to determine the sorption of toluene in the organic components of the Atsion soil identified humic acid as the prime organic sorption component. Since the Atsion soil contained three times more organic matter than the Keyport soil, it was expected that the total penetration of toluene would have been significantly lower in the Atsion soil than in the Keyport soil. However, toluene that is released to soil tends to volatilize quickly. Although the rate of volatilization from soil depends on temperature, humidity, and soil type, under typical conditions, more than 90% of the toluene in the upper soil layer volatilizes to air within 24 h (Thibodeaux and Hwang, 1982; Balfour et al., 1984). Volatilization losses as high as 95% for toluene decreased the amount of chemical that was available for dermal penetration in this study, indicating that the volatility of toluene was the predominant factor in reducing the dermal penetration of the chemical. With soil contact, the dermal penetration of toluene was 16-fold to 21-fold less than toluene without soil.

Lipophilic compounds such as BaP have a tendency to form reservoirs of the chemical in skin (Chu et al., 1996) as was observed in the present study. The formation of a dermal reservoir of BaP is important because of the ability of skin enzymes to biotransform BaP to a carcinogenic metabolite (Scribner, 1985; Ng et al., 1992). While most of the applied BaP dose was detected in skin, only 0.2% of the initial dose was found in receptor fluid after pure treatment; decreasing to 0.1% after chemical aging in either soil. Roy and Singh (2001) showed that as a result of 110 days of chemical aging in a coal tar contaminated field soil, 50% less coal tar BaP penetrated human abdominal skin sections into receptor fluid compared to freshly spiked 3H-BaP. Yang et al. (1989) and Wester et al. (1990) also reported significant reductions in dermal bioavailability when BaP was sorbed to soil but their studies did not include chemical aging. In general, it is difficult to make direct comparisons between present and previous dermal penetration studies because of differences in experimental conditions (e.g., source of skin, soil composition, receptor fluid, chemical concentration).

For BaP, surface adsorption was faster in the Keyport soil than in the Atsion soil. The adsorption of BaP onto the Atsion soil was evidenced by the 89% decrease in total penetration for freshly spiked BaP. Then, sequestration of BaP in the Atsion soil occurred with time ("aging"). This was reflected in the further reduction in total penetration (95%) after aging in the Atsion soil. In contrast, surface adsorption was greater in the Keyport soil since the decrease in the total penetration of BaP in freshly spiked Keyport soil was equal to that after aging in the Atsion soil. Furthermore, the total penetration of BaP in the Keyport soil (freshly spiked or after aging) was significantly lower than in freshly spiked Atsion soil and after aging in the Atsion soil. Most likely this was due to the 10-fold higher percentage of clay in the Keyport soil than in the Atsion soil. Clays, which typically have high surface areas, can enhance sorption through weak physical interactions and can impede chemical mass transfer due to clay aggregation and clay interlayers (Ake et al., 2001; Pu et al., 2004). Although organic matter acts primarily as a partition medium, mineral matter acts as an adsorbent for organic chemicals in soil (Karickhoff et al., 1979; Gschwend and Wu, 1985; Haderlein and Schwarzenbach, 1993; Chiou et al., 2000). Therefore, with increasing organic matter content and sometimes

clay content, retention of an organic chemical increases and the rate of release decreases, potentially decreasing overall chemical availability (Pu et al., 2004).

Skin is a critical organ of arsenic toxicity. Because of the affinity of arsenic for sulfhydryl groups, it can accumulate in skin (Hostynek et al., 1993) and penetrate slowly into the systemic circulation after exposure ends (Dutkiewicz, 1977). In the present study, soil decreased the total penetration of arsenic (mainly due to the amount of chemical in the skin reservoir). Iron, manganese, and aluminum oxides; clay content; and organic matter content are soil constituents that are strongly related to arsenic sorption (Galba and Polacek, 1973; Thanabalasingam and Pickering, 1986; Yan-Chu, 1994; Balasoju et al., 2001). However, soils with a higher clay content have been shown to retain more arsenic than soils with a lower clay content (Woolson and Kearney, 1973; Elkhatib et al., 1984). This was evidenced in the current study where the total penetration of arsenic in freshly spiked soil and after aging were lower in the Keyport soil than in the Atsion soil.

The decrease in the total penetration of mercury was similar in the two soils. Yin et al. (1997) showed that organic matter was the principal component of soil that was responsible for the resistance of divalent mercury to desorption from soil in their studies on three sandy loams and a stony loam. From the investigations by Andersson (1979), it was concluded that the only effective sorbent for inorganic mercury in acidic soils (pH < 4.5-5) is the organic material, but iron oxides and clay minerals may become more effective in neutral soils (pH > 5.5-6). Since both soils in the present study are acidic (pH 4.2 and 5), it is suggested from Andersson (1979) that even a small amount of organic matter (1.6% in the case of the Keyport soil) is very effective in sorbing significant quantities of mercury.

Soil pH is an important property of soil in the sorption of nickel. When King (1988) examined the ability of 13 soils (pH range 3.9-6.5) to retain metals, he determined that with increasing pH (differences as little as 0.2 units), nickel retention increased substantially in their study. Soil pH and to a lesser extent, clay content and the amount of hydrous iron and manganese oxides, most influenced nickel sorption in batch adsorption experiments by Anderson and Christensen (1988) on 38 different agricultural soils. In the nickel study reported here, the higher pH as well as the clay content of the Keyport soil most likely were factors in decreasing the total penetration of nickel in that soil compared to the Atsion soil.

The soil load (47 mg/cm<sup>2</sup>) that was used in these studies was based on soil adherence values reported in the literature (10-3 to 102 mg/cm<sup>2</sup>) which depended on soil properties, occupational and recreational activities, and different parts of the body (Kissel et al., 1996, 1998; Holmes et al., 1999). However, Yang et al. (1989), Duff and Kissel (1996), and Roy and Singh (2001) showed that only chemical in the monolayer of soil that is in direct contact with the skin surface is likely to be absorbed by skin. Monolayers of 3-9 mg/cm<sup>2</sup> were reported by those investigators and their studies showed that increasing the soil load decreased the percent of the applied dose of chemical absorbed. However, the soil loading that will achieve a monolayer is dependent on the particle size distribution of the soil being tested (Driver et al., 1989; NEPI, 2000b). For example, a soil load of 40 mg/cm<sup>2</sup> was used in Wester et al.'s (1993) studies on sodium arsenate in soil. Their studies showed a total penetration of 0.8% from soil on human cadaver skin and a dermal bioavailability of 3.2-4.5% in monkeys. Because the soil particle sizes were very large

(180-300  $\mu\text{m}$ ) in their studies, the soil loading was only slightly higher than a monolayer (Duff and Kissel, 1996) Particles less than 150  $\mu\text{m}$  in diameter have been shown to have greater adherence to skin than larger size fractions (Driver et al., 1989; NEPI, 2000b). For the two soils used in the studies reported here, only 17-22% of the soil particles have an arithmetic mean particle size diameter less than 150  $\mu\text{m}$ . This suggests that monolayer coverage was slightly exceeded. With a lower soil load, the dermal penetration of the studied chemicals may be a little higher.

Another factor that must be considered in addition to the soil load is the amount of chemical applied per unit area of skin. Although there were no significant differences in the percutaneous absorption of arsenic between a trace dose of arsenic in soil ( $4 \times 10^{-5} \mu\text{g}/\text{cm}^2$ ) and a higher dose ( $0.6 \mu\text{g}/\text{cm}^2$ ) in Wester et al.'s (1993) study in monkeys, the penetration rate of pure mercuric chloride through human skin in vitro was shown by Wahlberg (1965) to be concentration dependent.

## 5. CONCLUSIONS

Health risk assessments are often based on exposure to the total concentration of a chemical in a contaminated site. The total concentration is usually determined by rigorous extraction procedures such as acid digestion, sonication, or Soxhlet extraction to remove the chemicals from soil (USEPA, 1986, 1992; Tang et al., 1999). This approach can result in an overestimation of risk because when humans are exposed to contaminated soil, only a fraction of the total concentration (the bioavailable fraction) may be absorbed into the systemic circulation. The data presented in this paper highlight the need to incorporate bioavailability data into the health risk assessment of exposure to contaminated soils. The overall conclusion from this study is that soil decreased the dermal bioavailability of the organic chemicals and heavy metal compounds examined. Moreover, differences in soil composition and residence time in soil produced significant quantitative differences in bioavailability. However, further experiments should be performed at lower soil loads and additional concentrations to determine the effects of the soil layer thickness and the amount of chemical per unit area of skin on dermal penetration.

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