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Development of a Biokinetic Model to Evaluate Dermal Absorption of Polycyclic Aromatic Hydrocarbons from Soil

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ABSTRACT

The high carcinogenic potency of polycyclic aromatic compounds often results in the dermal pathway indicating significant risk to human health at sites with contaminated soils, resulting in the establishment of conservative, risk-based remediation goals. The sorptive properties of soil sequester chemical contaminants, making them less available for uptake by receptors. Recent studies of desorption from soil indicate that PAHs follow a nonlinear desorption pattern that can be estimated by two phases: a rapid, followed by a slow, desorbing fraction. In this work, we adapt a fugacity-based model to evaluate the availability of polycyclic aromatic hydrocarbons (PAHs) from soil to human skin. Incorporating two-site desorption kinetics into the fugacity model renders a less available fraction of chemical in soil for absorption, decreasing predicted dermal uptake. We explore the impacts to dermal bioavailability of removing the "fast-desorbing" fraction of chemical from the soil. The model predicts uptake within a factor of two when compared with experimental data on dermal uptake. Soil moisture and soil loading rates emerge as potential limiting variables; however, the model is most sensitive to the size of the fast desorbing fraction of chemical in soil.

Key Words: fugacity model, dermal absorption, bioavailability, two-site kinetics, uptake fraction.

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I. INTRODUCTION

Restoration of sites with contaminated soils often relies on human health and environmental risk assessment to establish remediation goals. A class of contaminants frequently found in hydrocarbon-contaminated soils are polycyclic aromatic hydrocarbons (PAHs). PAHs are byproducts of combustion processes and can be found in coal tar, petroleum refinery sludges, as well as in most urban environments. Many PAHs are considered human carcinogens. Because of their potency and ubiquity in the environment (Menzie *et al.* 1992), PAHs often contribute greatly to total site risk, in some cases becoming risk drivers, and therefore, significantly affecting the cost of soil remediation.

Current methods for estimating human health risk associated with exposure to PAHs in soil rely on conservative assumptions about the exposure to and availability of these compounds from laboratory studies, and do not account for possibility that site-specific soil conditions limit the availability of compounds. The U.S. Environmental Protection Agency (USEPA) (2001) draft guidance suggests the use of a dermal absorption factor for PAHs based on the results of an *in vivo* study (Wester *et al.* 1990) in which the dermal absorption of benzo(*a*)pyrene from soil was 13 ± 3%. The risk to human health due to dermal exposure to chemicals in soil according to these methods may be overestimated.

Further, efforts to remediate PAH-contaminated soils are fraught with difficulties due to their reticence in aged soils. Resources expended to remediate compounds in soil beyond levels that pose a risk to public health or the environment may be better spent on reducing greater sources of risk. Current risk estimation methods generally do not consider reduced availability in their calculations.

An understanding of the effects of sequestration on uptake can lead to better estimates of risk. In this work, we incorporate recent findings on the desorption characteristics of PAHs in soil into an investigative tool to evaluate the potential impact of soil characteristics on human uptake of PAHs from soil through dermal exposure.

A. Chemical Characteristics

Due to their low solubility in water and high affinity for organic carbon, PAHs tend to accumulate in soil. Karickhoff (1984) and Means *et al.* (1980) have demonstrated that PAH-sorption to soils is linear and can be predicted from the chemical-specific octanol water partition coefficient, K_{ow}. However, others have reported that desorption of compounds in soil is nonlinear and exhibits a "hockey stick" effect (Northcott and Jones 2001; Loehr and Webster 1996; Alexander 1995; Pignatello 1990a,b). This "hockey stick" effect is reflective of nonlinear desorption, which can be approximated in two stages, a fast and slow phase (Cornelissen *et al.* 1997; Huang and Weber 1997; Luthy *et al.* 1997; Young and Leong 1997; Linz 1996; Weissenfels *et al.* 1992). PAHs have a tendency to bind to the soil such that remediation and microbial degradation of contaminated soils may be incomplete (Erickson *et al.* 1993), indicating that PAHs in the "slow" phase may not completely desorb.

Although PAHs are considered semivolatile, their concentration in air is significantly lower than in soil, particularly for the three and four ring compounds considered carcinogenic by USEPA (USEPA, 1993). Therefore, the important di-

rect human exposure pathways to PAHs in soil are through incidental soil ingestion and dermal absorption. PAHs are lipophilic, meaning they prefer lipids to water. When skin becomes exposed to PAH-contaminated soil, the PAHs are absorbed into the skin due to the attraction of PAHs to the lipids in the skin.

Some studies have found that certain PAHs can become bound to the skin, and are metabolized to the toxic dihydrodiol form (Ng *et al.* 1991). However, passive diffusion through the stratum corneum is likely to be the main pathway for absorption of PAHs into human skin. In this work, we focus on the effect of the kinetics of PAH release from soil, rather than human metabolic pathways, on the rate of dermal uptake of PAHs. In doing so, we assume the entire dermally absorbed compound is potentially available for metabolism in the body.

II. FUGACITY MODEL

Fugacity relates the partial pressure of a chemical in one medium to that of the same chemical in another medium. The concept of fugacity can be applied to estimate the amount of contaminant in a soil matrix that would be absorbed by the skin under various conditions (Duff and Kissel 1996; McKone and Howd 1992; Mackay 1991; McKone 1990). Fugacity models have also been used to define a limiting soil layer thickness beyond which dermal absorption does not occur (Duff and Kissel 1996) and to estimate chemical transfer from the soil matrix to the skin (McKone and Howd 1992; McKone 1990). In this paper, we adapt McKone and Howd's (1992) model to evaluate dermal absorption of PAHs from soil.

A. The McKone and Howd Model

The fugacity model divides the soil matrix into soil solids, moisture, and vapor. These three compartments are related by mass transfer coefficients, K_p, which predict the fraction of the chemical that will be transferred between each phase of the soil matrix. A soil-skin mass transfer coefficient is then used to predict the amount of the chemical that is expected to be absorbed by the skin.

The compartment-specific mass transfer coefficients are calculated based on the thickness of the soil layer on the skin, diffusion rate of the chemical through the soil, the thickness of the boundary layer into which the chemical is diffusing (*i.e.,* air, water, or skin), and the fugacity capacities of the compartments involved (McKone and Howd 1992). The mass transfer coefficients are combined to determine the overall uptake fraction of chemical from the soil into the skin.

The general equation for the uptake fraction is (McKone and Howd 1992):

$$UF_{skin} = \left(\frac{K_p(soil,skin)}{K_p(soil,skin) + K_p(soil,air)} \right) * \left[1 - \exp(-b * ET) \right]$$

where	UF_{skin}	=	uptake fraction of chemical into the skin	(unitless)
	K_p(soil,skin)	=	overall mass transfer coefficient from soil through	(cm/hr)

		skin/soil layer	
K_p(soil,air)	=	overall mass transfer coefficient from soil through soil/air layer	(cm/hr)
b	=	inverse of chemical residence time on skin	(1/hr)
ET	=	exposure time	(hr).

The uptake fraction is the amount of chemical absorbed into the skin relative to the total amount of chemical available in the soil for uptake. The overall mass transfer coefficients are rates at which chemicals move from one compartment to another. The chemical residence time on the skin is a measure of the length of time the chemical in the soil matrix remains on the skin, and the exposure time is the length of time that the skin is exposed to the contaminated soil matrix.

B. Adaptation of Model

To evaluate the effects of nonlinear desorption kinetics of compounds from soil, we modified the McKone and Howd's (1992) model with respect to soil to air transfer, soil to water transfer, and chemical-soil desorption characteristics. Figure 1 shows the compartments and mass transfer coefficients employed in this adaptation. In using this model, we assume a single event exposure to soil that results in an application of soil to the skin that remains for a period of time of typically 8 or 24 hours, before being washed off or otherwise removed.

1. Soil to Air Mass Transfer

The mass transfer from soil to air in McKone and Howd's (1992) model assumes an arbitrary air layer above the soil matrix to which the contaminant can also partition. In a bounding analysis we found that uptake of chemical into the skin is driven solely by the size of this air layer. The use of this arbitrary air layer thickness reduces the uptake fraction for the skin by several orders of magnitude. Because the model is sensitive to the thickness of the air layer, we assume the air layer occurs only within the soil matrix, at a thickness equal to the air porosity of the soil, and the boundary layer excluded.

2. Soil to Water Mass Transfer

The transfer from soil to water is not considered a separate compartment in McKone and Howd's (1992) equation. For semivolatile chemicals, such as PAHs, this pathway may significantly affect dermal absorption. Therefore, in our model, we modified the uptake equation to account for soil-water transfer:

$$UF_{skin} = \left(\frac{K_p(soil,skin)}{K_p(soil,skin) + K_p(soil,air) + K_p(soil,water)} \right) * \left[1 - \exp(-b * ET) \right]$$

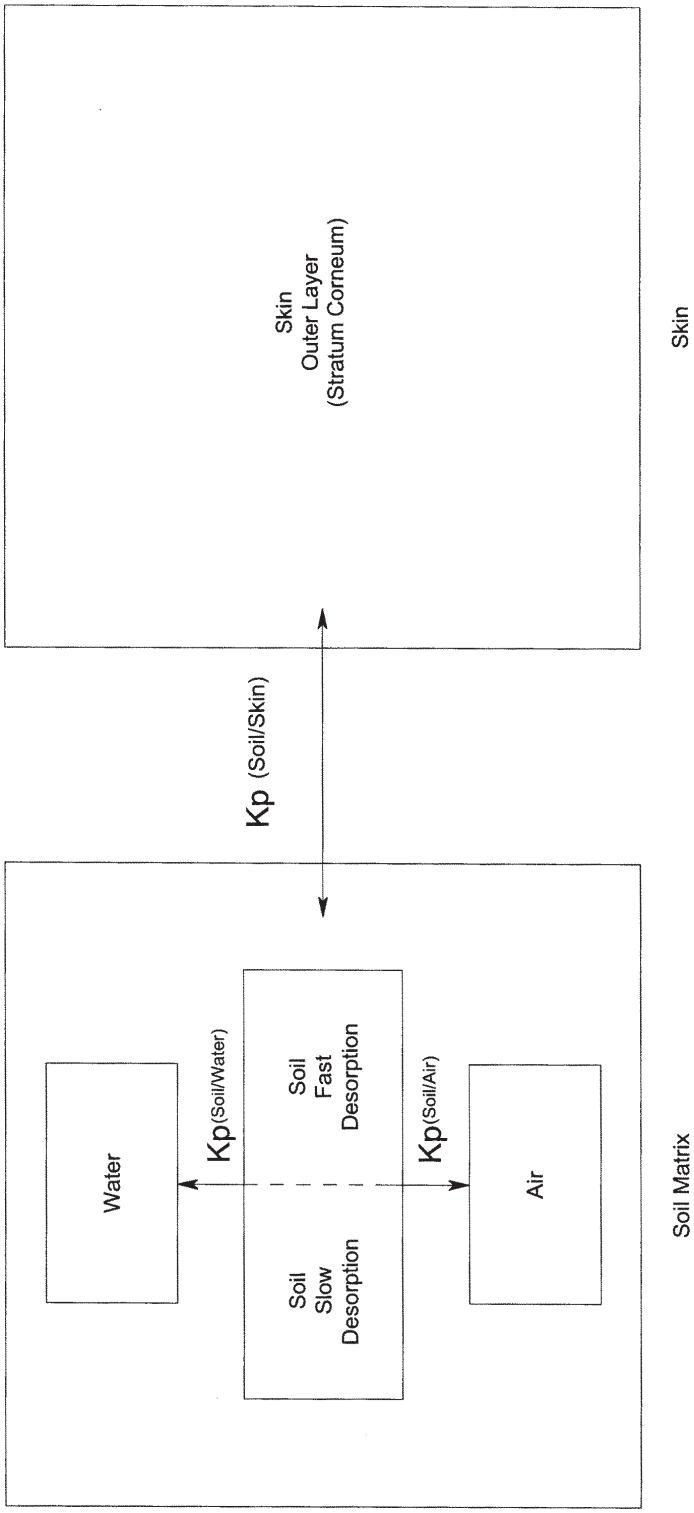

Figure 1. Fugacity model incorporating two-site kinetics. Two-site model.

This modification allows us to assess the importance of soil-water transfer of contaminants of concern relative to dermal uptake, as well as the impacts of soil moisture content on contaminant availability. The K_p(soil, water) is calculated by:

$$K_p(soil, water) = \left[\frac{\delta_{soil}}{2D_{soil}} + \frac{\delta_{wat}Z_{soil}}{D_{wat}Z_{wat}}\right]^{-1}$$

where	K_p(soil,water)	=	overall mass transfer coefficient from soil through soil/water layer	(cm/hr)
	δ_{soil}	=	soil layer thickness	(cm)
	D_{soil}	=	chemical-specific diffusion coefficient through soil	(cm^2/hr)
	Z_{soil}	=	chemical-specific fugacity capacity of the soil	(mol/mL-Pa)
	δ_{wat}	=	water layer thickness	(cm)
	D_{wat}	=	chemical-specific diffusion coefficient through water	(cm^2/hr)
	Z_{wat}	=	chemical-specific fugacity capacity of the water.	(mol/mL-Pa)

3. Chemical Desorption from Soil

The fugacity model, as described thus far, relies on the assumption that the partitioning of chemicals from soil to skin follows a linear relationship (Karickhoff 1984), such that whatever fraction of chemical that is not bound to the soil's organic carbon is available for uptake (McKone and Howd 1992):

$$K_{D,soil} = K_{oc}f_{oc}$$

where	$K_{D,soil}$	=	chemical-specific partition coefficient from soil to skin	(mL/g)
	K_{OC}	=	chemical-specific partition coefficient from soil to organic carbon	(mL/g)
	f_{OC}	=	fraction organic carbon in soil.	(unitless)

K_{oc} is oftentimes based on the octanol-water partition coefficient, K_{ow} (Karickhoff 1984). We reject this approach, however, because it masks the true effects of soil organic carbon content on uptake. It assumes octanol to be an organic carbon surrogate, when in fact organic carbon and octanol do not have similar sorptive capabilities. The relationship between K_{oc} and K_{ow} may not be predictive for semivolatile compounds, such as PAHs (Karickhoff 1984). K_{oc} values can vary over several orders of magnitude depending on the nature of organic matter in soil (Krauss and Wilcke 2001; Lucking *et al.* 2000; Kögel-Knabner *et al.* 2000). Further-

more, using K_{ow} as the basis for soil to skin partitioning does not allow us to evaluate the effects of soil organic carbon on dermal absorption, because the effect will appear linear for every compound. Instead, we rely on literature reported values of K_{oc}.

Brusseau and Rao (1989) suggest the following relationship between the partition coefficient, K_p, and the first order decay constant of the chemical, k:

$$\log k = 0.301 - 0.668 \log K_p$$

where	k	=	chemical-specific first order decay constant	(1/hr)
	K_p	=	chemical-specific partition coefficient.	(mL/g)

However, the wide range in the values of k and K_p reported by Brusseau and Rao (1989), resulting from the choice in experimental techniques used to determine either parameter shows that this relationship cannot be relied upon for general predictions of uptake. Therefore we consider non-linear desorption of PAHs as an alternative.

4. Two-Phase vs. One-Phase Kinetics

In McKone and Howd's (1992) model, uptake is predicted based on the overall mass transfer of chemical between the soil, air, and skin compartments according to first-order desorption kinetics. The model assumes transfer from soil occurs uniformly, and that PAHs desorb linearly with respect to time according to their mass transfer coefficients.

However, the desorption of PAHs from the soil matrix has been demonstrated to decrease nonlinearly with time (Northcott and Jones 2001; Reeves'*et al.* 2001; Cornelissen *et al.* 1997; Young and Leong 1997). Initially, a large quantity of PAHs is rapidly released from the soil. Following the initial rapid release of PAHs, a slower desorption rate is observed. This observation is often referred to as the "hockey-stick" effect. Taking into account this non-linear desorption kinetics is likely to impact the predicted uptake of PAHs into the skin. In this work, we incorporate nonlinear kinetics into the fugacity-based uptake fraction equation to evaluate the potential effect on the dermal absorption of PAHs from soil.

With the above exceptions, all equations were as published in McKone and Howd (1992). Chemical parameters were obtained from Mackay *et al.* (1992). Unless published, we assumed a soil organic carbon content of 1%, soil bulk density of 1.5 g/cm^3, 15% soil moisture content, and total porosity of 30% (15% air filled porosity). Initial model runs indicate the uptake fraction is not overly sensitive to these parameters.

III. TWO-PHASE KINETICS

To address the observed nonlinear kinetic desorption process, we incorporate a two-site model for PAH desorption from the soil matrix into the fugacity-based

dermal absorption model. The two-site model is a simplification of the actual process of chemical sorption onto a heterogeneous medium such as soil. Recent reports on the nature of soil and organic matter sorptive mechanisms identify subregions of soil particles that represent different sorption and desorption capacities. Desorption kinetics for these various soil phases have been measured for several PAHs (Lucking *et al.* 2000; White and Pignatello 1999; Poerschmann and Kopinke 2001). Various models for describing the nonlinear desorption behavior of nonionic organic chemicals from soils have been proposed (*e.g.* Mulder *et al.* 2001; White and Pignatello 1999; Cornelissen *et al.* 1997; Johnson *et al.* 1995; Connaughton *et al.* 1993; Brusseau *et al.* 1991; Weber and Miller 1988).

While the current debate on appropriate representation of the nonlinear desorption process is unresolved, the two stage (fast, slow) approximation is generally accepted as a simplification, and provides a reasonable model for evaluating effects on dermal bioavailability. For example, Northcott and Jones (2001) report correlation coefficients in the range of 0.909 to 0.999 between their two-stage fitted model and experimental desorption data for three PAHs.

Several studies have measured the fraction of total sorbed compound in the labile versus the resistant phases of soil, and the different desorption rates between these two fractions in a variety of soils.

Northcott and Jones (2001) measured the rate of desorption and effect of soil aging of PAHs spiked onto sewage sludge-amended soils. Two stage desorption rate equation parameters were estimated by modifying an XAD resin extraction method by Carroll *et al.* (1994; cited in Northcott and Jones 2001). Parameters were estimated by nonlinear regression analysis in SPSS, and include the fraction in the fast desorbing or labile phase (F_{fast}), the fast desorbing rate constant, k_1, and the slow desorbing (resistant) fraction k_2 for pyrene, phenanthrene, and benzo(a)pyrene. While aging of soils produced little effect on phenanthrene and pyrene desorption rates, benzo(a)pyrene was released more slowly after 21 days of aging and beyond. The reported rates are specific to the soil and experimental setup, but are useful for evaluating the potential effects of nonlinear desorption on dermal bioavailability.

In a study of the effect of chemical aging on oral bioavailability, Reeves *et al.* (2001) measured desorption rate constants (F_{fast}, k_{fast}) for phenanthrene, pyrene, and benzo(a)pyrene in coal tar-amended unaged and aged soils. Desorption was measured by the method of Cornelissen *et al.* (1997) using Tenax TA beads; no significant differences were observed between unaged and aged soils for the measured parameters.

In a recent study to quantify the desorption-resistant fraction of phenanthrene-contaminated soils, supercritical CO_2 extraction was used to experimentally determine the F_{slow}, k_{fast} and k_{slow} constants for phenanthrene in four different soils of varying properties (Young and Leong 1997). Soil samples were spiked and then allowed 30 days contact time. CO_2 was flushed through the soil mixture, and then removed at certain temperatures (50°C and 150°C) and time steps using a commercial supercritical fluid extraction unit. The extracted solvent was then analyzed for phenanthrene content. Because of the elevated temperature and solvent used (supercritical CO_2 in the study as opposed to water in real world situations), these two-stage kinetic values may not be representative of desorption at ambient temperatures or other solvents, such as water.

Table 1 shows some kinetic rate parameters from the three studies used to evaluate the model. The studies reflect desorption measurements of different sources of PAHs in different soils by different techniques, however, provide the parameters needed for evaluating the effects of nonlinear desorption from soil on dermal bioavailability in a fugacity model. Two of the studies also reported the effect of soil aging, by measuring changes in rates over time. No significant changes in desorption rates over time were found. The fast- and slow-desorbing fractions and kinetic constants vary with compound and soil type. However, for the purpose of evaluating the effect of soil properties on dermal uptake of chemicals, these data are useful, as long as the results are interpreted as relative, not absolute dermal uptake fractions.

To evaluate the effect of complex desorption kinetics for PAHs in aged soil, we use the two-site model to represent the effect of non-linear desorption of PAHs from soil.

Figure 1 demonstrates how two-phase desorption kinetics are incorporated into the fugacity model. The two-site model has three additional fitting parameters: the fraction of chemical in the "fast" desorption phase, F_{fast}, and the kinetic rate constants for both the "fast" and""slow" desorbing fractions, k_{fast} and k_{slow} (Cornelissen et al. 1997; Young and Leong 1997). These parameters are combined to model desorption from the soil matrix from both the fast and slow desorbing regions. The fraction of chemicals remaining in the soil at time, t, is described by:

Table 1. Two-phase kinetic soil desorption rate parameters.

SOIL	Chemical	Soil Organic Carbon[b] (%)	F_{Fast}[c] (unitless)	k_{fast}[d] (1/min)	k_{slow}[e] (1/min)	Source
Webster	Phenanthrene	2.97	0.176	0.236	8.43×10^{-4}	Young and Leong 1997
Chelsea	Phenanthrene	5.60	0.257	0.267	1.59×10^{-3}	Young and Leong 1997
Houghton	Phenanthrene	46.24	0.179	0.472	4.38×10^{-4}	Young and Leong 1997
Ohio Shale	Phenanthrene	2.44	0.713	0.205	6.88×10^{-3}	Young and Leong 1997
Silty Clay Loam	Phenanthrene	1.7	0.56 ± 0.28	0.44 ± 0.41	Not Reported	Reeves *et al.* 2001
Silty Clay Loam	Benzo(a)pyrene	1.7	0.24 ± 0.04	0.05 ± 0.24	Not Reported	Reeves *et al.* 2001
Sandy Loam	Phenanthrene (day 10)[f]	2.25	0.69	0.39	0.014	Northcott & Jones 2001
Sandy Loam	Benzo(a)pyrene (Day 53)[g]	2.25	0.1	0.04	0.0008	Northcott & Jones 2001

[a]Young and Leong (1997)
[b]Weber and Young (1997)
[c]rapidly desorbing chemical fraction
[d]decay constant for rapidly desorbing chemical fraction
[e]decay constant for slowly desorbing chemical fraction
[f]Study measured rates over 525 days. Parameters were not significantly different over time
[g]Measured rates over 525 days. Parameters did not change significantly after 53 days.

$$SF = \frac{m_t}{m_o} = F_{fast} \exp(-k_{fast} t) + F_{slow} \exp(-k_{slow} t)$$

where	SF	=	mass fraction of chemical sorbed in soil at time, t	(unitless)
m_t	=		mass of chemical remaining in soil at time, t	(g)
	m_t	=	mass of chemical initially in soil (t = 0)	(g)
	F_{fast}	=	mass fraction of chemical that rapidly desorbs from soil	(unitless)
	k_{fast}	=	decay constant of rapidly desorbing fraction	(1/hr)
	t	=	time	(hr)
	F_{slow}	=	mass fraction of chemical that slowly desorbs from soil	(unitless)
	k_{slow}	=	decay constant of slowly desorbing fraction.	(1/hr)

To incorporate the two-phase kinetics into the fugacity model, the uptake fraction is modified to account for a soil with both slow and fast desorbing sites:

$$UF_{skin} = \left(\frac{K_p(soil, skin)}{K_p(soil, skin) + K_p(soil, air) + K_p(soil, water)} \right) *$$

$$\left[1 - F_{fast} \exp(-k_{fast} * ET) - F_{slow} \exp(-k_{slow} * ET) \right]$$

where	UF_{skin}	=	uptake fraction of chemical into the skin	(unitless)
	K_p(soil,skin)	=	overall mass transfer coefficient from soil through skin/soil layer	(cm/hr)
	K_p(soil,air)	=	overall mass transfer coefficient from soil through soil/air layer	(cm/hr)
	K_p(soil,water)	=	overall mass transfer coefficient from soil through soil/water layer	(cm/hr)
	F_{fast}	=	mass fraction of chemical that rapidly desorbs from soil	(unitless)
	k_{fast}	=	decay constant of rapidly desorbing fraction	(1/hr)
	ET	=	exposure time	(hr)

F_{slow}	=	mass fraction of chemical that slowly desorbs from soil	(unitless)
k_{slow}	=	decay constant of slowly desorbing fraction.	(1/hr)

This, then, becomes the general equation that is used in our model to describe dermal absorption of PAHs from soil.

IV. RESULTS

The dermal absorption equation in Section III was entered into a Microsoft® Excel spreadsheet to enable the user to vary parameters such as exposure time, soil characteristics, and compound of interest. The predicted dermal uptake fraction is evaluated as a function of these input parameters.

A. Adapted Model vs. Published Model Results and Trends

A recent study measuring the flux over time of benzo(*a*)pyrene spiked into manufactured gas plant tar-contaminated soils in an *in vitro* flow through cell (Roy *et al.* 1998a) was used as a comparison study to test the plausibility the model. No existing studies are available to validate the model, because no studies have measured both dermal absorption and soil desorption rates.

Three different soils each at three different doses were applied, for a total of nine different experiments. Soils were sieved to less than 150 μm size particles. Each skin section was dermatomed to 350 μm thickness and sliced to a 3 by 3 cm portion. The skin was placed on a Franz diffusion cell and dosed for 144 hours. Twenty-five mg/cm^2 soil was applied to the dermatomed skin, an infinite (nonlimiting) dose condition. Benzo(*a*)pyrene was radiolabeled to measure dermal uptake of PAHs from human skin, which was obtained from cadavers (Roy *et al.* 1998a). B(a)P can be used as a surrogate for measuring dermal flux (*in vitro*) and estimating the dermal bioavailability of PAHs from coal tar derived mixtures. The uptake of B(a)P was within a factor of 2 for 40 out of 60 PAHs tested and within a factor of 3 for 55 out of 60 PAHs tested (Roy *et al.* 1998b). Radiolabeled B(a)P uptake was extrapolated for the model using this equation:

$$\text{Total B(a)P } (mg/cm^2) * \text{PADA} = \text{B(a)P uptake fraction}$$

where: PADA = Percent of Dermally Applied Dose.

The data do not allow a true model validation, because we are applying soil parameters from different soil types, in comparison to unknown soil types in the *in vitro* assays. Because the soil type was not reported, loamy sand and silt soil parameters were used as model inputs. The Utah State University Analytical Laboratory measured organic carbon content of eight of the soils. All known experimental parameters were used as model inputs, including: thickness of soil layer, time, fraction organic carbon, skin thickness, and skin area. Unknown parameters from the *in vitro* study which were estimated for modeling include: soil type, air filled porosity, water filled porosity, F_{fast}, and fast and slow desorption rates (k_{fast} and k_{slow}).

In Figure 2, the measured uptake fraction in the nine soils is plotted as triangles, and error bars representing two standard deviations of the mean uptake fraction are shown as a solid line. Two model runs with fitted two stage desorption parameters from Reeves *et al.* (2001) are shown in comparison to the measured range of benzo(a)pyrene uptake fractions from the nine soil experiments. Model predictions range from 10 to 34% uptake in 24 hours, within the range of measured dermal uptake for benzo(*a*)pyrene of 8 to 74% (eight of nine experiments had uptake below 30%).

Average model values are within the lower error bars of the range, while the maximum parameters are above the range of eight of nine measurements, but below the maximum measured. Neither data source provides adequate detail to directly compare the model prediction to measurement, but the overlapping range indicates potential for the model to be useful in evaluating the effect of soil parameters on uptake.

We also compared the predicted dermal uptake fraction from our model with published *in vitro* measurements of absorbed chemical from soil across human and rat skin. We did not have all of the soil parameters from these published experiments that were needed to enter into our model, and therefore made some assumptions about soil characteristics.

For each comparison, soil parameters that were not reported in the *in vitro* comparison studies were kept constant. Table 1 shows the comparison of published uptake fractions from three studies of percutaneous uptake of soil bound benzo(*a*)pyrene vs. model predicted values. As shown in Table 2, the model predicts uptake of benzo(*a*)pyrene to within a factor of 2 of the experimental data.

B. Model Parameter Sensitivity

The results of the adapted model also support the theory of a soil layer thickness beyond which the chemical is no longer available for uptake into the skin. Duff and Kissel (1996) describe the existence of a monolayer soil thickness beyond which dermal absorption is limited. Yang *et al.* (1989) found that the total uptake did not change in rats exposed to 9 mg/cm^2 benzo(*a*)pyrene in soil vs. 56 mg/cm^2, but the percent of dose absorbed decreased, supporting the theory that above a monolayer of soil coverage on skin, little transfer from soil to skin occurs. This finding was also noted during *in vitro* experiments with benzo(*a*)pyrene in which the soil layer thickness inhibited uptake below 10 mg/cm^2, but not above this thickness (Roy 2001). Figure 3 demonstrates the model also predicts this phenomenon with varied soil layer thickness.

As shown in Figure 4, the model also predicts that low soil moisture can limit uptake, if below 10%. This finding remains consistent with the fact that increased soil moisture may increase diffusion of the chemical to the skin surface, but because of the low water solubility of PAHs, has a (predicted) maximum of 25% decrease on uptake.

The model does not predict a clear correlation between soil organic carbon content and uptake fraction (data not shown). This implies that factors other than soil organic carbon content may play a significant role in dermal uptake of contaminants from skin.

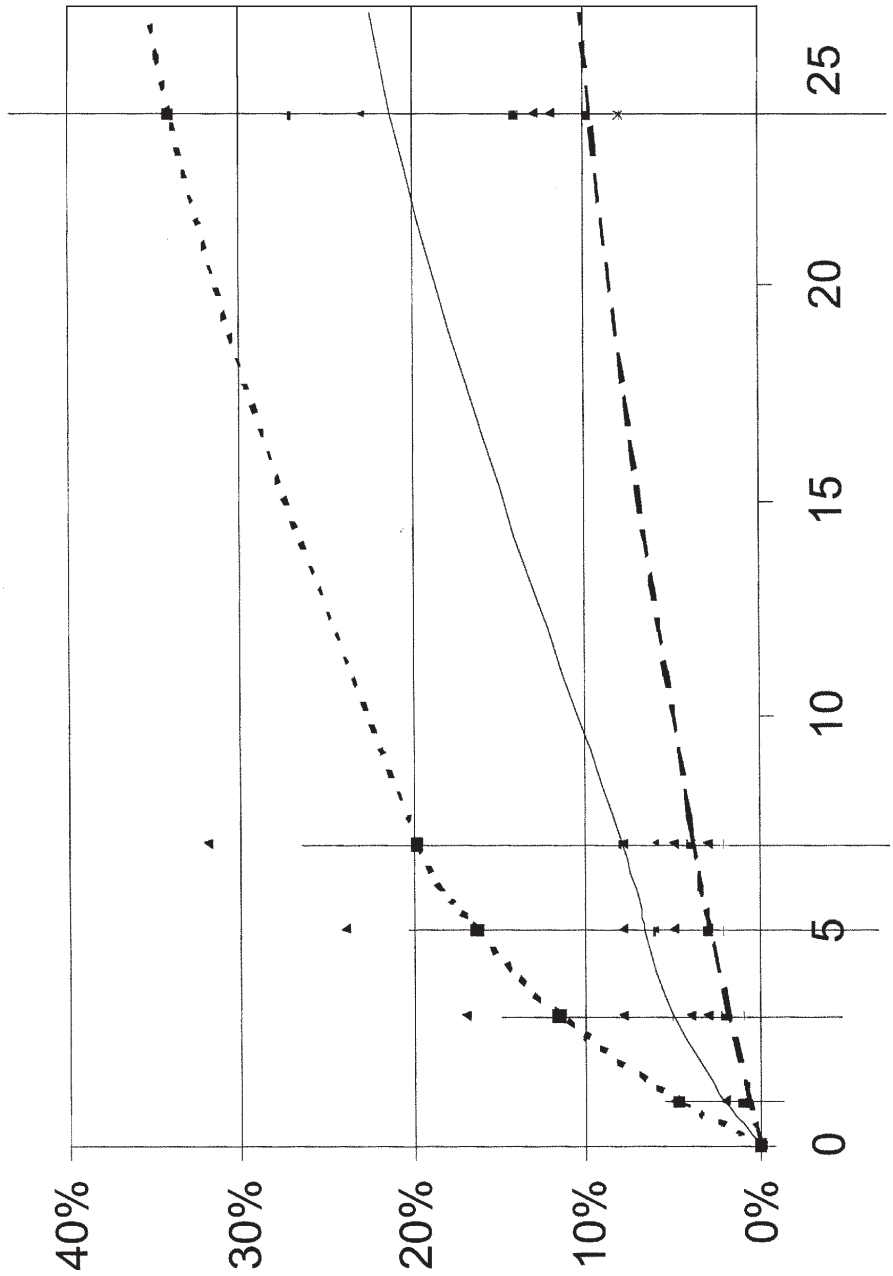

Figure 2. Two Stage Model prediction vs. 9 measurements of benzo(*a*)pyrene uptake. The solid line is the mean measure uptake fraction. Triangles are individual data points. Model predicted uptake fractions (Mean and Mean plus 1 SD) are shown as dotted lines.

Table 2. Model validation with published results.

Source	Study Type	Receptor	Temp. (°C)	Time (hr)	Soil Organic Carbon Content (%)	Soil Loading (mg/cm^2)	Skin Surface Area (cm^2)	Skin Layer Thickness (μm)	Published Benzo(a)Pyrene Uptake Fraction	Model Predicted Benzo(a)–Pyrene Uptake Fraction
Roy *et al.* 1998a	*In vitro*	human	37	96	-	25	9	350	$1.7 \times 10^{-2} - 6.1 \times 10^{-1}$ (mean 4.4E-1)	1.9×10^{-1}
Wester *et al.* 1990	*In vitro*	human	37	24		40	3	500	1.4×10^{-2}	3.3×10^{-2}
Yang *et al.* 1989	*In vitro*	rat	37	96	1.64	9	7	350	8.4×10^{-2}	8.8×10^{-2}

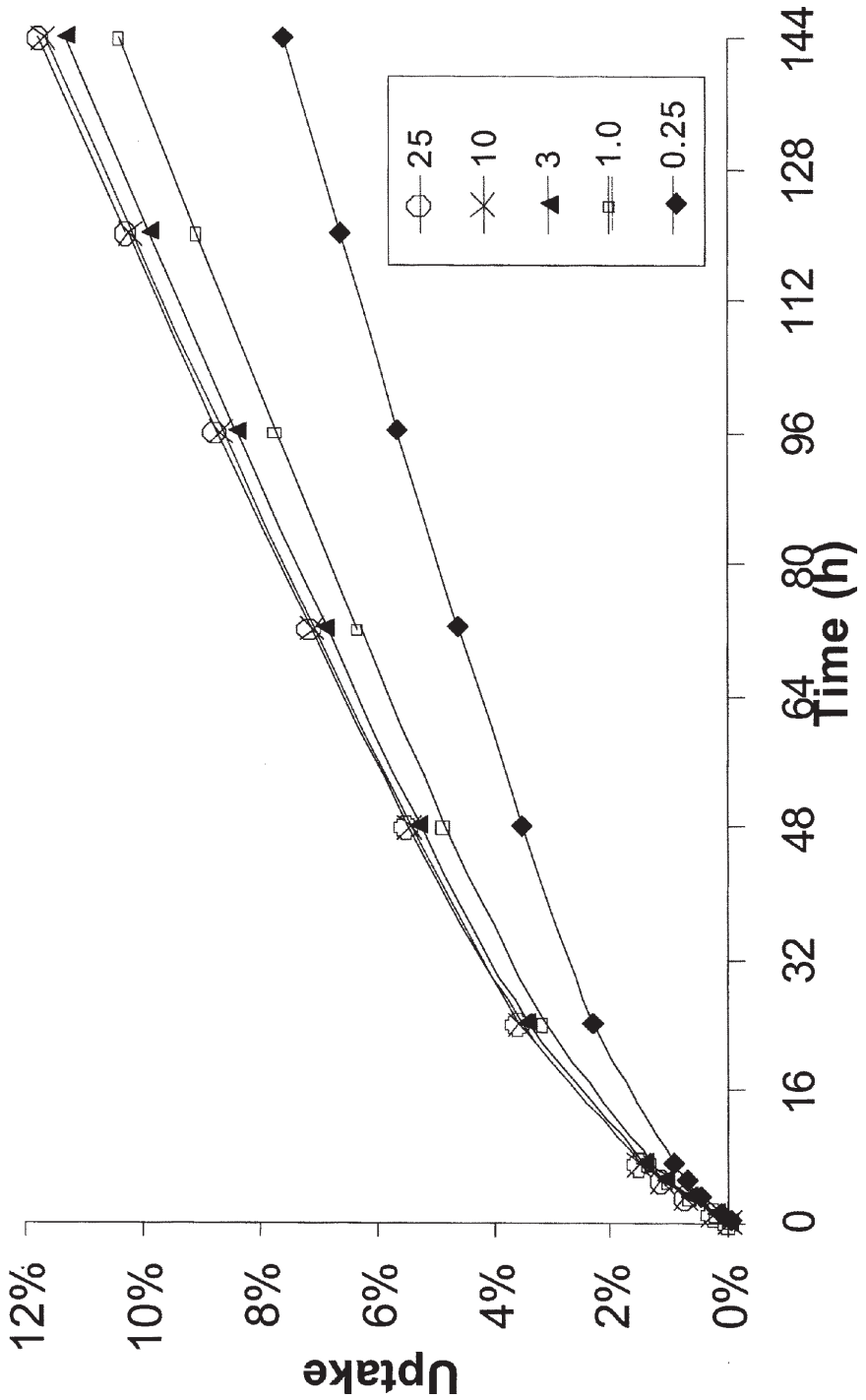

Figure 3. Model prediction of dermal uptake fraction at five soil loading rates.

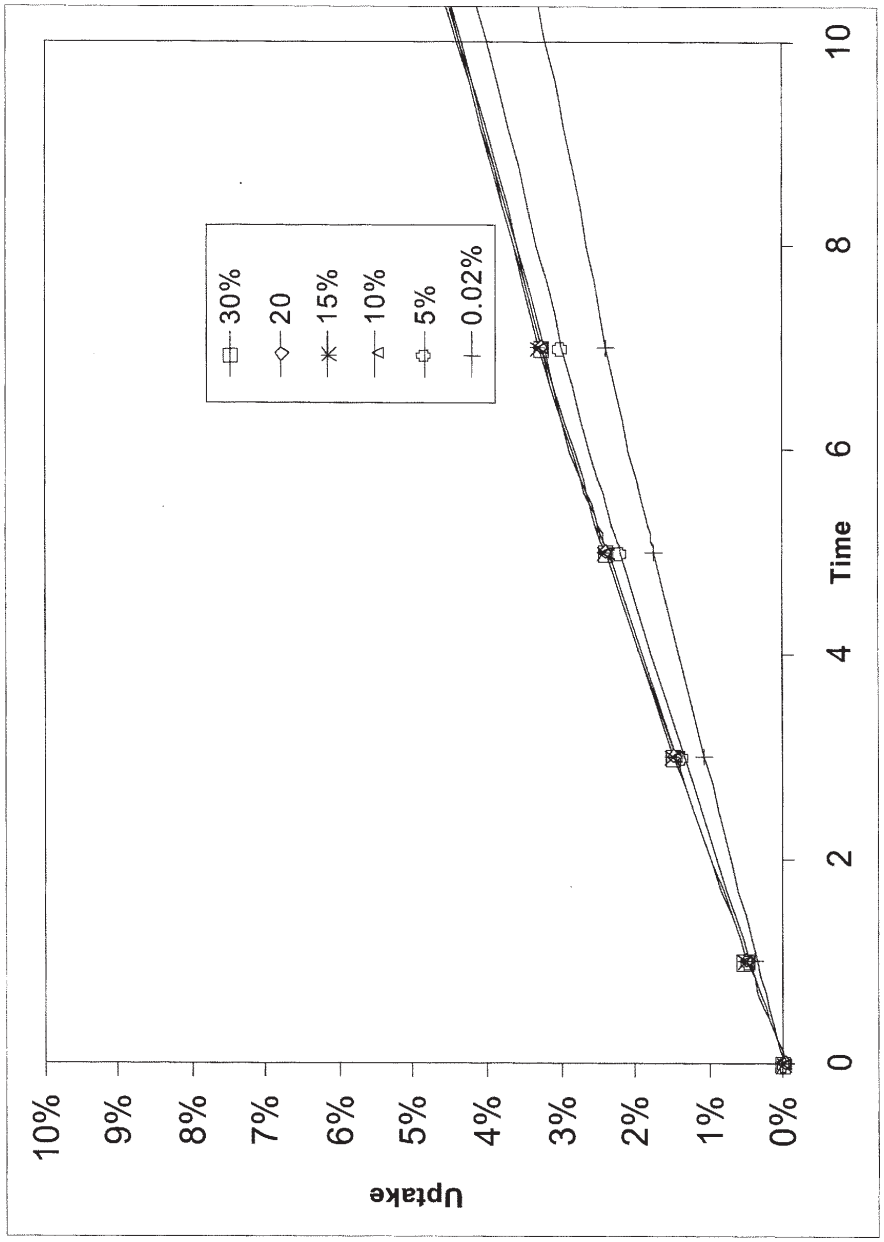

Figure 4. Effect of soil moisture content on predicted uptake fraction of benzo(*a*)pyrene.

C. Dermal Absorption as a Function of Fast- and Slow-Desorbing Chemical Fractions

We compared the predicted dermal uptake in four different soil types, using desorption data from studies of supercritical CO_2 extraction of phenanthrene at 50°C (Young and Leong 1997), and soil characteristics data from Weber and Young (1997). However, we assumed the soil/skin system to be at 25°C. Therefore, what is shown in Figure 5 is the *relative* uptake fraction for the four soils. Uptake appears inversely related to organic carbon content in soils to some degree, because greater uptake is observed in the Webster (f_{oc} = 2.97) vs. Houghton (f_{oc} = 46.1%) soils. However, the size of the fast-desorbing fraction (F_{fast}) clearly dominates the uptake into skin. The predicted uptake of phenanthrene in the Ohio soil is two to three times the uptake in the Webster soil, both of which have about 2% organic carbon, whereas the F_{fast} in Ohio soil is 71% vs. 18% in the Webster soil. In contrast, the Webster and Houghton soils have similar F_{fast} (18%), with significant differences in organic carbon content (2.44% vs. 46.1%), and the predicted uptake differs by less than a factor of two.

Two studies used as a source of nonlinear kinetic rate parameters measured the effect of aging on the parameters (Northcott and Jones 2001; Reeves *et al.* 2001). While the F_{fast} for benzo(*a*)pyrene decreased from 0.4 at 10 and 21 days to 0.04 at 53 days in one study (Northcott and Jones 2001), no significant effect was observed in either study. Thus, aging was not explored as a soil parameter of interest in this evaluation.

In Figure 6, we explore the impact of decreasing the fraction of fast-desorbing chemical on the predicted dermal uptake. For example, if one reduces F_{fast} from 75% to 25% (*e.g.,* through remediation), the uptake fraction for the remaining benzo(*a*)pyrene decreases from 45% to 15%. The balloons in Figure 6 compare the predicted uptake from recent experiments in desorption of benzo(a)pyrene where F_{fast} was 24% and 10%, respectively (Reeves *et al.* 2001; Northcott and Jones 2001), indicating that even in unaged soils, F_{fast} is predicted to limit dermal uptake. F_{fast} has a greater impact on predicted uptake than any other model parameter, including organic carbon. This finding may have implications for remediation of PAHs and potentially for other compounds as well. If one can reduce the concentration of easily desorbed fraction of a contaminant in soil, F_{fast}, the chemical remaining in the soil can have a much lower dermal availability, and is therefore associated with lower risk. Of course, we are assuming the dermal pathway is significant relative to overall risk from soil.

These preliminary findings indicate that an important area for further study is to learn what factors affect F_{fast} and F_{slow}, as well as how the kinetic rate constants vary across chemicals and soils. This would enable development of predictive relationships for these parameters for a variety of chemicals in differing soils, to develop methods to measure F_{fast} in the field, and to evaluate bioavailability when F_{fast} is reduced.

It is worthy of note that benzo(*a*)pyrene has a much lower F_{fast} than the smaller PAHs measured by Reeves *et al.* (2001). It would be valuable to have two phase desorption data for a wider range of chemicals, particularly larger PAHs, to further evaluate the potential importance of F_{fast} on dermal bioavailability.

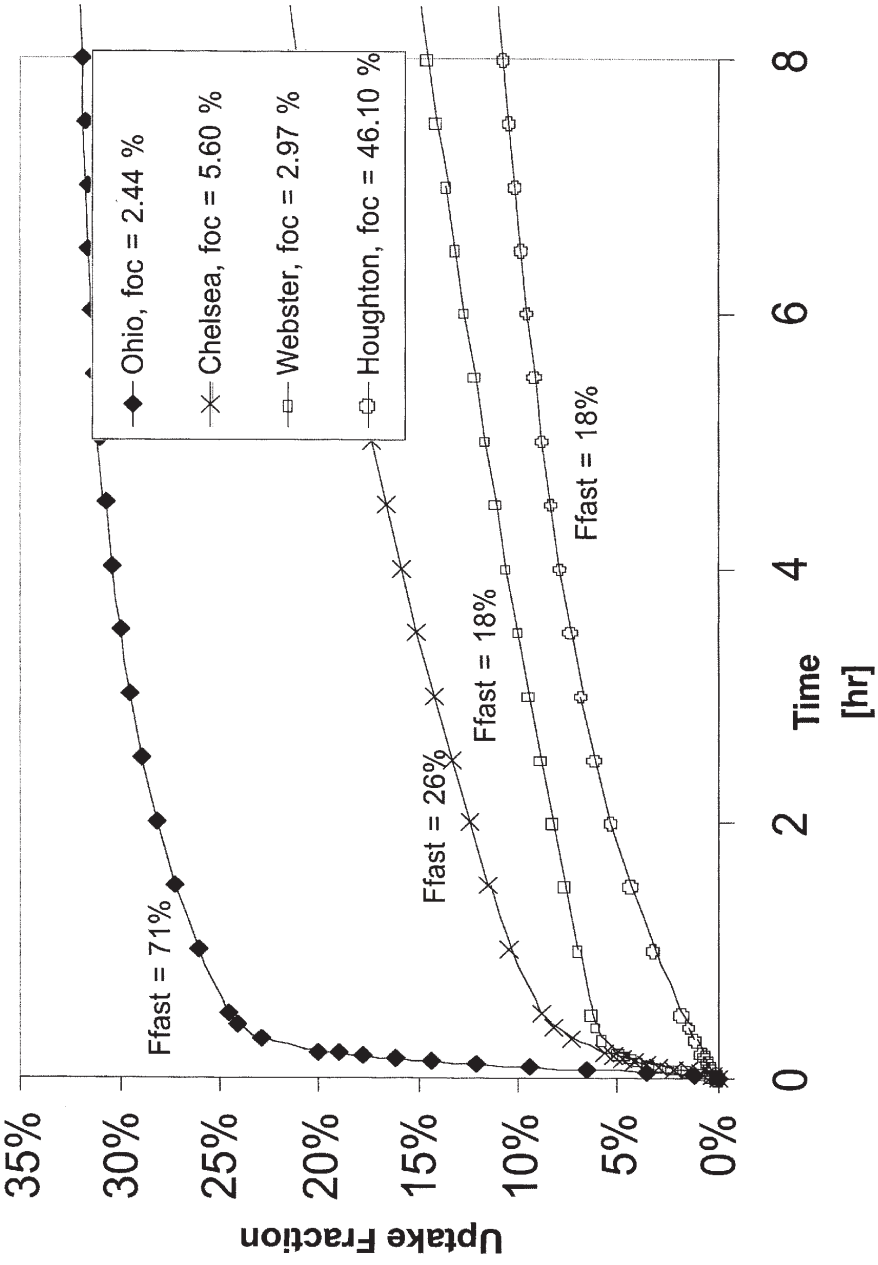

Figure 5. Dermal uptake of phenanthrene for four different soil types. Uptake fraction v. time. ('Uptake Fraction' refers to the amount of chemical absorbed into the skin as compared to the total amount of chemical in the soil available for uptake.). Soil data from Young and Leong, 1997, and Weber and Young, 1997.

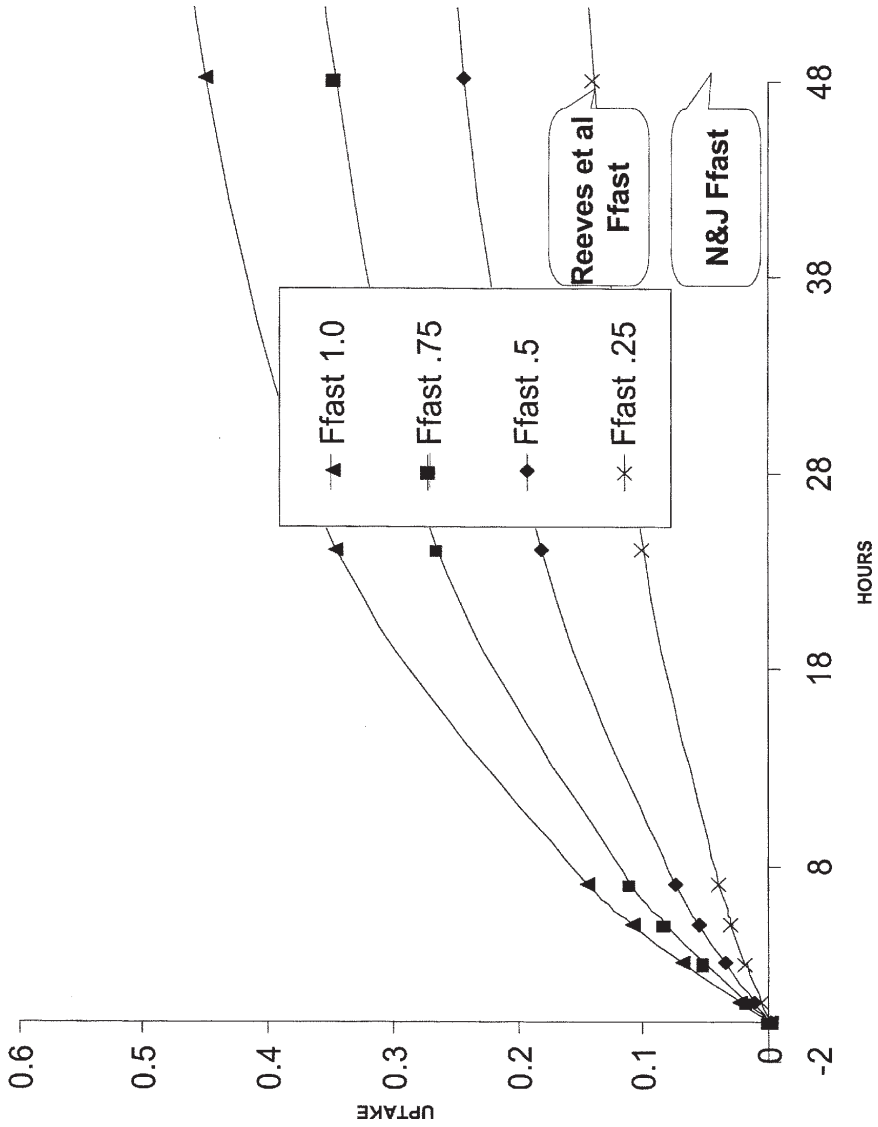

Figure 6. Effect of varying F_{FAST} on predicted dermal uptake of benzo(*a*)pyrene. Predicted uptake fraction with measured F_{FAST} values from Reeves et al. (2001) and Northcott and Jones (2001) are shown in balloons.

CONCLUSIONS

Two-stage desorption kinetics data were incorporated into a fugacity-based model to evaluate the potential effect of varying the available soil fraction, soil type content, soil loading, soil moisture content and other parameters, on dermal bioavailability of PAHs from a contaminated soil matrix.

The model predicts that incorporating nonlinear desorption kinetics results in less of the chemical being available for uptake by the skin, and hence lower dermal uptake when evaluated vs. time, the fast-desorbing soil fraction (F_{fast}), soil moisture content, and soil loading rate on skin. The predicted dermal uptake fraction increases with time and with soil loading rate on skin; in each case, uptake fraction reaches a plateau above which it does not increase.

The model was most sensitive to the fast and slow-desorbing chemical fraction. A higher fraction of fast desorbing chemical results in a quicker availability for, and hence, higher, dermal uptake. This finding may have implications for remediation of contaminated soils, in cases where the dermal pathway contributes significantly to overall risk.

It would be valuable to measure the nonlinear soil desorption parameters for other chemicals that are oftentimes risk drivers at sites. Also, additional data on soil characteristics during two-stage desorption experiments would be especially useful in understanding which soil characteristics, such as moisture content, grain size, porosity, *etc.*, might preferentially impact fast and slow desorption rates for chemicals.

It would be useful to measure soil desorption rates in conjunction with dermal uptake of chemicals in *in vitro* studies. It would be useful to learn which factors affect F_{fast} and F_{slow}, as well as how the kinetic rate constants vary across chemicals and soils both for soil desorption, as well as for dermal penetration of chemicals. With this additional information, we might be able to develop a predictive relationship for uptake for a variety of chemicals in differing soils, to develop methods to measure F_{fast} in the field, and to evaluate bioavailability when F_{fast} is reduced.

Currently, the paucity of data limits the use of fugacity models to predictive research tools. With coordinated studies comparing soil information to oral and dermal bioavailability measurements, computer simulation models may be valid approaches for evaluating chemical bioavailability in risk assessments of contaminated soils.

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