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Soil/Air Partitioning of Semivolatile Organic Compounds. 1. Method Development and Influence of Physical−Chemical Properties

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Soil is the primary sink of semivolatile organic compounds (SOCs) in the terrestrial environment, while the atmosphere is the primary vector of these substances to humans via the agricultural food chain. Hence, the exchange of SOCs between soil and air is of paramount importance to their environmental fate and potential risk to humans. In this paper, a method is developed to determine soil/air partition coefficients (K_{SA}) of SOCs. On the basis of the solid-phase fugacity meter developed for plants, the method was initially tested using a soil contaminated in the laboratory with chlorinated benzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. A systematic validation exercise demonstrated that the method is not subject to a wide range of potential artifacts. It was then shown that K_{SA} in moist soil (relative humidity = 100%) is independent of the water content of the soil. The method was then extended to the measurement of K_{SA} in the original soil, which contained background levels of the SOCs. Good agreement was found between the K_{SA} values measured with the original soil and with the laboratory contaminated soil, confirming that the studies with contaminated soil can be extrapolated to environmental conditions and demonstrating that it is possible to directly measure K_{SA} at current background levels of soil contamination. The K_{SA} values of the compounds studied ranged over almost 4 orders of magnitude. There was an excellent linear relationship between K_{SA} and the quotient of the octanol/water and air/water partition coefficients (K_{OW}/K_{AW}), indicating that the Karickhoff model commonly applied to soil/water partitioning can be extended to the soil/air system. An equally good regression was obtained between K_{SA} and measured octanol/air partition coefficients (K_{OA}).

Introduction

Soils are the primary sink of semivolatile organic compounds (SOCs) in the terrestrial environment. For instance, soils have been estimated for 93% of the polychlorinated biphenyl (PCB), 94% of the polycyclic aromatic hydrocarbon (PAH), and 95% of the polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) burden in the environment of the United Kingdom (*1*−*3*).

Air is the primary vector of SOCs to humans. SOCs in air are deposited on animal feed such as grass; the contaminated feed is consumed by livestock; and the SOCs are absorbed in the digestive tract and deposited in fatty tissue or milk fat, which in turn are the primary sources of human exposure to these compounds (*4, 5*). Soil ingestion by livestock or humans is generally of little importance for human exposure to SOCs (*6, 7*).

With soil being the major sink and air being the primary vector leading to human exposure, the exchange of SOCs between soil and air is of paramount importance for the human risk posed by SOCs in the environment. When soil is a net sink for SOCs in the atmosphere, it removes contaminant that might otherwise enter agricultural food chains through the atmosphere, hence serving to decrease human exposure. When soil is a net source of SOCs to the atmosphere, environmental residues are remobilized and introduced into agricultural food chains, increasing human exposure.

There is considerable evidence that soils are currently a source of some SOCs to the atmosphere, especially PCBs. These compounds display an annual cycle in the atmosphere characterized by a positive relationship between the gaseous concentration and the ambient temperature (*8*−*11*). This observation led to the hypothesis that a temperature-controlled revolatilization of PCBs from environmental reservoirs such as soils determines the atmospheric levels (*8, 12*). Support for this hypothesis has come from a study showing that there is a measurable exchange of PCBs between the laboratory atmosphere and naturally contaminated soils (*13*) and from a fate model, indicating that volatilization from soil is the most plausible explanation for the observed decrease in PCB levels in U.K. soils in the last decades (*14*).

The exchange of gaseous chemical between the atmosphere and soil can be expected to play an important role in the global distillation or cold condensation hypothesis of distribution and fate of SOCs (*15*). In warm climates, SOCs have a higher tendency to volatilize from the soils into the atmosphere. In the atmosphere, they are transported to cooler regions, where the lower temperatures result in an increased tendency for partitioning from the air to soil. This together with increased wet and dry particle-bound distribution combine to give relatively higher soil concentrations.

The exchange of gaseous chemical between the atmosphere and soil is a diffusive process. The direction and magnitude of the diffusion gradient is determined by the concentrations in the air and soil and by the soil/air equilibrium partition coefficient K_{SA}. However, although K_{SA} is the crucial parameter for this process, we are not aware of any measured values of K_{SA} for SOCs. In the absence of measured values, the current practice is to calculate K_{SA} from the soil/water partition coefficient K_{SW} and the air/water partition coefficient K_{AW} (*16, 17*):

$$K_{SA} = \frac{K_{SW}}{K_{AW}} \tag{1}$$

A commonly used expression for K_{SW} is that derived from the pioneering work of Karickhoff (*18*):

$$K_{SW} = f_{OC}K_{OC} = 0.411\, f_{OC}\rho K_{OW} \tag{2}$$

where f_{OC} is the organic carbon fraction of the soil, K_{OC} is the organic carbon/water partition coefficient, ρ is the soil density, and K_{OW} is the octanol/water partition coefficient. Substituting this into eq 1 yields

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$$K_{SA} = 0.411\, f_{OC}\rho\left(\frac{K_{OW}}{K_{AW}}\right) \quad (3)$$

which predicts that the soil/air partition coefficient is linearly proportional to the quotient of the octanol/water and air/water partition coefficients.

This paper is the first of a series dealing with soil/air partitioning of SOCs. It describes the development of a method to experimentally determine soil/air partition coefficients. This method is then applied to studying the partitioning of PCBs and PAHs in a soil. The resulting data provide an experimental basis for evaluating the validity of eq 3 as a basis for describing the influence of physical−chemical properties on K_{SA}. In a subsequent paper, the same method will be employed to examine the influence of temperature and relative humidity.

Experimental Methods

The soil/air partition coefficients were measured using a solid-phase fugacity meter. In the solid-phase fugacity meter, air is passed over a solid phase in such a way that an equilibrium is achieved between the air and the surface of the solid phase. Upon leaving the solid phase, the air is collected on a sorbent trap, and the concentrations of the chemical in the air are measured. The concentrations in the solid phase are also measured. The solid phase/air partition coefficient can be calculated from the quotient of the solid phase and air concentrations, providing that a number of conditions that are discussed below are satisfied.

This method is very similar to the gas saturation method for measuring vapor pressures. The gas saturation method has also been applied to the determination of pesticide vapor pressures in soil (*19*). The principal differences lie in the much shorter air residence times, the lower concentrations employed in this work, and the focus on partition coefficients.

Description of the Experimental Apparatus. A solid-phase fugacity meter developed for plant samples (*20, 21*) was modified for this work (see Figure 1). After the incoming airstream was cleaned, it was passed through a gas wash bottle filled with water to achieve 100% relative humidity. The air then flowed through a dew point controller, which set the desired relative humidity before the air entered the soil column. All components between the dew point controller and the sorbent trap were made of glass. Temperature was measured directly in the soil column. Temperature and relative humidity could also be measured in the airstream before and after the soil column. The downstream sensor was always removed together with the glass sensor holder between the soil column and the sorbent trap during fugacity measurements to avoid sorption artifacts. With the exception of the air cleaning and air metering components, the complete apparatus was placed in a climate chamber to ensure isothermal conditions throughout. There was no lighting in the climate chamber to prevent photodegradation.

Two different versions of this device were employed. The smaller had a capacity of 0.55 L ($\phi = 50$ mm, $h = 280$ mm) and was typically filled with 500 g of soil that rested on a glass frit. It was operated using compressed air and with florisil (in most cases) or XAD 2 (for the 1:100 dilution of the contaminated soil and the PAH measurements—see below) as the sorbent to capture the gaseous contaminants. The larger version with a capacity of 11 L ($\phi = 200$ mm, $h = 350$ mm) was filled with 2−4 kg of soil, which rested on a glass fiber filter. It was operated using a vacuum pump to draw air through the apparatus and with XAD 2 as the sorbent. The larger version was used for measurements of uncontaminated soil and the 1:1000 dilution of the contaminated soil, while the smaller device was used for all other measurements.

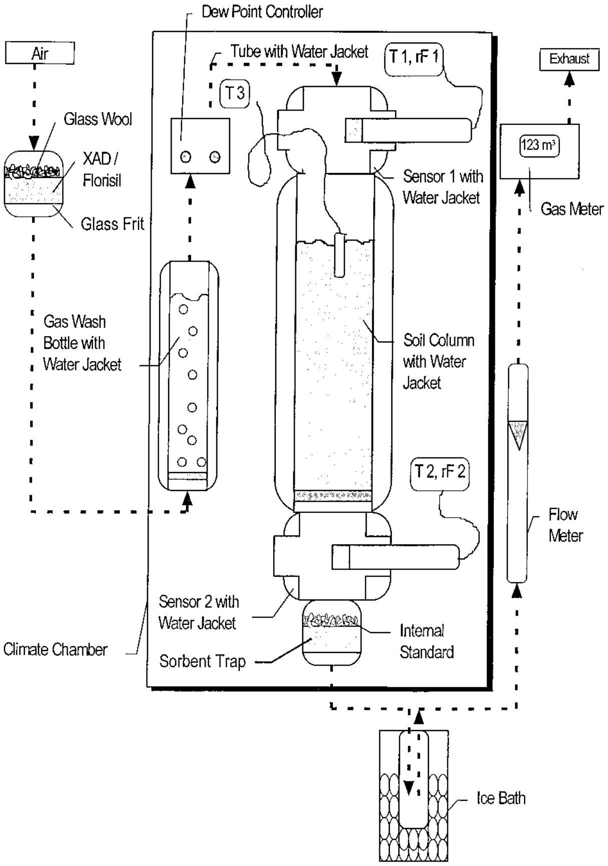

FIGURE 1. Schematic view of the fugacity meter.

Description of the Soil. The soil used for all experiments was a silty sand collected from a plowed field close to Bayreuth. It was air-dried and sieved to 2 mm prior to use. It contained 80% sand, 16% silt, 4% clay, and 1% organic carbon. The surface area was 1.63 $m^2\,g^{-1}$ as determined by nitrogen adsorption using a Gemini II 2370 from Micrometrics. The bulk density of the soil after sieving was 1.27 $g\,cm^{-3}$. The density of the soil material was assumed to be equal to that of quartz (2.65 $g\,cm^{-3}$) based on its high sand content. The concentrations of PCBs in the soil (~10 ng of ΣPCB g^{-1}) were typical for unmodified agricultural soils from the Bayreuth area, indicating that the PCB contamination originated primarily from atmospheric deposition, which was highest during the 1960s and 1970s (*22*).

In order to facilitate the method development, most of the experiments were conducted with contaminated soil, which was prepared as follows: 360 g of soil was covered with *n*-hexane. A standard mixture containing pentachlorobenzene (QCB), hexachlorobenzene (HCB), phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chry), and triphenylene (Tri) and a 1:1:1 mixture of Aroclors 1248, 1254, and 1260 dissolved in *n*-hexane was added. The solvent was evaporated to dryness on a rotary evaporator. A total of 3240 g of uncontaminated soil was added, and the soils were mixed on the rotary evaporator at room temperature without vacuum for 3 h. Seven batches of contaminated soil of 500 g each were filled into brown glass bottles, which were sealed and stored for 3 months at room temperature. After 3 months, six of the bottles were transferred to the freezer and frozen at −20 °C until use. This artificial contamination resulted in concentrations that were, dependent on the compound, a factor of 2500−66 000 higher than in the environmental sample. One of the batches was later used to prepare dilutions by mixing it with untreated soil. These dilutions (1:10, 1:100, and 1:1000 of the contaminated soil) were sealed in brown glass bottles and stored at room temperature for a further 13 months.

For one of the experiments, different soil water contents were required (see below). To obtain a high water content, one of the contaminated soil batches was spread out in a thin layer and sprayed with water. The moist soil was transferred to a brown glass bottle, sealed, and stored for 1 week. The water content was then adjusted downwards in steps by freeze-drying.

Analytical Methods. The sorbent traps of the small apparatus were prepared using either 10 g of activated florisil ($\phi = 3$ cm) or 15 g of precleaned XAD-2 ($\phi = 3$ cm). The sorbent traps of the large apparatus ($\phi = 6$ cm) were filled with 25–30 g of precleaned XAD-2. Preliminary experiments using backup cartridges verified that this quantity was adequate to prevent breakthrough of the compounds studied. Glass wool was placed on top of the sorbent, and an internal standard mixture containing ^{2}D-labeled isotopes of Phe, Flu, BaA, and Chry; ^{13}C-labeled isotopes of QCB and HCB; and the PCB congeners 28, 52, 101, 138, 153, and 180 was applied to the glass wool. The trap was then immediately attached to the fugacity meter apparatus. Following collection of the sample, the florisil traps were eluted with *n*-hexane/diethyl ether (20:1), and the extracts were reduced to 30 μL for analysis. The XAD traps were extracted with *n*-hexane/diethyl ether (10:1). After immersing the XAD in the extraction solvent for 0.5 h, the solvent was drained off and the XAD was rinsed several times with fresh solvent. The combined extract was applied to a column containing activated florisil/4% water, eluted with *n*-hexane, and reduced to 30 μL for analysis.

Soil samples were analyzed before every series of fugacity measurements. The samples were not dried due to the risk of sample contamination/loss of SOCs. Preliminary tests showed that the water content had no influence on the extraction efficiency. Two extraction methods were evaluated for the study: Soxhlet extraction and sonification, both using *n*-hexane/acetone (2:1). It was found that the two methods gave comparable results for the chlorinated compounds in the contaminated soil, but that the Soxhlet extraction was more efficient for the PAHs in the contaminated soil and for all compounds in the uncontaminated soil. The internal standard mixture described above was added to the solvent before beginning the extraction. The extracts were dried using Na_2SO_4 and cleaned up on a florisil column in the same manner as the air samples. Those samples analyzed for PAHs were cleaned up using a silica gel/alumina column (*23*).

All samples were analyzed using high-resolution gas chromatography with a mass selective detector (HP5970) or—when the concentrations were low—with a high-resolution mass spectrometer (Finnigan MAT 8230 or VG Autospec Ultima). The isomers were identified using single compound standards and—for several of the PCB congeners—using published chromatographic data (*8, 24, 25*). BaA, Chry, and Tri were quantified together due to inadequate chromatographic separation.

Description of the Experiments. In validating this method of determining soil/air partition coefficients of SOCs, the following factors were considered:

(1) Homogeneity of the soil contamination. This was evaluated by analyzing six parallel samples of the contaminated soil and eight parallel samples of the uncontaminated soil.

(2) Gaseous origin of the contaminants captured on the sorbent trap. The presence of particle-bound material in the air downstream of the soil column could falsify the results. This was evaluated by installing a glass fiber filter (Schleicher & Schüll, No. 8) between the soil column and the sorbent trap and analyzing the filter after the fugacity measurement was finished.

(3) The presence of a (near) equilibrium between the air and the soil surface. This was evaluated by varying the residence time of the air in the soil column. In the case of a non-equilibrium, one would expect the concentrations in air to increase as the residence time of the air in the soil column increased, since the air would have more time to approach equilibrium with the soil. When the concentration in air no longer increases with increasing residence time, this indicates that a (near) equilibrium between the air and the soil surface has been achieved.

(4) Reversibility of the sorption/partitioning to the soil. Interactions apart from reversible sorption/partitioning such as irreversible sorption, biodegradation or photodegradation could falsify the measurements. Potential degradation was tested by performing mass balances of the contaminants in the fugacity meter. Soil samples were taken when the soil batch was first placed in the fugacity meter and when the soil was removed from the fugacity meter. The loss of contaminant from the soil was compared with the amount collected in the fugacity measurements conducted with this soil batch. The reversibility of the sorption/partitioning was examined by measuring the loss of contaminant from the top of the column. Because of the plug-flow nature of the fugacity meter, contaminant is lost from the top of the soil column to the clean inflowing air. A decrease in soil concentration at the top of the column is an indication that at least this fraction was reversibly bound.

(5) Disturbance of the soil/air equilibrium as a result of the measurement. It has been reported that soils behave as a multi-compartment system and that the fast-reacting surface compartment has a small capacity and contains only a small fraction of the contaminant in the soil (*26*). If during the measurement a significant fraction of this surface compartment is depleted and not replenished from subsurface compartments, the measured air concentrations will be too low. This behavior has been observed for fugacity meter measurements with spruce needles (*20*). This potential artifact was evaluated by conducting sequential fugacity measurements. If the emptying of the surface compartment is a problem, the air concentrations should decrease when the measurements are conducted immediately after one another. When this is followed by a long pause, the air concentrations should recover to the initial level.

(6) Influence of the soil water content. Although the water content of the soil was not expected to influence the K_{SA} values due to the hydrophobic nature of the compounds studied, an experiment was conducted to ensure this was the case. The water content of the soil was varied between 12.4% (close to the maximum water content at which the fugacity meter could be operated without water being expelled from the soil column by the air) and 1.9% (close to the lowest water content at which 100% relative humidity was maintained). Initially five fugacity measurements were conducted at a water content of 12.4%. Then the soil was taken out of the glass column and freeze-dried to a lower water content. A small quantity of the soil was taken for chemical analysis and determination of the water content, and the remainder was placed back in the fugacity meter for the next measurement. This was repeated several times until a water content of 1.9% was reached. Then the soil was remoistened to 12.4%, and six further parallel fugacity determinations were conducted.

(7) Finally, since all of the above experiments were conducted with artificially contaminated soil, it had to be demonstrated that the results could be extrapolated to naturally contaminated soils. To this end a partitioning/sorption isotherm was measured using the contaminated soil and the three dilutions of this soil to establish whether

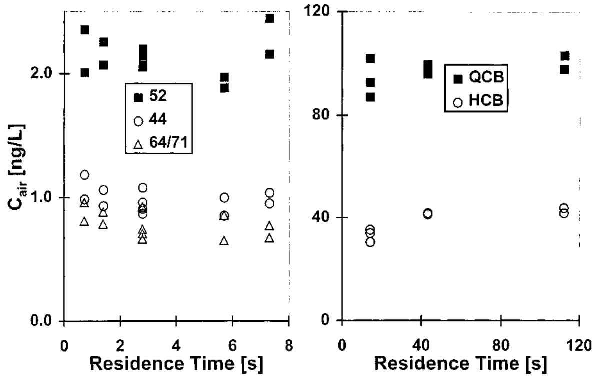

FIGURE 2. Dependence of the air concentration of several compounds on the air residence time in the fugacity meter.

the contaminated soil lay in the linear portion of the partitioning/sorption isotherm. Then K_{SA} values were measured for the naturally contaminated soil and compared with the values obtained for the artificially contaminated soil.

All measurements presented in this paper were conducted at 21 °C.

Results of the Method Validation

Homogeneity of the Soil Contamination. The coefficient of variation for the six parallel analyses of the contaminated soil (1 g each) averaged 15% for the compounds analyzed. The average for the eight analyses of the naturally contaminated soil (100 g) was 23%. It can be concluded that the soil contamination was quite homogenous.

Gaseous Origin of the Contaminants Captured on the Sorbent Trap. The analyses of the particle filter installed between the soil column and the sorbent trap did not yield detectable quantities of any compound. Since the concentrations in the sorbent trap were at least 25 times higher than the detection limits for the filter sample, the concentrations on the filter were in all cases at least 25 times lower than in the sorbent trap. Hence, it can be concluded that there was no artifact due to particles being deposited on the sorbent trap when the apparatus was operated without a filter. As a further check, the detection limit for PCB 203 in the sorbent trap (PCB 203 was never detected in the trap) was used together with the concentration of this compound in the soil to estimate the maximum amount of soil that could be in the sorbent trap. This soil quantity was then multiplied by the concentrations of the other compounds in soil to obtain an estimate of the maximum quantity of a compound in the sorbent trap that could be attributed to soil particles. This was for all compounds in all experiments <1% of the amount present in the trap, confirming that soil particles from the column did not contaminate the trap.

Equilibrium between the Air and the Soil Surface. The presence of equilibrium was tested by changing the residence time of the air in the soil column between 0.7 and 112 s. This was done at soil water contents of 1.8, 9.1, and 12.5% (a total of 29 fugacity measurements). As shown for several compounds in Figure 2, the air concentrations remained constant, indicating that the air and the soil surface were in equilibrium. For all of the chlorobenzenes and PCBs there was no evidence of non-equilibrium over the range of residence times investigated. Residence times of 7.2 s for the small apparatus and 2.8 s for the large version were used for the remaining experiments.

Reversibility of the Sorption/Partitioning to the Soil. Mass balances of the chlorinated benzenes and PCBs were conducted for four soil batches, some of which were in the fugacity meter for several weeks. The average recovery was 97 ± 5%, which indicates that degradation did not affect the results.

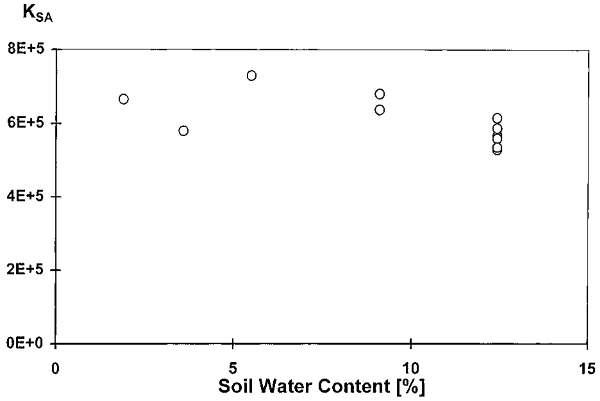

FIGURE 3. Dependence of the soil/air partitioning coefficient K_{SA} on the soil water content for PCB 52.

The soil sampled from the top 2 cm of the column after several fugacity measurements had significantly lower concentrations of many compounds than the soil from the bottom 5 cm (note that the concentrations in the bottom 5 cm were similar to those at the beginning of the experiments; i.e., there was no evidence of contaminant depletion in the lower part of the column). In the top 2 cm, 99% of the chlorobenzenes and 98% of the PCBs 4/10−32/16 were lost, indicating that these compounds were virtually completely reversibly bound to the soil. For the other compounds, the fraction lost decreased with decreasing volatility, from 92% for PCB 31/28 to 19% for PCB 110. However, this was to be expected given the increase in K_{SA} values with decreasing volatility (see below). No evidence was found indicating that a significant fraction of the chlorinated benzenes or PCBs was irreversibly bound to the soil.

Disturbance of the Soil/Air Equilibrium as a Result of the Measurement. Using one soil batch, 16 consecutive fugacity measurements were made, varying the interval between the runs from 1 min to 40 days. The air concentrations of all chlorobenzenes and PCBs remained constant, with an average coefficient of variation of 12%. This not only indicates that the measurements did not disturb the soil/air equilibrium; it also demonstrates the excellent reproducibility of the fugacity meter measurements.

Influence of the Soil Water Content. In Figure 3, the K_{SA} values of PCB 52 are plotted as a function of water content. No influence of soil water content on K_{SA} was observed for this or any of the other PCBs or chlorobenzenes. Taking the K_{SA} values for the different water contents together, the coefficient of variation was less than 25% for all compounds. However, as the next paper will show, when the water content becomes so low that the relative humidity drops below 100%, K_{SA} is affected.

Extrapolation to Naturally Contaminated Soil. The concentration measured in air was in all cases at least 1000 times smaller than the saturation concentration of the compound in air, and hence it was likely that the measurements were conducted in the linear range of the partitioning/sorption isotherm. This was confirmed by comparing the K_{SA} values in the contaminated soil and in the three dilutions of this soil. The isotherms were linear over a concentration range of 1000.

In Figure 4, the K_{SA} values measured for PCB 153 in contaminated soil, the three dilutions of this soil, and in uncontaminated soil are plotted. The error bars represent the concentrations calculated using the minimum soil/maximum air and maximum soil/minimum air concentrations. There is good agreement between the K_{SA} values for the different dilutions of the contaminated soil and for the K_{SA} value for the naturally contaminated soil. This indicates that the results obtained with the contaminated soil can be

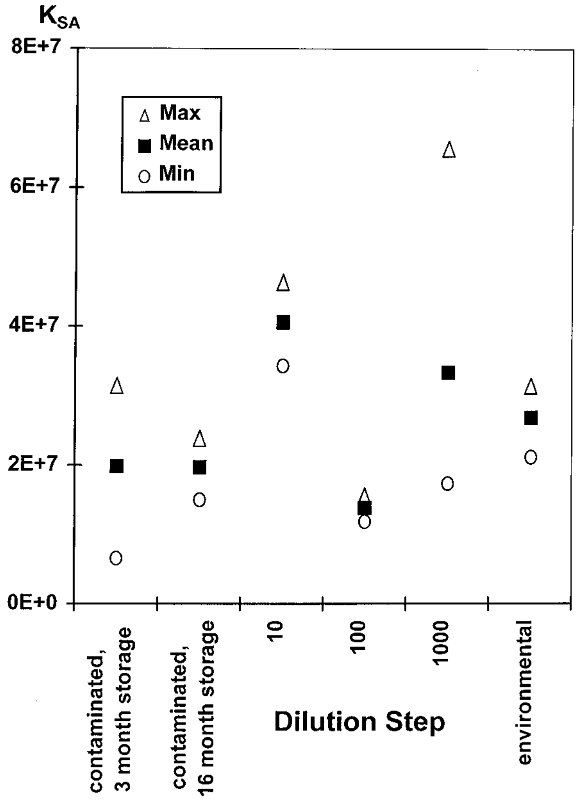

FIGURE 4. Plot of the soil/air partition coefficient K_{SA} of PCB 153 indicating the influence of contamination level and post-contamination storage.

extrapolated to the uncontaminated soil. Similar agreement was obtained for the other PCBs and chlorinated benzenes.

This agreement is to some degree surprising, given the discussion of aging as an important factor affecting the availability of organic chemicals in soils (*27, 28*). The contaminated soil in this study had aged for 3 months, the dilutions of the contaminated soil for 16 (3 + 13) months, and the naturally contaminated soil for 15 years or more, yet no significant differences in the soil/air partition coefficients were measured. This indicates that for this soil aging has no measurable effect on the soil/air exchange of these compounds.

This study demonstrates that it is possible to directly measure K_{SA} for chlorobenzenes and PCBs in soil containing current background levels of these substances, with the caveat that good laboratory blanks and an analytical method with low detection limits are required. A single measurement of the uncontaminated soil in the large fugacity meter lasted 20 h. This opens up the possibility of using this method to directly study the tendency of SOCs to volatilize from soils in field situations.

In all of the experiments described to this point, the PAHs could not be quantified in the sorbent trap. However, an influence of storage on the soil/air partitioning was apparent from the soil analyses. Whereas the PCB concentrations in the dilutions of the contaminated soil were the same after 13 months of storage, only 6% of the fluoranthene and 4% of the pyrene present at the time of dilution were measured in the soil 13 months later. The recovery of the more strongly bound benz[*a*]anthracene, chrysene, and triphenylene was 90%. It could not be established whether the losses of fluoranthene and pyrene were due to degradation or to the formation of bound residues.

Influence of Physical–Chemical Properties on K_{SA}. Table 1 summarizes the results of 42 different K_{SA} determinations for the chlorinated benzenes and PCBs conducted on three different batches of contaminated soil as well as on the dilutions of the contaminated soil and the naturally contaminated soil at varying water contents. Despite this wide range in experimental variables, the coefficient of variation was on average only 61%, indicating that the method precision is about a factor of 2.

TABLE 1. Measured Soil/Air Partition Coefficients (21 °C)

compound	K_{SA}	cv (%)	*n*
QCB	3.02E+04	57	42
HCB	9.57E+04	56	42
PCB 4/10	1.60E+05	71	32
PCB 8/5	3.41E+05	67	33
PCB 18/17	3.89E+05	55	35
PCB 32/16	4.76E+05	39	35
PCB 31/28	8.10E+05	42	38
PCB 52	9.67E+05	48	40
PCB 44	1.50E+06	62	40
PCB 64/71	1.74E+06	54	40
PCB 95	3.91E+06	38	41
PCB 101/84	5.24E+06	37	41
PCB 110	1.02E+07	66	40
PCB 149	1.48E+07	81	39
PCB 153	2.29E+07	109	37
PCB 138[a]/163[b]	3.83E+07	96	24
PCB 187	7.03E+07	81	26
PCB 180	1.09E+08	41	13
Phe	1.32E+06		2
Flu	8.06E+06		2
Pyr	9.93E+06		2

[a] PCB 163 includes PCB 164. [b] PCB 138 includes PCBs 158 and 160.

The PAHs could not be determined routinely due to inadequate limits of detection. Two separate determinations using large air volumes were conducted with the contaminated soil which had been stored for 3 months to circumvent this problem. The resulting K_{SA} values are also listed in Table 1.

In Figure 5, log K_{SA} is plotted against log K_{OW}/K_{AW}. The K_{OW} values were taken from ref 29 for the PCBs, from ref 30 for the chlorobenzenes, and from ref 31 for the PAHs. The K_{AW} values were calculated from the Henry's law constants in ref 32 for PCBs, in ref 30 for the chlorobenzenes, and in ref 31 for the PAHs. The quotient of K_{OW}/K_{AW} was corrected from 25 to 21 °C using the enthalpy of vaporization as described in ref 21. The enthalpies of vaporization were taken from ref 33 for the PCBs, from ref 34 for the PAHs, and from ref 35 for the chlorobenzenes.

An excellent linear relationship between log K_{SA} and log (K_{OW}/K_{AW}) was obtained ($r^2 = 0.972$). The fact that all three families of chemicals fall on the same line indicates that K_{OW}/K_{AW} is a good predictor of the interchemical variability in K_{SA}. The linear regression of the data yielded

$$\log K_{SA} = 0.987 \times \log \frac{K_{OW}}{K_{AW}} - 1.686 \tag{4}$$

or

$$K_{SA}(\text{meas}) = 0.0206 \left(\frac{K_{OW}}{K_{AW}}\right)^{0.987} \tag{5}$$

The slope of the regression in Figure 5 was nearly 1.0 as predicted by the modified Karickhoff model (eq 3). When the f_{OC} of 0.01 and ρ of 2.65 for the experimental soil are substituted into eq 3, a result very similar to eq 5 is obtained:

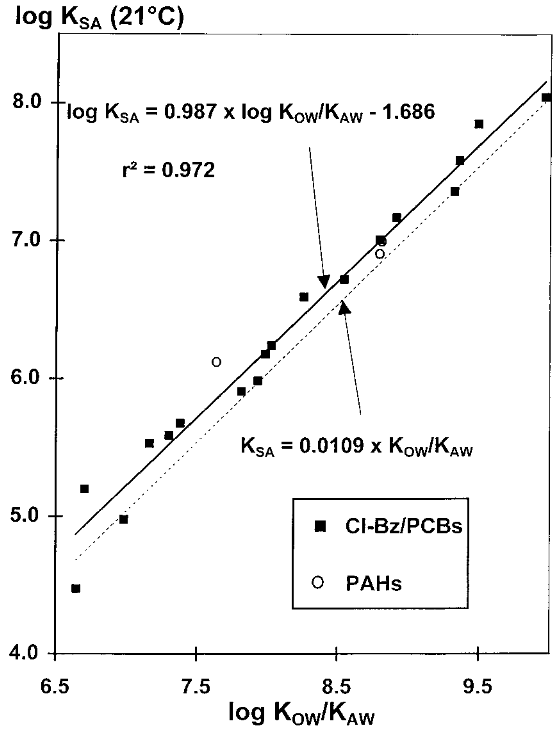

FIGURE 5. Plot of the average soil/air partition coefficient K_{SA} against the quotient of the octanol/water and air/water partition coefficients. The upper equation is the linear regression of all data points; the lower equation is the Karickhoff model for soil/water partitioning extended to soil/air partitioning.

$$K_{SA}(\mathrm{pre}) = 0.0109\left(\frac{K_{OW}}{K_{AW}}\right) \qquad (6)$$

This equation is also plotted in Figure 5. The agreement between the measured and predicted K_{SA} values was good, with the predicted K_{SA} values lying systematically about 1.5 times lower. This shows that the modified Karickhoff model does a good job predicting the partitioning behavior.

Recently our group and others have begun measuring octanol/air partition coefficients (K_{OA}) of SOCs (*36–38*). The thought behind this work is that K_{OA} should be a better predictor for interactions of airborne organic chemicals with organic matrices than K_{OW}/K_{AW}, if only because the former can be directly measured while the latter is calculated from two difficult to measure entities. Using measured K_{OA} values from ref 36 for the PCBs, from ref 37 for the chlorobenzenes, and from ref 38 for the PAHs, a linear regression between log K_{SA} (21 °C) and log K_{OA} (21 °C) was calculated:

$$\log K_{SA} = 0.951 \times \log K_{OA} - 1.754 \qquad (7)$$

or

$$K_{SA}(\mathrm{meas}) = 0.0176\, K_{OA}^{\ 0.951} \qquad (8)$$

A good correlation was obtained for all compounds (r^2 = 0.970), and again the slope of the log–log relationship was close to the ideal value of 1. Within the uncertainties associated with the K_{OW}/K_{AW} and K_{OA} values, these two parameters are equally good predictors of the interchemical variability in K_{SA}.

Other chemical descriptors besides K_{OW}/K_{AW} may be equally good for predicting K_{SA}. Soil/air partitioning/sorption of more volatile organic compounds is often interpreted using an adsorption model (*39–41*). In this case, the interchemical variability is described by the subcooled vapor pressure (P_L) for nonpolar compounds (*42*). In Figure 6, log K_{SA} is plotted against log P_L. The P_L values were calculated for 21 °C from the same references as the enthalpies of vaporization (*33, 34*). A good linear relationship between log K_{SA} and log P_L is apparent for the chlorinated compounds (r^2 = 0.974). However, the points for the PAHs lie distinctly above this line (r^2 = 0.910 for all compounds). Hence P_L is not as good a descriptor of the interchemical variability in K_{SA} as K_{OW}/K_{AW}. This may be attributable to the fact that the more hydrophobic SOCs in this study partition/sorb into the organic material of the soils, whereas the VOCs are thought to sorb primarily to the surfaces of minerals and micropores (*39*).

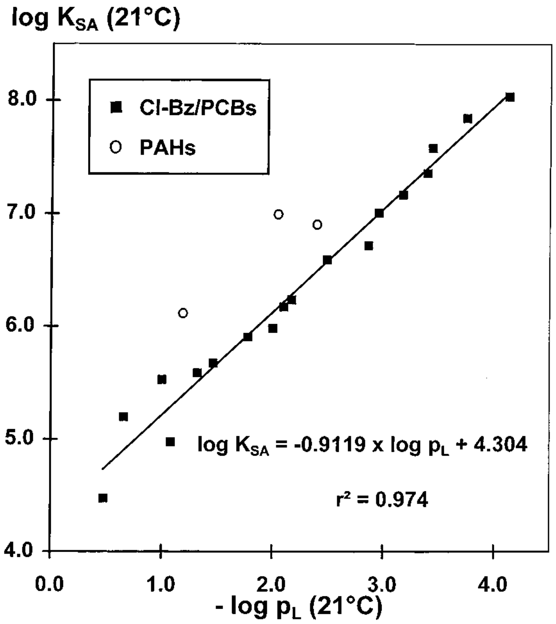

FIGURE 6. Plot of the average soil/air partition coefficient K_{SA} against the subcooled liquid vapor pressure. The equation is the linear regression of all data points excluding the PAHs.

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