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PCB163, 74472-44-9; PCB159, 39635-35-3; PCB161, 74472-43-8; PCB165, 74472-46-1; PCB128, 38380-07-3; PCB130, 52663-66-8; PCB132, 38380-05-1; PCB157, 69782-90-7; PCB138, 35065-28-2; PCB140, 59291-64-4; PCB133, 35694-04-3; PCB135, 52744-13-5; PCB162, 39635-34-2; PCB146, 51908-16-8; PCB148, 74472-41-6; PCB136, 38411-22-2; PCB164, 74472-45-0; PCB149, 38380-04-0; PCB150, 68194-08-1; PCB169, 32774-16-6; PCB167, 52663-72-6; PCB168, 59291-65-5; PCB153, 35065-27-1; PCB154, 60145-22-4; PCB155, 33979-03-2; BMBT, 103445-71-2; Apolane 87, 75536-64-0; cytochrome P-450, 9035-51-2; 1-octanol, 111-87-5; water, 7732-18-5.

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Received for review February 6, 1989. Revised manuscript received September 12, 1989. Accepted July 3, 1990.

Influence of Organic Matter from Soils and Sediments from Various Origins on the Sorption of Some Chlorinated Aliphatic Hydrocarbons: Implications on K_{OC} Correlations

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■ Sorption of nonionic compounds is strongly dependent on the content as well as the nature of the organic matter in soils and sediments. The composition and the structure of organic matter varies due to its origin and geological history and strongly influences the sorption affinity for nonionic organic compounds. Organic matter in unweathered shales and high-grade coals shows enhanced sorption (>1 order of magnitude) compared to organic matter in recent soils or geologically young material and low-grade coals. The results obtained indicate a decrease in sorption with increasing proportions of oxygen-containing functional groups in natural organic substances. A first approximation to estimate sorption coefficients for various organic matter is provided by an empirical correlation between the hydrogen/oxygen (H/O) atomic ratio as an index of the oxidation of the organic matter and the organic carbon normalized sorption coefficients (K_{OC}). This approximation also permits adjustment of K_{OC} values derived from K_{OW} data.

Introduction

The sorption of nonionic organic compounds by sediments and soils is commonly referred to as partitioning and is often described by a single partition coefficient K_d (1–3):

$$K_d = C_S/C_W \quad (1)$$

where C_S and C_W are the concentrations of the compound sorbed onto the solids and dissolved in water, respectively. This presumes linear sorption isotherms and implies that sorption is not dependent on the pollutant concentration in the soil. However, other researchers (4) have described nonlinear isotherms for the uptake of nonionic pesticides by soils and have suggested that the partition coefficient alone is insufficient to describe sorption over large concentration ranges. Linear isotherms are often observed for narrow concentration ranges and low concentration levels, whereas nonlinearity frequently appears when large concentration ranges are involved.

Nonlinear isotherms are frequently described by the Freundlich equation:

$$C_S = K_F C_{eq}^{1/n} \quad (2)$$

C_{eq} represents the equilibrium concentration in soil water or soil air. K_F and $1/n$ are empirical constants. K_F equals the partition coefficient between soil and air or soil and water, for $1/n = 1$ and $C_{eq} = 1$. In all other cases ($1/n \neq 1$) the concentration dependency of the sorption (and thus K_d—the concentration ratio between solids and liquid or gas phase) must be taken into account.

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Table I. Empirical Constants for K_{OC} Estimation (eq. 4)

compd log K_{OW}	a	b	ref
>2	1.00	−0.21	Karickhoff et al. (*7*)
2.1–5.6	0.90	−0.54	Chiou et al. (*3*)[a]
1.0–2.4	0.356	1.15	Sontheimer et al. (*25*)[b]
2.4–7.4	0.807	0.068	Sontheimer et al. (*25*)[b]
1.25–6.06	0.72	0.5	Giger et al. (*26*)

[a] Conversion of data based on organic matter content (K_{OM}) with $K_{OC} = 1.724K_{OM}$. [b] Includes data from Karickhoff et al. (*7*), Briggs (*27*), Schwarzenbach and Westall (*28*), and Chiou et al. (*3*).

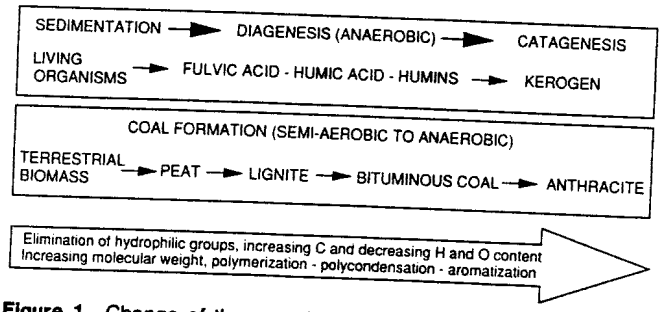

Figure 1. Change of the organic matter during burial.

Numerous studies have shown that the sorption of hydrophobic organic compounds in soils is strongly dependent on the organic carbon content of the soil (*1, 5–7*). Consequently, sorption can be normalized to the soil organic carbon content (OC%):

$$K_{OC} = K_d/\mathrm{OC\%} \times 100 \qquad (3)$$

Other studies have shown that K_{OC} for a given compound correlates well with the respective octanol–water partition coefficient (K_{OW}) through a linear free energy relationship:

$$\log K_{OC} = a \log K_{OW} + b \qquad (4)$$

Published values for the empirical constants a and b are available for a variety of compounds (Table I). K_{OC} can also be estimated from the water solubility (S):

$$\log K_{OC} = 4.04 - 0.557 \log S\ (\mu\mathrm{mol/L})\ (2) \qquad (5)$$

This K_{OC} concept assumes that the soil organic matter acts as a quasi-solvent for nonionic compounds (partitioning) and that the uptake of compounds is controlled solely by the organic matter. K_{OC} is commonly considered to be reasonably constant regardless of the nature of the soil or sediment sample.

Natural organic matter, however, has distinctive origins and histories. A large diversity of natural organic substances is known in nature and a variety of processes change the composition of these substances. Figure 1 presents a scheme of the change in the composition of organic matter during sedimentation and burial. Coalification describes the process of biochemical and geochemical alteration of the residues of plants (mostly terrestrial in origin) under semiaerobic or anaerobic conditions. In the marine environment, microorganisms (phytoplankton and zooplankton) are the most abundant source of the organic material in sediments. In both cases biopolymers (carbohydrates, lipids, protein, lignins, tannin, pigments, etc.) are degraded and condensed to form geopolymers such as fulvic acid, humic acid, humin, and kerogen (*8*). During diagenesis, catagenesis, and coalification, the geopolymers are subjected to further alteration, the final product of which is graphite (crystalline carbon). As a result of these processes, the composition and structure of the organic material is changed. These changes usually result in a decrease in the hydrogen/carbon (H/C) and oxygen/carbon (O/C) atomic ratios, and an increase in organic carbon content due to polymerization and condensation effects. On the other hand, fossil organic matter such as kerogen may be also subject to weathering processes, which result in increasing the O/C ratios (*9*). Also, a shift of compounds from the aromatic to polar fraction in bitumen extracts with decreasing depth in coal dumps exposed to weathering has been reported (*10*).

Table II. Physicochemical Properties of Choroaliphatic Chemicals (20 °C)

	water sol,[a] ppm	vapor density,[b] mg/L	Henry's law constant[c] 20 °C	Henry's law constant[c] 9.6 °C	octanol–water-partition coeff log K_{OW}[d]
TCM	7925	1027	0.12	0.065	1.94
TCA	1500	726	0.57	0.33	2.49
TCE	1100	415	0.31	0.16	2.29
PCE	150	126	0.58	0.29	2.60

[a] Horvath (*29*). [b] Verschueren (*30*). [c] Gosset (*31*), data interpolated for 20 °C. [d] Hansch and Leo (*32*).

Due to this resultant diversity in composition and structure of OM similar sorptivities for organic chemicals are unlikely. Indeed, several researchers (*11–14*) have observed a variation in the sorptivity of organic compounds for different fractions of organic matter such as humic and fulvic acids, lipids, and humins. Also water solubility enhancements of relatively water-insoluble organic solutes by dissolved organic matter was found to be dependent on the source of the humic substances involved, which was attributed to differences in their molecular weight and polarity (*15*). Such findings suggest limitations in applying K_{OC} values from the literature to calculate sorption coefficients without considering the nature of the organic matter involved.

This paper presents data (K_{OC}) to demonstrate the different sorption properties of various types of organic matter in soils and sediments. The results suggest a relationship between the elemental composition of natural organic matter and K_{OC}. The investigation is based on 39 soil and sediment samples from different geological formations and areas (mostly in southern Germany) and their vapor-phase Freundlich isotherms for four nonionic organic compounds: trichloromethane (TCM), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and perchloroethylene (PCE). These halogenated compounds are widely used as industrial solvents and have been detected in many aquifers and soils.

Materials and Methods

Chemicals. The pure compounds were purchased from Aldrich Chemicals (HPLC grade) and used as received. Their physicochemical properties are given in Table II.

Soil and Sediment Samples. Most of the samples were collected from various sites in southwestern Germany (Baden-Württemberg). They include sandstones, mudrocks, shales, and silt (from Triassic to Quaternary) at different stages of weathering, as well as various soil samples taken from distinct soil horizons and aquifer material. In addition, some humic coals (peat, lignite, subbituminous coal, and anthracite), as well as two pure clays (kaolinite and montmorillonite) were also used. The samples used covered a variety of paleoecological and diagenetic conditions and hence showed wide ranges in mineralogical composition, grain-size distribution, organic carbon content, and nature of the organic matter.

Table III. Sorption Coefficients log K_{SG}, $1/n$ (in Parentheses) and OC % for Some Samples (±1 SD, $r^2 \geq 0.98$, $15 > n > 9$)

	TCM	TCA	TCE	PCE	OC%
shale (tertiary)	2.58 ± 0.016[a]	2.35 ± 0.117	2.83 ± 0.078	3.28 ± 0.036	26.8
	(0.99 ± 0.017)	(0.97 ± 0.021)	(0.96 ± 0.015)	(0.87 ± 0.004)	
shale (jurassic)	2.84 ± 0.100	2.62 ± 0.063	2.94 ± 0.054	3.18 ± 0.055	9.7
	(0.89 ± 0.017)	(0.88 ± 0.010)	(0.92 ± 0.010)	(0.91 ± 0.010)	
peat	2.36 ± 0.039	1.99 ± 0.028	2.49 ± 0.056	2.81 ± 0.040	33.4
	(0.90 ± 0.007)	(0.90 ± 0.005)	(0.88 ± 0.009)	(0.84 ± 0.006)	
lignite	2.22 ± 0.044	1.87 ± 0.063	2.43 ± 0.058	2.70 ± 0.024	18.5
	(0.86 ± 0.015)	(0.90 ± 0.021)	(0.88 ± 0.019)	0.87 ± 0.009)	
bituminous coal	3.50 ± 0.111	2.99 ± 0.093	3.85 ± 0.062	3.85 ± 0.065	83.6
	(0.88 ± 0.027)	(0.92 ± 0.035)	(0.82 ± 0.023)	(0.79 ± 0.014)	
anthracite	3.85 ± 0.093	3.51 ± 0.154	4.26 ± 0.076	4.28 ± 0.072	80.1
	(0.78 ± 0.023)	(0.86 ± 0.048)	(0.80 ± 0.027)	(0.70 ± 0.020)	

[a] A total of 98.55% of the TCM is sorbed (X_S), 1.19% is dissolved in water (X_W), 0.19% is in the vapor phase (X_G), and 0.06% is lost from the system within 1 day according to the blanks.

Sample Preparation. Soil samples were air-dried and homogenized; soil aggregates, shales, and mudstones were fractured to aggregate sizes of less than 2 mm. Further treatment of the samples was avoided to minimize any changes in their natural sorption properties. Prior to the vapor-phase sorption experiment, the samples were mixed with deionized water to match the water contents observed in situ. Very low water contents were achieved by storage of the sample in desiccators at different relative humidities for 2 weeks.

Sample Characterization. Grain-size distributions were determined by dry-sieving and sedimentation methods. Organic carbon content (OC%) was measured by wet oxidation with $K_2Cr_2O_7$ after pretreatment of the soil with H_2SO_4 to remove inorganic carbon. In addition, the specific surface area (N_2 adsorption–BET isotherms) and cation-exchange capacities were determined. The methods used have been described in detail elsewhere (*16*).

Analytical Procedures. Vapor-phase analyses were performed with a Carlo Erba gas chromatograph (Mega 5160) equipped with two detectors (ECD and FID) connected in series. For separation, a 50-m fused-silica capillary column (Carlo Erba) with 0.32 μm i.d. and a 1-μm stationary phase (SE 30) was used. For each analysis 100 μL of the vapor phase was withdrawn from the sample vial and injected directly into the gas chromatograph. The precision of the sampling and analytical method in general was better than 10%.

Sorption Experiments. The sorption isotherms were determined by a headspace method, which allowed the calculation of the amount of chemical sorbed without separation of the soil water and soil solids phase. Hence, problems associated with the separation of colloid-size soil material (*17, 18*) are avoided. This method is based on the assumption that Henry's law is valid and implies that water adsorbed to mineral surfaces in soils behaves as bulk water. Dorris and Gray (*19*) observed that the surface properties of water coated onto glass beads at relative humidities above 80% very closely resemble those of bulk water. Some samples in the current study also showed that, beyond a certain minimum level, sorption becomes independent of the water content, (published elsewhere; see refs 16 and 20). This level is generally achieved under field conditions where relative humidities are usually 98% or greater (*21*). At this relative humidity all mineral surfaces are coated by an adsorbed film of water and micro- and mesopores are filled with condensed water. However, at relative humidities below this level, a strong increase in sorption is due to interactions with dry mineral surfaces (*16, 20, 22, 23*).

Moist material samples (20 g) were placed in 20-mL glass vials sealed with Teflon-lined butyl rubber septa. To prevent the competitive sorption of solvents often used for stock solutions (e.g., methanol), known quantities of pure compound were added microliter syringes. For low vapor-phase concentrations (0.01–1 μg/L), 1–100 μL of pure compound was vaporized in a 1-L gas bulb and 100 μL of the vapor mixture was injected into the sample vial with a gas-tight syringe. In most of the experiments a vapor-phase concentration range of 10^{-1}–10^4 μg/L was used. A minimum of three replicates was run for each sorption experiment.

Table IV. log K_{OC} (20 °C)

sorbents	TCM	TCA	TCE	PCE	ref
soil, sand, loess[a]	1.44	1.65	2.09	2.64	this study
weathered shale, mudrock[a]	1.98	2.22	2.56	3.29	this study
unweathered shale, mudrock[a]	2.79	3.02	3.43	4.03	this study
soil[b]		2.26	2.03	2.56	34
humic acid[c]			1.79		23
humins			1.76–2.28		11
calcd by using eq 4[d]	1.85	2.08	1.97	2.39	25
	1.92	2.29	2.15	2.57	26

[a] Includes temperature corrections from 10 to 20 °C (TCM, −0.31; TCA, −0.31; TCE, −0.29; PCE, −0.23) as determined by isotherms at 5, 10, and 15 °C (*16*). [b] Converted from K_{OM}. [c] Humic acid coated aluminum oxide. [d] Compare Table I.

To approach natural subsurface conditions the sorption experiments were carried out at 10 °C. After 1 day for equilibration, the compound concentrations in the vapor phase of the vials were measured. A control experiment involving shale and mudstone samples confirmed this time to be sufficient for equilibration as no further sorption could be observed after an additional 3 days of equilibration. Soil aggregates and fragments of shale and mudstones in general have relatively high intraparticle porosities (>10%), and this may allow a fast diffusion of the compounds and therefore a relatively fast approach to equilibrium.

To determine the mass of each compound lost from the sample vials (primarily through the Teflon-lined butyl rubber septa), several blank vials were run with each batch of sorption experiments. Teflon is known to adsorb and to be permeable to volatile organic substances. In the blanks a continuous loss of the compounds was observed. Average losses in the blank vials after 1 day at 10 °C were as follows: TCM, 23%; TCA, 21%; TCE, 34%; PCE, 55%. This effect prevented distinguishing the sorption of these compounds for a few samples with very low sorption capacity (e.g., where the sorption in the sample was significantly lower than the loss in the system). However, this loss was insignificant for the strong sorbing samples such

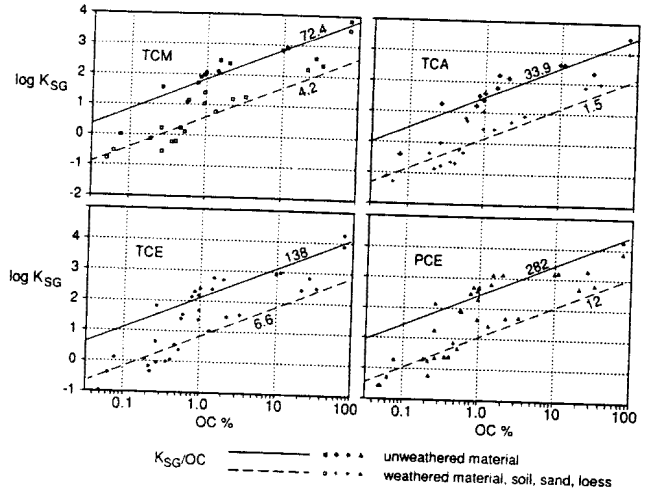

Figure 2. Dependency of the vapor-phase sorption coefficient K_{SG} on the organic carbon content at 10 °C. For several samples with very low organic carbon content, such as fluviatile sands, loess, Keuper marl, and kaolinite no sorption could be measured. Numbers on lines indicate average K_{SG}/OC ratios.

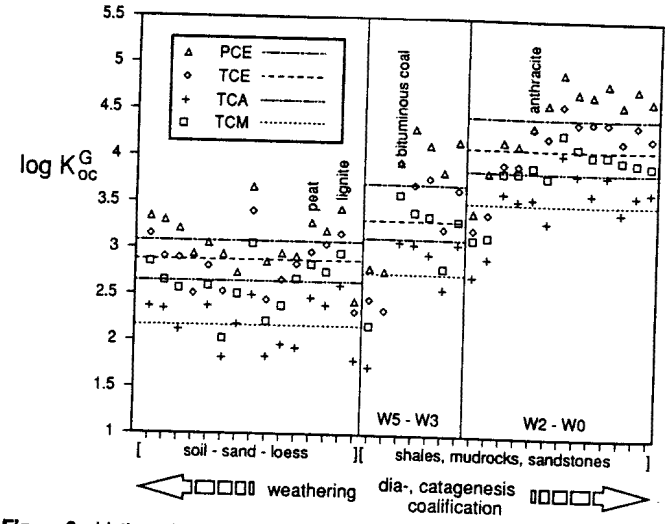

Figure 3. Listing of soil and sediment samples classified in three groups depending on weathering or coalification with their K^G_{OC} values at 10 °C. Stages of weathering according to Einsele et al. (*33*) from WO = unweathered, fresh rocks to W4/W5 = completely weathered material.

as those shown in Table III. Also, the observed rate of loss from the blank vials was much smaller than the rate of sorptive uptake of the compound by the sample.

Analysis of Data. The quantity of compound sorbed onto the soil solids (X_S) was calculated as follows:

$$X_S = X_{tot} - X_G - X_W - X_{sys} \quad (6)$$

where X_{tot} is the total mass of compound added (μg), X_G is the mass present in the vapor phase [concentration measured in the vapor phase (C_G)(vapor-phase volume)], X_W is the mass dissolved in water [as calculated from the vapor-phase concentration by using Henry's law constant (H)—(C_G/H)(water volume)], and X_{sys} is the mass sorbed by the septum or lost from the system, as determined from blank vials (corresponding to the respective vapor-phase concentration).

Freundlich isotherms were obtained by linear regression of the logarithmic data:

$$\log C_S = 1/n \log C_G + \log K_{SG} \quad (7)$$

where C_S is the sorbed concentration (μg/kg) and C_G is the vapor-phase concentration (μg/L). K_{SG} represents the Freundlich sorption coefficient K_F in the system soil-gas phase; some examples are given in Table III. In the case of nonlinear isotherms ($1/n \neq 1$), K_{SG} equals the concentration ratio between the solid and gas phase at C_G = 1 μg/L and would thus correspond to a partition coefficient obtained from a linear isotherm fit within a narrow concentration range around 1 μg/L. Isotherms in low concentration ranges are frequently considered to be linear. In addition K_{SG} values were normalized to the respective organic carbon content:

$$K^G_{OC} = K_{SG}/\text{OC\%} \times 100 \quad (8)$$

Results and Discussion

The Freundlich isotherms obtained were, in most cases, nonlinear over the concentration range studied (4–5 orders of magnitude), indicating heterogeneities of the sorption sites depending on the concentration level for some samples. The term $1/n$, the degree of nonlinearity of the Freundlich isotherm, varied for most samples between 0.8 and 1.

No significant correlations between the vapor-phase sorption coefficients K_{SG} and the surface-associated properties such as cation-exchange capacity and specific surface area or the clay mineral fraction were observed. Even in samples with a high content of expandable clay minerals (but very low organic carbon content) or pure kaolinite and montmorillonite, little or no sorption of highly volatile chlorinated hydrocarbons was measurable. By contrast, plots of log K_{SG} versus log OC for the four halogenated compounds (Figure 2) suggest that, for all samples, the sorption of these compounds is largely governed by the soil organic carbon content as previously reported (*1, 3, 5–7*).

The considerable scattering of the data in Figure 2 indicates that sorption may be dependent strongly on the nature as well as the percentage of the organic matter in the sorbent. Soils and recent sediments (e.g., loess) demonstrate relatively weak sorption compared to unweathered mudstones and shales. For example, K_{SG} for an entirely weathered shale (Opalinuston) is reduced by a factor as high as 30 compared to the almost unweathered counterpart from the same site. Sorption is therefore strongly influenced by the change in composition and structure of organic matter. Figure 3 shows log K^G_{OC} values (gas-phase-based K_{OC}, eq 8) for all samples listed in three groups according to their degree of weathering, where soils, sand, and loess samples represent the group with the highest influence of weathering and shales and rocks the group with the lowest. The change of organic matter during weathering processes has previously been described as "retrograde coalification" (*24*). If sorption decreases with an increase in the degree of weathering of the organic matter, an increase in sorption could be expected for coals with increasing degree of coalification. This is confirmed by the K^G_{OC} values for peat, lignite, bituminous coal, and anthracite (Figure 3). These data indicate that sorption is dependent on the degree of weathering or coalification of the organic matter.

These results suggest a relationship between sorption of nonionic compounds and the composition of the organic matter. Since, to a large extent, the changes in the composition of organic matter during burial and weathering result in a decrease or increase of the relative amounts of oxygen-containing functional groups (e.g., carboxyl, hydroxyl), it can be inferred that sorption decreases with increasing proportions of oxygen content. High amounts of oxygen-containing functional groups may result in an increase in the overall polarity of organic polymers com-

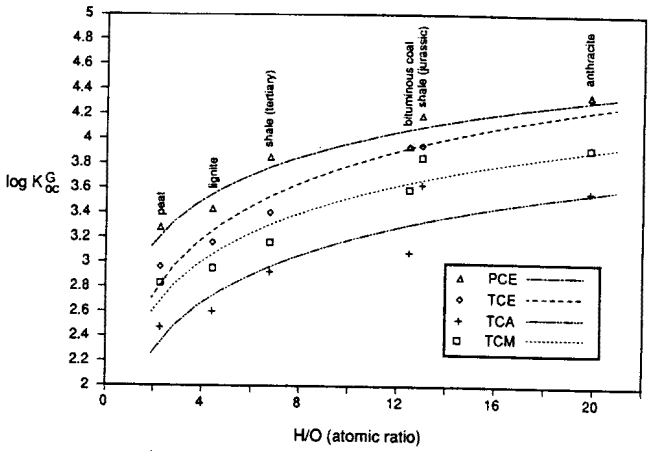

Figure 4. log K_{OC}^{G} versus the H/O ratio for some high organic carbon samples.

posing natural organic matter and thus in a lower affinity for nonionic compounds thereby decreasing the sorption capacity. Organic matter is commonly characterized by the H/C and O/C atomic ratios (e.g., by Van Krevelen diagrams); similary, the H/O atomic ratio can be used as an index of the degree of oxidation of the organic matter. A high H/O ratio indicates relatively low amounts of oxygen-containing functional groups (corresponding to a relatively low polarity and high hydrophobicity) and therefore a high sorption affinity of nonionic organic compounds by the organic matter. To calculate these atomic ratios, reliable data for the composition of organic matter (e.g., elemental analysis) are necessary. Such data are primarily available for material with relatively high organic carbon content such as bituminous shales, peat, and coals or organic matter extracts and fractions. The elemental composition or H/C and O/C atomic ratios of several kerogen-containing shales and coals used in this study are readily available from the literature. These samples and their sorption coefficients (K_{SG}, $1/n$) as well as their organic carbon content are listed in Table III. The corresponding H/C, O/C, and H/O atomic ratios are compiled with others in Table V. Figure 4 shows a plot of log K_{OC}^{G} for TCE versus the H/O ratios for these samples. This data set indicates that a relationship exists between the sorption of nonionic organic compounds and the elemental composition of natural organic matter. Sorption increases considerably with an increasing H/O ratio.

Comparison with Reference Data

To obtain comparisons with existing reference data for aqueous systems, vapor-phase concentrations were converted to equivalent aqueous concentrations by using Henry's law. This yields the sorption coefficients in the aqueous system K_{SW} and K_{OC}.

$$K_{SW} = C_S/C_W^{1/n} \quad (9a)$$

$$K_{SW} = K_{SG}H^{1/n} \quad (9b)$$

$$\log K_{OC} = \log K_{SG} + 1/n \log H - \log f_{OC} \quad (9c)$$

where K_{SW} is the sorption coefficient in an aqueous system (equals K_d for $1/n = 1$), H is the Henry's law constant (C_G/C_W), and f_{OC} is the fraction of organic carbon (OC%/100).

Table IV includes averaged data (arithmetic mean) converted to aqueous systems for the three groups of samples used in this study as well as values of log K_{OC} given in the literature or calculated according to eq 4. The data in the literature were obtained mostly from the linear part of the isotherm (low-concentration range). The K_{OC} values for the samples with the highest degree of weathering (e.g., soil, sand, loess, weathered shale, and mudrock) from this study are in good agreement with the K_{OC} values reported from previous studies, whereas the K_{OC}'s for unweathered samples are considerably higher compared with the literature data.

To verify a possible correlation between the H/O ratio and K_{OC}, the data were supplemented by data published by Garbarini and Lion (*11*) on the sorption of TCE (and toluene) to organic sorbents such as humic, fulvic, and tannic acids, lignin, zein, and cellulose. The data used are compiled in Table V. A plot including this additional data set (Figure 5) also supports the existence of a direct relationship between K_{OC} and the elemental composition (expressed as H/O atomic ratio) for TCE with some of the investigated sorbents. Only minor agreement was found for the three sorbents with the lowest H/O atomic ratios (tannic acid, fulvic acid, cellulose). This could be due to a lower degree of polymerization and aromatization of these sorbents compared to the kerogen-containing samples. However, there is good agreement for lignin and humic acids, which are the most abundant constituents of soil organic matter. A linear regression based on the data from this study (only shales and coals) yields the following relationship between log K_{OC} and log [H]/[O]:

$$\log K_{OC} = 1.52 \log [H]/[O] + 1.54 \quad (r^2 = 0.95;\ n = 6) \quad (10)$$

Although this correlation is based on a preliminary data set and involves the difficulties in comparing data from different studies obtained by dissimilar methods, it provides a reasonable first approximation for calculating the sorption coefficient of TCE for organic matter of different compositions. It also permits correction of K_{OC} values derived from K_{OW} data. Assuming that the existing correlations between log K_{OC} and log K_{OW} are based mostly on soil humic material with a H/O ratio of ~3, this yields the following correction for eq 4:

$$\log K_{OC} = a \log K_{OW} + b + (1.52 \log [H]/[O] - 0.73) \quad (11)$$

This correction is based on the K_{OC} for TCE but probably indicates a general trend; further work is needed to ascertain the validity of this correlation for other nonionic compounds.

Conclusions

Many of the K_{OC} values and K_{OW}-derived values for K_{OC} reported in the literature for nonionic compounds (such as chloroaliphatics) fail to account for variations in the composition of natural organic matter and are therefore likely to be misleading when used to predict sorption coefficients such as K_d. The data presented here emphasize the importance of the nature of the organic matter for the sorption of nonionic compounds. The results suggest that an empirical relationship exists between K_{OC} and the elemental composition (here expressed as the atomic H/O ratio) in natural organic matter. The use of the H/O ratio to adjust the K_{OW}-based estimates of K_{OC} may be regarded as tentative until more data confirm the correlation. This relationship may be used to provide a better assessment of K_{OC} for organic matter occurring in the subsurface environment. As a first approximation, the composition of the organic material may be estimated by the origin and geological history of the material (e.g., the degree of coalification or the stage of weathering for ker-

Table V. O/C, H/C, and H/O Atomic Ratios and K_{OC} for TCE

sample	log K_{OC}(TCE)	H/C	O/C	H/O
shale (tertiary)[a]	2.63	1.35	0.20	6.75
shale (jurassic)[b]	3.19	1.30	0.10	13.00
peat[c]	2.23	1.20	0.53	2.26
lignite[c]	2.43	0.80	0.18	4.41
bituminous coal[c]	3.24	0.78	0.06	12.48
anthracite[c]	3.64	0.32	0.02	19.85
humic acid[d]	1.76	1.95	0.84	2.32
humic acid (Aldrich)[d]	1.83	0.71	0.26	2.70
fulvic acid[d]	0.62	2.20	1.19	1.85
lignin[d]	2.08	1.05	0.29	3.64
zein[d]	2.05	1.50	0.26	5.75
cellulose[d]	0.30	1.61	0.80	2.00
tannin acid[d]	1.24	0.89	0.68	1.30

[a] H/C and O/C ratios from Durand (*9*). [b] H/C and O/C ratios from Küspert (*35*). [c] H/C and O/C ratios according to the degree of coalification–vitrinite reflection [Given (*36*)]. [d] K_{OC} and elemental analyses for organic substances from Garbarini and Lion (*11*).

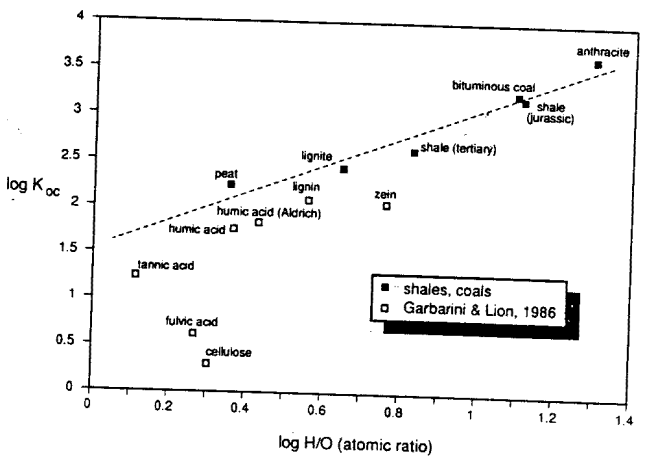

Figure 5. log H/O versus log K_{OC} for TCE. Includes data from Garbarini and Lion (*11*). Regression (dotted line) based on shale and coal samples from current study (eq 10).

ogen-containing shales, mudrocks, etc.). The results reported here support rather an extension of the K_{OC} concept for organic matter of different composition than a limitation. However, there is a need for further research to relate the structure and composition of natural organic matter to sorption processes. Also tools such as solid-state ^{13}C nuclear magnetic resonance spectroscopy might provide insights into the composition and structure of organic matter and contribute to a better understanding of organic matter influenced processes in the subsurface environment. Although the data presented here are for the sorption of nonionic compounds, the variability in the natural organic matter may also be important for other contaminants and processes taking place in soils and sediments.

Acknowledgments

I would like to thank Prof. G. Einsele for his advice and continuous interest in this study and R. Seelig, F. Forster, and A. Voutta for experimental support (Institute for Geology and Paleontology, Tübingen). The paper also benefited from reviews by J. E. Barbash and G. P. Curtis (Environmental Engineering and Science, Stanford University).

Registry No. TCM, 67-66-3; TCA, 71-55-6; TCE, 79-01-6; PCE, 127-18-4.

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Received for review February 6, 1990. Revised manuscript received June 22, 1990. Accepted June 28, 1990. This study was financed in part by Harress Geotechnik GmbH (8856 Harburg/Schwaben, West Germany). Further funding was provided by the state of Baden-Württemberg, West Germany (Projekt Wasser-Abfall-Boden, PA 86030).

Statistical Analysis of Mass-Transfer Parameters for Sorption Processes and Models

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■ The determination of mass-transfer parameters for sorption processes involving microporous solids such as activated carbon, ion-exchange resins, and soil particles and aggregates is an important element in the modeling and design of separation and purification processes and in the description of sorption phenomena in natural and environmental systems. Such determinations are typically carried out by fitting appropriate mathematical models to sets of rate data obtained in laboratory or field-scale experiments. An aspect of such determinations that has been largely neglected is the evaluation of statistical confidence. Determination of confidence for sorption parameters is made difficult by the use of nonlinear mathematical models and the existence of multiple, jointly determined parameters. This paper presents a method for determining preliminary estimates of confidence intervals for two jointly determined mass-transfer parameters describing sorption by microporous solids in fixed-bed reactors. An application of the method to examine the statistical significance of dissolved background organic substances on rates of adsorption of a specifically targeted compound, *p*-dichlorobenzene, from different complex aqueous solutions is presented.

Introduction

Microporous adsorbents such as activated carbon and macroreticular resins are used widely to remove organic and inorganic contaminants from waters, wastes, and industrial process streams. The design of appropriate adsorber systems is traditionally performed by executing pilot-scale tests to determine configurations and dimensions required for the full-scale process. An alternative and/or complementary approach is to use mathematical design models in conjunction with bench-scale tests to reduce the number and length of pilot plant experiments required to carry out a reasonable design procedure. Weber and Smith (*1*) have summarized such models and their applications and limitations.

Recent work by Smith and Weber (*2*) demonstrates a typical modeling approach to adsorber design. The method involves determination of model parameters by calibration to experimental data obtained from bench- or pilot-scale investigations; the calibrated model is then used to predict the behavior of larger scale systems. Such modeling exercises should be carried out in a standardized manner to ensure that the determined parameter values are the best possible estimates. Because adsorption models are generally mathematically nonlinear, standard residual minimization techniques are frequently difficult to apply. In addition, an aspect of these determinations that is frequently neglected is the estimation of statistical confidence for the model parameters. The examination of statistical confidence for adsorption parameters is important to demonstrate the efficacy and reliability of system designs. As is the case for the determination of model parameters, the nonlinearity of most adsorption models makes the determination of confidence difficult. This paper develops a methodology for statistically evaluating mass-transfer parameters for adsorption models and for making estimates of corresponding confidence limits. An example of the application of these methods for determining the significance of potential interferences of dissolved background organic substances on the mass-transfer rates for adsorption of compounds specifically targeted for removal by granular activated carbon adsorbers is presented. Similar types of mass-transfer-based sorption models are increasingly being used to characterize contaminant behavior in porous media associated with subsurface environments (*3–6*). The substance of this paper addresses such modeling applications as well.

Model Exposition

The model employed in the development of the search and statistical methods described here is a two-resistance model involving external mass transfer at the adsorbent/water interface and intraparticle mass transfer along the pore surfaces of microporous adsorbents (*1, 2*). The mass-transfer parameters associated with these two resistances are, respectively, an external "film" transfer coefficient, k_f (m/s), and an intraparticle surface diffusion coefficient, D_s (m^2/s). A brief recapitulation of the model is presented to clarify the parameters examined.

There are two governing equations for the fixed-bed version of the model, which applies to the type of reactor system illustrated schematically in Figure 1. The liquid-phase continuity equation written in one-dimensional form is

$$\frac{\partial C}{\partial t} = -v_z\frac{\partial C}{\partial z} + D_h\frac{\partial^2 C}{\partial z^2} - \rho\frac{1-\epsilon}{\epsilon}\frac{\partial q}{\partial t} \qquad (1)$$

where C is the liquid-phase concentration of solute (kg/m^3) at column position z and time t, z being distance along the (axial) direction of fluid flow; q is the solid-phase concentration of solute (kg/kg of adsorbent) at radial position r within an adsorbent particle and time t; v_z is the interstitial velocity in the direction z(m/s); t is time (s); ρ is the apparent particle density (kg of adsorbent/m^3); ϵ is the bed void fraction (ϵ is the volume of fluid accomodated by the bed divided by the total volume of the bed) (dimensionless); and D_h is the axial hydrodynamic dispersion coefficient for one-dimensional flow (m^2/s).

The other governing equation describes the solid-phase (intraparticle) continuity relationship for the solute:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \qquad (2)$$

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