

Interactions between a Hydrophobic Organic Chemical and Natural Organic Matter: Equilibrium and Kinetic Studies

WENDELA SCHLEBAUM,^{†,‡}
ALEKSANDRA BADORA,^{‡,§}
GOSSE SCHRAA,[‡] AND
WILLEM H. VAN RIEMSDIJK^{*,†}

Department of Environmental Sciences, Subdepartment Soil Science and Plant Nutrition, Wageningen Agricultural University, P.O. Box 8005, 6700 EC Wageningen, The Netherlands, and Laboratory for Microbiology, Wageningen Agricultural University, H. van Suchtelenweg 4, 6703 CT Wageningen, The Netherlands

Interactions between a well-characterized, purified, peat humic acid and pentachlorobenzene were studied in equilibrium and kinetic experiments. The kinetic experiments, performed with a gas-purge method, showed the presence of a fast-desorbing, labile fraction and a slow-desorbing, nonlabile fraction. Increased contact time did not change the measured continuous desorption curves. A desorption experiment with interrupted flow and the measured isotherm suggested nonlinear sorption behavior. A first-order model consisting of two parallel "sites" could describe the continuous desorption curves but failed to describe the adsorption isotherm and the desorption curve with interrupted flow. A Langmuir model with one site was able to describe the characteristics of the desorption experiments and of the adsorption isotherm, but it did not describe the observed nonlabile fraction. Expanding the model with an additional Langmuir or first-order site did not lead to a good description of the various experiments. We speculate that the nonlabile fraction is a consequence of a change of conformation of the humic acid after the binding of pentachlorobenzene. This structural change leads to entrapment of pentachlorobenzene within the humic acid structure.

Introduction

Remediation of polluted soils or sediments may be hindered by the binding of hydrophobic organic chemicals (HOCs) on or into the soil matrix. For risk evaluation of polluted soils or to be able to predict the outcome of remediation projects, one should be able to describe the binding. Equilibrium partitioning expressions can be used to describe the binding when the time scale of transport and degradation is larger than the time scale of sorption. When equilibrium expressions are used, sorption is regarded to be instantaneous. However, sorption processes may have time scales of weeks

or months, thus prescribing the use of kinetic expressions (1).

The release of HOCs from soils and sediments often shows biphasic desorption behavior with a fast-desorbing, labile fraction and a slow-desorbing, nonlabile fraction. The important role of organic matter in the overall binding is well established as demonstrated by the use of organic carbon-normalized partition coefficients. However, only in recent literature the possible role of organic matter in slow sorption has received more attention. It is suggested that the labile fraction is composed of relatively open humic structures and the nonlabile fraction is composed of more condensed, rigid humic structures (2–4).

Rigid humic structures may be formed by humin or kerogene-like materials (3), but also humic acids may have condensed and rigid regions (1, 4–6). This implies that for rigid humic acid structures slow sorption kinetics can be observed. Only a few studies have been focused on the kinetics of interactions between humic substances and neutral HOC. McCarthy and Jimenez (7) and Hassett and Milicic (8) were unable to detect biphasic desorption for aqueous solutions of a commercial humic acid (Aldrich humic acid), but Aochi and Farmer (6) did detect biphasic sorption behavior for 1,2-dichloroethane in the vapor state and dry soil humic acids. The latter study also demonstrated that slow sorption kinetics were correlated to the presence of rigid structures in the humic acids.

To investigate the interactions between a nonionic hydrophobic organic pollutant (pentachlorobenzene) and organic matter in soils, we used a well-characterized peat humic acid (9, 10). For the peat humic acid studied, a molecular weight of 23 000 has been given as an upper limit (9). On the basis of proton titrations and this molecular weight, the radius of the humic acid particles has been determined to be between 2 and 4 nm, depending on the salt level (10). Since pentachlorobenzene has a radius of 0.32 nm, we do not regard radial diffusion or intraorganic matter diffusion as a rate-limiting process for the interactions between pentachlorobenzene and peat humic acid. Sorption on or into rigid structures, however, may take place.

To get a better understanding of the kinetics of the interactions and the nature of the binding between pentachlorobenzene and peat humic acid, equilibrium and kinetic experiments were performed. The adsorption isotherm was measured in a batch system, while desorption kinetics were studied in a gas-purge system. Furthermore, desorption kinetics were measured continuously and in an experiment with interrupted flow. As the experiments differ in experimental setup, they can be used to test the predictive capability of different models.

Experimental Section

Materials. Humic acids were prepared from "Irish Peat" following the extraction procedure of the International Humic Substances Society, as modified by Reid et al. (11). Pentachlorobenzene (QCB, Merck, 98% pure) was used as the hydrophobic organic pollutant. The purified peat humic acids (ppHA) solutions for adsorption and desorption experiments had a concentration of 500 mg L⁻¹, were set to pH = 5, and had a background electrolyte concentration of 0.01 M NaNO₃. To ensure an equilibrium conformation of ppHA, all ppHA solutions were prepared 24 h before adsorption of QCB took place.

To determine the QCB concentration in humic and aqueous solutions, samples were extracted with hexane at

* Corresponding author e-mail address: willem.vanriemsdijk@bodsch.benp.wau.nl; phone: +31 317 482339; fax: +31 317 483766.

[†] Subdepartment Soil Science and Plant Nutrition.

[‡] Laboratory for Microbiology.

[§] Present address: Department of Agricultural Chemistry, Agricultural University of Kraków, Akademicka 1, 20-950 Lublin, Poland.

room temperature for at least 24 h. QCB in the hexane phase was analyzed with a Hewlett-Packard 5890 series II gas chromatograph equipped with a HP 5 column and a Hewlett-Packard mass selective detector (series 5971) in selective ion monitoring mode.

The loading of an aqueous solution with or without humic acids was done via the gas phase at 20 °C. Air was pumped through a glass tube filled with pure QCB. The air with QCB in the vapor state was led through the aqueous solution under continuous stirring. Gas flow in the adsorption studies was approximately 70 mL min⁻¹. In this way, a controlled loading of the humic acids was achieved.

Adsorption Isotherm. The equilibrium dialysis method (12) was used to determine the adsorption isotherm. A 5-mL sample of a ppHA solution (500 mg L⁻¹, pH 5, 0.01 M NaNO₃) was added to a dialysis bag (Spectra/Por 7, mol wt cutoff of 1000) and placed in a 125-mL glass jar containing 100 mL of an aqueous solution of QCB (pH 5, 0.01 M NaNO₃) at different concentrations. The jar was sealed with a Viton-lined cap and shaken (end-over-end) in the dark at 20 °C for 6 days. After 6 days, the QCB concentration was measured inside and outside the bag. In initial experiments, the time needed to reach constant concentrations inside and outside the dialysis bag was determined to be less than 6 days.

Desorption Experiments. The gas-purge experimental setup was based on the one used by Karickhoff and Morris (13). The purge bottles, which had a diameter of 5 cm and a suspension volume of 100 mL, were thermostated at 20 °C. Experiments were done in triplicate as three bottles could be purged (parallel, with individual flow meters) at the same time. Some data sets consist of duplicates as a result of gas leakage in one of the three bottles. The solutions were purged with 500 mL min⁻¹ nitrogen. QCB was trapped on columns with approximately 2 g of Tenax (Tenax TA 60–80 mesh Chrompack, used as received). Tenax columns were extracted with 10 mL of hexane. In preliminary experiments, it was determined that 10 mL of hexane was sufficient for total extraction of QCB from the Tenax column. The hexane samples were concentrated under air after the addition of an internal standard, 1,2,4,5-tetrachlorobenzene (Aldrich, 98% pure) in hexane, and analyzed. At the end of a desorption experiment, the residual concentration was measured in 5-mL samples from the bottles (extracted with 1 mL of hexane). The initial total concentration for the desorption experiments was calculated by combining the amount recovered on the Tenax columns and the residual amount in the solution. The recoveries were 80%–120%. A solution of QCB in water was purged to determine the rate with which the chemical is stripped from the water phase. The value obtained for the gas-purge rate constant, k_{gp} was 5.28 h⁻¹.

Desorption was followed continuously in ppHA solutions with a high and a low initial QCB concentration. Humic acid solutions with a high initial QCB concentration were obtained after an 8 day period of adsorption via the gas phase. After this adsorption period, adsorption via the gas phase was stopped, and desorption kinetics were measured either at day 0, after 2 days, or after 29 days. The results from day 0 and day 29 were from the same adsorption batch. Half of it was used to measure desorption kinetics directly; the other half was set aside for 29 days at 10 °C in the dark, after which desorption kinetics were measured again. To measure the desorption kinetics of ppHA solutions with low initial QCB concentrations, concentrated humic acid solutions (pH 5, 0.01 M NaNO₃) were dissolved in an aqueous solution of QCB (pH 5, 0.01 M NaNO₃) resulting in the usual final ppHA concentration. These solutions were stored for 7 and 42 days at 20 °C. Both solutions were stirred in the first week. In none of the stored ppHA solutions were indications of microbial QCB degradation observed. The desorption experiment with interrupted flow started at a high initial

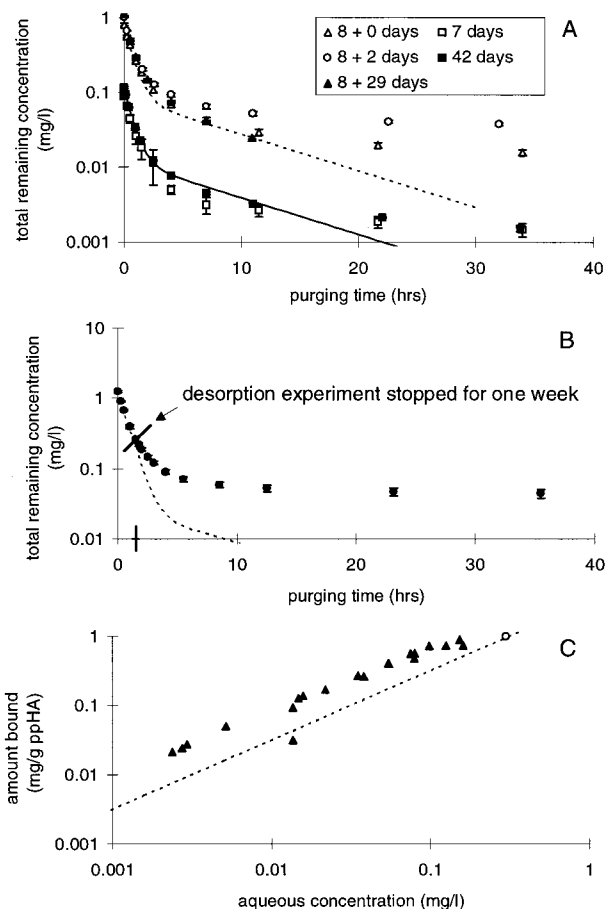


FIGURE 1. Measured data are represented by symbols, error bars (in A and B) represent standard deviations but may fall within the symbol. Fitted (solid line) and predicted (dashed line) curves are obtained with first-order model. (A) Continuous desorption of QCB from ppHA. For curves with a low initial concentration (± 0.1 mg L⁻¹), the given times indicate the contact time between QCB and ppHA (7 or 42 days) prior to desorption. The closed squares experiment was fitted. For curves with a high initial concentration (± 1.0 mg L⁻¹), the given times indicate the duration of loading via the gas phase (8 days) plus the additional period between the end of the adsorption via the gas phase and the start of the desorption experiment (0, 2, or 29 days). The open triangles experiment was predicted. (B) Desorption of QCB from ppHA with interrupted flow; the moment at which the purging is interrupted is indicated in the curve and on the x-axis. Note that the x-axis is continuous, indicating total purging time. (C) Adsorption isotherm. The partition coefficient, as calculated from maximum loading via the gas phase, is also given (open circle).

QCB concentration. After an 8 day period of adsorption via the gas phase, the ppHA solution was transferred to gas-purge bottles, and desorption was followed for 1.5 h. After 1.5 h, the purging was stopped, and the bottles were closed with Teflon-lined caps. The bottles were then shaken (end-over-end) for 7 days at 20 °C, after which the purging was resumed and desorption was followed again.

Results

Continuous desorption curves of ppHA solutions with a high (± 1 mg L⁻¹) and a low (± 0.1 mg L⁻¹) initial QCB concentration are shown in Figure 1A. High initial QCB concentrations were obtained by pumping air with QCB in the vapor state through an aqueous solution of ppHA. To investigate the effect of contact time between QCB and ppHA, desorption started either 0, 2, or 29 days after the end of the adsorption via the gas phase (high initial QCB concentrations) or 7 or

42 days after dissolving a ppHA solution in an aqueous solution of QCB (low initial QCB concentrations). The increased contact time between QCB and ppHA does not result in slower desorption. This implies that, for both the high and the low initial QCB concentrations, equilibrium binding is reached before the desorption experiment starts. Furthermore, the curves with a low and high initial concentration are remarkably similar. If, for all curves, the remaining concentrations (*y*-axis) are normalized to their initial concentrations, the low initial QCB concentration curves fall between the curves with a high initial concentration. Assuming that equilibrium has indeed been reached at the start of the experiments, it indicates that the desorption rate is independent of the total initial concentration. This is a typical characteristic of first-order kinetics that is based on linear sorption or partitioning.

Although desorption of the majority of QCB is fast (within 3–5 h), the desorption curves do show biphasic desorption, suggesting the existence of a slow desorbing fraction. The residual concentration is 1.3–3.7% of the total initial concentration. The slow desorbing fraction is not the result of insufficient purging, since it is not influenced by the QCB concentration in the aqueous phase.

The results of the desorption experiment in which the purging was interrupted for a period of 7 days are shown in Figure 1B. The temporary stop of the purging does not result in a visible discontinuity of the predicted desorption curve. No redistribution of QCB from the nonlabile fraction to the labile fraction is visible after 1 week of rest. This implies that either the rate constants are so small that no significant redistribution occurs during the period that no purging took place or that the system is very close to, or at, equilibrium when the purging stops. The latter is possible when the sorption behavior is nonlinear.

The adsorption isotherm of QCB and ppHA, measured with the dialysis method, and the calculated partition coefficient are shown in Figure 1C. The measured isotherm levels off above an aqueous concentration of 0.1 mg L⁻¹, indicating nonlinear sorption behavior. The partition coefficient of QCB and ppHA was calculated by measuring the maximum total concentration of QCB in aqueous and humic acid solutions after the loading of the solutions with QCB. If equilibrium is reached and maximum binding is achieved, the concentration in the water phase (*C*_(aq)) is equal to the solubility of QCB. The measured solubility of QCB in water was 0.30 ± 0.02 mg L⁻¹, and the apparent solubility in the humic acid solution was 0.81 ± 0.07 mg L⁻¹, which resulted in a bound concentration of 0.51 mg L⁻¹. This had been measured in experiments that lasted 20 days and in which equilibrium seemed to be reached after 7 days (data not shown). With an organic carbon (OC) content of approximately 50%, this gives an OC-normalized partition coefficient (*K*_{OC}) of 6800 or a log *K*_{OC} of 3.8. This value is comparable to values reported in the literature for soils and sediments (14).

Modeling Desorption Kinetics. Two models were tested to describe the interactions between QCB and ppHA, a first-order kinetic model and a kinetic model based on Langmuir sorption. A first-order model, which is based on a linear sorption isotherm, was tested since the desorption rate of the continuous desorption curves is independent of the total initial concentration. As both the adsorption isotherm and the desorption curve with interrupted flow seem to suggest nonlinear sorption, the second kinetic model tested is based on Langmuir sorption.

Different first-order models have been used in the literature to describe desorption from soils or sediments (13, 15–18). The most often used model is the two-compartment model with two “sites” in series (13, 15, 16). This model is usually related to diffusion into particles, which we do not

regard as a rate-limiting process for the interactions between QCB and ppHA. It is usually assumed that the two compartments differ only in kinetics and not in their affinity for the HOC (13, 15). The model used in this study is a parallel model with two discrete sites that may have different affinities for HOC and different sorption kinetics. Such a model may correspond to sorption on or into different humic structures that vary in hydrophobicity or rigidity. The equations defining the model are as follows, for *i* = 1, 2:

$$q_i = K_{p,i} C_{(aq)} \quad (1)$$

$$\frac{dq_i S}{dt} = -k_{d,i} q_i S + k_{a,i}^{app} C_{(aq)} S \quad (2)$$

and

$$\frac{dC_{(aq)}}{dt} = \sum_{i=1}^2 k_{d,i} q_i S - \sum_{i=1}^2 k_{a,i}^{app} C_{(aq)} S - k_{gp} C_{(aq)} \quad (3)$$

where *q_i* is the amount of QCB bound [mg of QCB (kg of ppHA)⁻¹] to site *i*; *C*_(aq) (mg L⁻¹) is the aqueous concentration of QCB; *K*_{*p,i*} (L kg⁻¹) is the partition coefficient for site *i*; *k*_{*d,i*} (h⁻¹) and *k*_{*a,i*}^{app} (h⁻¹) are the desorption and adsorption rate constants; *k*_{gp} is the gas-purge rate constant, and *S* (kg L⁻¹) is the sorbent concentration. Equations 1 and 2 are correlated since at equilibrium *dq_iS/dt* = 0, which gives *K*_{*p,i*} = *k*_{*a,i*}^{app} / (*k*_{*d,i*} *S*). As it is virtually impossible to determine the actual size of each site, the amount sorbed to each site is expressed as milligram per kilogram of sorbent instead of milligram per kilogram of site *i*. Note that it is necessary to use the amount of QCB bound (*q_i*) times the sorbent concentration (*S*) to be able to relate the amount bound to the concentration in the water phase (eqs 2 and 3). As the above equations imply that the adsorption rate constant is linear with the sorbent concentration, it is an apparent *k*_{*a,i*}. As the concentration of site *i* is unknown, the apparent adsorption rate constant (*k*_{*a,i*}^{app}) may be normalized by the total amount of sorbent present (*S*).

The Langmuir model may correspond to sorption on or into specific ppHA structures or holes (4). The equations defining a kinetic model based on Langmuir sorption behavior are

$$q = \frac{q_{max} K C_{(aq)}}{1 + K C_{(aq)}} \quad (4)$$

$$\frac{dqS}{dt} = -k_d qS + k_a^{app} C_{(aq)} (q_{max} S - qS) \quad (5)$$

$$\frac{dC_{(aq)}}{dt} = k_d qS - k_a^{app} C_{(aq)} (q_{max} S - qS) - k_{gp} C_{(aq)} \quad (6)$$

where *q*_{max} (mg kg⁻¹) is the capacity of the Langmuir site, *K* (L mg⁻¹) is the Langmuir binding coefficient, and *k*_{*a*}^{app} (L mg⁻¹ h⁻¹) is the apparent adsorption rate constant. The other symbols are as defined above (as only one site is present the subscript *i* is removed).

Starting from an initial guess, the unknown parameters for both models were fitted to the experimental data using a least-squares criterion and a Newton–Raphson method. Each iteration step involved numeric integration of the set of differential equations. We used a standard fourth-order Runge–Kutta method for this purpose. The initial condition for the desorption curves is dependent on the adsorption method. For the curves with a low initial QCB concentration, adsorption occurred via the water phase and for a known adsorption period. Therefore, the amount bound to the two sites at the start of the desorption period can easily be

TABLE 1. Parameters Obtained from the Fit with the First-Order Model and with the Langmuir Model^a

first-order		Langmuir	
$k_{a,1}^{app}$ (h ⁻¹)	4.02	k_a^{app} (L mg ⁻¹ h ⁻¹)	4.55
$k_{d,1}$ (h ⁻¹)	2.98	k_d (h ⁻¹)	1.66
$k_{a,2}^{app}$ (h ⁻¹)	0.027	q_{max} (mg kg ⁻¹)	2.74×10^3
$k_{d,2}$ (h ⁻¹)	0.11	K (L mg ⁻¹)	2.75
$K_{p,1}$ (L kg ⁻¹)	2.69×10^3		
$K_{p,2}$ (L kg ⁻¹)	4.82×10^2		

^a For the first-order model, the continuous desorption curve with a low initial concentration and an adsorption period of 42 days was fitted. For the Langmuir model, desorption with interrupted flow and the isotherm were fitted simultaneously.

calculated with the parameters that are fitted to the desorption curve. For the high initial QCB concentrations, an additional factor would have to be introduced to describe the adsorption via the gas phase. Since increased contact time did not result in lower desorption rates, equilibrium binding at the start of the desorption was assumed for the desorption curves with a high initial QCB concentration.

The validity of the first-order kinetics model was tested by fitting it to a continuous desorption curve with a low initial QCB concentration. The fitted parameters were then used to predict (1) continuous desorption with a high initial QCB concentration, (2) the measured adsorption isotherm, and (3) desorption with interrupted flow. These results are shown in Figure 1. The values for the parameters, obtained from the fitted data and used for the predicted curves, are given in Table 1. The fit of the continuous desorption curve with a low initial QCB concentration and an adsorption period of 42 days and the predicted high initial QCB concentration curve measured directly after the loading with QCB via the gas phase are given in Figure 1A. The fitted and predicted desorption curve are identical after normalizing the remaining concentration (y-axis) to the total initial concentration. The fit indicates that, for adsorption via the water phase, equilibrium is reached within 1 week (data not shown). This justifies our assumption that, for all the continuous desorption experiments, equilibrium was reached before desorption started. The model fails to describe the last data points, suggesting the presence of an additional site or even a distribution of sites. However, since only the last two data points are not described, these data are insufficient to justify the addition of another site to the model.

The prediction of the desorption experiment with interrupted flow follows the data closely until the data point at 1.5 h where the purging was temporarily stopped. The temporary stop of the purging results in a visible discontinuity of the predicted desorption curve. The predicted desorption rate is increased after the purging is resumed. The increase of the desorption rate is due to redistribution of QCB from the nonlabile fraction to the labile fraction during the period that no purging took place. This calculated effect is clearly at variance with the experimental data.

The measured and predicted adsorption isotherms are given in Figure 1C. The prediction underestimates the adsorption for almost the complete concentration range. The partition coefficient, which was calculated for maximum loading via the gas phase, is described well, although the data to which the model was fitted were below this concentration.

The Langmuir model was tested by fitting it simultaneously to the adsorption isotherm and to the desorption curve with interrupted flow. The continuous desorption curves were then predicted with the obtained parameters. The results obtained with the Langmuir model are given in Figure 2, and the values for the parameters, obtained from

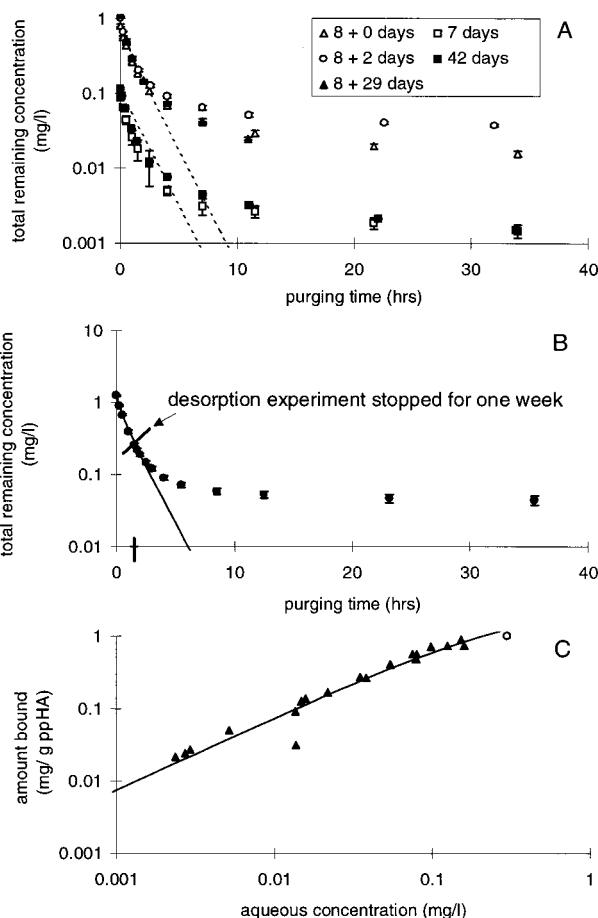


FIGURE 2. Fitted (solid line) and predicted (dashed line) curves obtained with Langmuir model. Measured data are represented by symbols and are also given and described in Figure 1. (A) Continuous desorption of QCB from ppHA. The open triangles and closed squares experiments are predicted. (B) Desorption of QCB from ppHA with interrupted flow. (C) Adsorption isotherm.

the fitted data and used for the predicted curves, are given in Table 1. The description of the adsorption isotherm is good (Figure 2C). Furthermore, the fact that the temporary stop of the purging does not result in a visible discontinuity of the desorption curve is now also well described (Figure 2B). The model description indicates that a slight redistribution of QCB occurs until 1.5 h after the end of the first desorption period. After the purging is resumed, the fitted curve follows the data closely for another hour. The tail of the desorption curve with interrupted flow cannot be described.

The measured and predicted continuous desorption curves are given in Figure 2A. The desorption curve with a high initial concentration can be described reasonably well for the initial 90% removed. For the desorption curve with a low initial concentration, the predicted desorption in the initial stage is less well described since the model underestimates the observed initial desorption rate. This is an intrinsic characteristic of the Langmuir model since Langmuir sorption implies that relatively more QCB is bound at lower concentrations, which will lead to lower desorption rates.

Discussion

Compared to the first-order model, the Langmuir model gives a better description of the adsorption isotherm, the desorption experiment with interrupted flow, and the continuous desorption experiments. For a better description of the tail of the desorption curves, the Langmuir model has to be

expanded. Although a model with two Langmuir sites is rather flexible with six fitting parameters, simulations (not shown) have indicated that this model cannot describe the complete set of data. To describe the nonlabile fraction, a Langmuir site with a high affinity (K) and small desorption rate constant (k_d) is needed. A high affinity will increase the relative amount of QCB bound to the nonlabile fraction at low initial QCB concentrations as compared to high initial QCB concentrations. This results in significantly lower desorption rates for the curves with a low initial concentration, which has not been observed experimentally. A small desorption rate constant and a moderate affinity will result in a small adsorption rate constant. With a small adsorption rate constant, increased contact time will increase the amount bound to the nonlabile fraction with a concomitant decrease of the desorption rates. This has also not been observed experimentally. In the Langmuir model with one site, this effect was small due to the relatively low affinity and large desorption rate constant of this site.

A model with a linear site to describe the labile fraction and a Langmuir site to describe the nonlabile fraction has been used by Xing and Pignatello (4) and Huang et al. (19). However, a fast adsorbing and desorbing linear site will lead to redistribution of QCB during the stop in the desorption experiment with interrupted flow. This was not observed in our experiments. Furthermore, as discussed above, the nonlabile fraction in the continuous desorption experiments could not be described with a Langmuir term.

As increased contact time did not result in lower desorption rates, slow adsorption or diffusion processes into rigid structures do not seem to occur for the interactions between QCB and ppHA. The biphasic desorption curves, however, suggest the presence of a slow desorbing fraction. The occupancy of this fraction increases linearly with the total amount initially sorbed. We could not find a model able to describe all our data. Although it may be very speculative, our results do show some similarity with the data from Kan et al. (20). They studied sorption kinetics of naphthalene to sediment and surrogate sediments in experiments consisting of several successive adsorption/desorption steps. Part of the amount sorbed seemed to resist desorption but could be extracted with an organic solvent and was defined to be "irreversibly" bound. The amount bound to this fraction increased proportionally to the initial naphthalene concentration. The term irreversible was used to imply that there is a rearrangement of the solid or organic carbon matrix in an irreversible manner and that desorption from this altered solid or matrix is not the reverse of the adsorption process. In our study, the residual concentration is also proportional to the initial concentration. Furthermore, part of the amount sorbed resists desorption. The latter was clearly visible in the desorption experiment with interrupted flow. For humic acids, a change of the conformation after adsorption of a pollutant may occur. This change of conformation may well lead to entrapment of QCB. For ppHA and QCB, the change occurs relatively fast since slow adsorption was not observed. Irreversible sorption or entrapment of QCB in the ppHA structure is not likely to be

described with simple equations. Furthermore, these phenomena are easily overlooked with most experimental methods. If only continuous desorption curves would have been measured, the nonlinear nature of the binding of QCB to ppHA would not have been detected. Our experiments demonstrate that the interactions between HOC and natural organic matter in soils or even purified humic acids are not yet fully understood. However, it is clear that simple linear sorption or partitioning is not able to describe the interactions between QCB and humic acid.

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