

Reports

A Gel Partition Model for Organic Desorption from a Pond Sediment

Abstract. Adsorption at the water-sediment interface has been correlated with the organic carbon content of natural sediment samples and with water-octanol partitioning equilibria. In deriving a new model for sorption in sediment, it is assumed that adsorption is due to humin-kerogen polymers associated with the clay component in the sediment. The model includes solubility parameter theory applied to solute-gel-liquid interactions and a theory of the liquid-polymer interactions that control gel swelling. Partially swollen gels are expected to exhibit impeded diffusion. These concepts are able to explain observations of limited desorption of certain organic compounds from natural sediments and soil minerals. Experiments were performed in which extractive solvents flowed through a liquid chromatographic column packed with dried estuarine and pond sediment samples and the effluent was analyzed for a test lipophilic compound, di(2-ethylhexyl) phthalate. The model predicts that the maximum desorption rate and the maximum extent of gel swelling should coincide and, conversely, that the desorption rate should be diffusion-limited if the polymer gel is only partially swollen. The conditions for maximum desorption and for diffusion-limited desorption were both observed experimentally.

There is growing interest in the fate of numerous natural and man-made organic chemicals in the environment. Transported and transformed by air, water, and biota, they are found as complex mixtures in soils and sediments, where they are difficult to measure (1). Organic compounds are not easily removed from such samples, and incomplete extraction is a source of error in subsequent measurements. The difficulty in making quantitative determinations was demonstrated in a recent interlaboratory study of environmentally persistent compounds in sediment. There were discrepancies of more than two orders of magnitude in the measurements (2). These considerations led to a search for ways to achieve more complete extraction of organic substances from a geological matrix.

As described in this report, we derived a sediment model to express the natural affinity of nonpolar compounds for the relatively nonpolar polymeric component (called humin or kerogen) that is present in most sediments. We then used physical considerations to derive criteria that minimize this affinity and maximize the ease of extraction. For comparison with the theory, we performed experiments on the liquid extraction of a lipo-

philic compound in a simplified situation where the compound was known to be present in high concentration in an industrial pond sediment. Before discussing these experiments, however, it is necessary to deal with a contradiction between reported water-sediment partitioning data that suggest an equilibrium process and reported desorptive impediments that imply the opposite.

Adsorption of lipophilic compounds at the water-sediment interface compares well with water-octanol partitioning equilibria with an explicit dependence on the organic carbon content of the sediment (3-5). Adsorption of organic substances by sediment may be reversible and, further, neutral organic compounds may undergo reversible desorption. However, it has been reported that desorption from soils can be strongly impeded by a "lock-in" mechanism (6) or by hypothesized cage effects (7). It is important to be able to distinguish experimentally between the achievement of equilibrium and the sorptive limitations due to slow dynamic processes. The model described in this report predicts the conditions under which either equilibrium or impeded desorption is favored.

We assumed that the sorptive proper-

ties of a sediment are due primarily to its organic structure and that sediments adsorb uncharged lipophilic organic compounds because of the humin-kerogen polymers, which are chemically bound to a mineral substrate. This is consistent with the cross-linked network structure suggested by Degens and Mopper (8). The humin-kerogen structure is pictured as consisting of highly branched polymer chains that form a three-dimensional, randomly oriented network. The density of cross-links, or chain interconnections, prevents the network from dissolving in liquids, except by reaction. Instead, the liquid may be absorbed, or imbibed; typically, this type of process is accompanied by network swelling to form a gel. The amount of imbibition depends on the network compatibility with the liquid. The swelling limit is fixed by the density of the cross-links. The observed gel-type swelling behavior of "humic acid" (9) and the swelling "spectrum" of coal (10) are consistent with this gel model of humin-kerogen polymers.

Sorption of diffusible lipophilic solutes in a liquid-gel partitioning system should be controlled by the relative solute affinities of the liquid and gel phases. Except for special circumstances that are not considered here, the partitioning effect is less likely to be due to the mineral support phase.

Several key properties of a liquid-gel system are expected to control solute sorption by the gel phase. The sorption of lipophilic solutes and the degree of solvent imbibition are both expected to be strongly dependent on the relative polarities, along with other interactive or acid-base properties, of the two phases. Solute selectivity in liquid-gel media occurs in addition to a molecular sieve effect. The overall selectivity also depends on diphasic liquid-gel-solute interactions, which have been treated by using a theory developed by Hildebrand and Scott (11) and by Scatchard (12). Combining both the sieving and the interactive effects (13), we derived the following expression for the solute partitioning coefficient K_i :

$$\ln K_i = A - BL_i + \frac{V_i}{RT} f(\delta) \quad (1)$$

where the coefficients A and $B > 0$ refer to the pore structure of the gel phase, L_i is the size of the partitioning solute i , V_i is the solute molar volume, R is the gas constant, and T is absolute temperature. Solute partitioning between liquid and gel depends on competing attractive effects due to solute-liquid and solute-gel interactions. The net solute preference for either phase is represented by the

solubility parameter function $f(\delta)$, where the square of the value of δ for a nonpolar molecule is defined as the energy of vaporization per unit volume, known as the cohesive energy density. The value of $f(\delta)$ is given by

$$f(\delta) = (\delta_i - \delta_m)^2 - (\delta_i - \delta_g)^2 \quad (2)$$

or

$$f(\delta) = (\delta_m - \delta_g)(\delta_m + \delta_g - 2\delta_i) \quad (3)$$

where subscripts m and g refer to the liquid and gel phases, respectively, and each δ value refers to the solubility parameter of the subscripted component. Equations 2 and 3 define a region of minimal solute sorption by the gel phase, that is, a region where $K_i \leq 1$. This occurs between the solubility parameter limits at $\delta_i = \delta_m$ and $\delta_m = \delta_g$. (In the following, matched substances are those having equal solubility parameters.)

Gel swelling effects were correlated by Flory (14) with polymer-solvent interaction parameters. In terms of the logically equivalent solubility parameters, maximum gel swelling is expected when the network and the liquid properties are matched, that is, when $\delta_g = \delta_m$. The swelling behavior of synthetic polymer networks (15) and natural ones such as coal (10) illustrates this effect. Huminkrogen swelling behavior should be consistent with the water-octanol model for water-sediment partitioning. Therefore the swelling maximum for these polymers is expected to occur near $\delta = 10.3$, since that is the value for *n*-octanol (16). Conversely, if the solubility parameters of the network and liquid are mismatched, correspondingly less swelling will occur. It follows that solute diffusion through a swollen gel should be significantly faster than that through the more densely entangled structure of a partially or completely deswollen gel.

Desorption of a solute also depends on its solubility in the extracting liquid. For convenience, we use the rule that like dissolves like and predict a solubility maximum when the solute and liquid are matched ($\delta_i = \delta_m$). The foregoing discussion of partitioning theory, gel swelling, and solubility considerations is illustrated in Fig. 1 with reference to the solutes and liquids described in the following section.

We conducted several experiments in an attempt to distinguish between equilibrium and nonequilibrium desorption from sediment. Homogenized clay-silt sediment samples were obtained from a reference site on Chesapeake Bay (76°16'N, 39°03'W) and from an industrial wastewater holding pond (17). Both samples contained notable amounts of an

adsorbed lipophile, di(2-ethylhexyl) phthalate (DEHP). After gentle drying to less than 1 percent residual water, these two samples had DEHP concentrations of 0.11 ± 0.01 ppm and 0.12 ± 0.01 percent, respectively. We also used two reference materials, a sample of fuller's earth (attapulgit, calcined at 1000°C and therefore practically carbon-free) and a sample of synthetic 12:1 styrene-divinylbenzene copolymer beads (PSDVB). Small amounts of DEHP in dichloromethane were added to the reference samples. The mixtures were homogenized and the solvent was removed. The modified samples were then found to contain 0.05 and 0.02 percent DEHP, respectively. Throughout this work, analysis was based on independent methods which showed that consistent desorption of the DEHP was obtained from the dried Chesapeake Bay sediment samples as a result of repeated batch ultrasonic agitation and Soxhlet extraction in dichloromethane. Significantly less complete extraction recovery was obtained with other solvents. We measured the DEHP by glass capillary gas chromatography-mass spectrometry with selected ion monitoring at mass-to-charge ratio (*m/e*) 149 and retention time confirmations at *m/e* 167, 177, and 279 (17, 18).

The following experiments were based on practically ideal test specimens due to

the naturally aged and conveniently high DEHP levels in the pond sediment. The experiments involved flow of pressurized solvent through 1-g samples of dry sediment that had been placed in liquid chromatographic (LC) columns (5 cm long; inner diameter, 4 mm). Initially, it was shown in a pair of tests (replicated five times) with dichloromethane that the batch ultrasonic extraction method gave 98 ± 5 percent removal of the DEHP while the column technique gave 101 ± 4 percent for 1-g samples. The LC column technique brings pure solvent to the head of the column; it facilitates sample fraction collection and is convenient for studying the effects of chemical or physical variables on the rate and degree of desorption. Desorption results obtained with several solvents are shown in Fig. 2. The extraction maximum, previously observed in batch tests with the estuarine sediment, is again apparent in the column extraction of the pond sediment.

The results in Fig. 2 show that desorption from the column also occurred rapidly when a nonoptimal solvent was used, but only a fraction of the DEHP was removed. The finding of a desorption maximum with dichloromethane is consistent with the gel partition model and inconsistent with adsorption due to the mineral components alone.

Elution of column sediment samples with flowing water proved far more difficult (19), and the amount of DEHP desorbed was well below our limit of detection (~ 10 ng). An attempt was made to improve sensitivity by the coupled column technique (20), but DEHP desorption was still not detected. We concluded that experiments with a continuous flow of liquid through the column could not be used to distinguish between a slow diffusion effect, since concentrations were soon below the limit of detection, and an irreversible adsorption effect, where the desorption rate would be zero. More sensitive experiments were needed.

The column experiments were modified by use of a pulsed-flow operating sequence. Column flow of hexane through the dried pond sediment was chosen for these experiments. The initial flow of liquid was allowed to continue until the collected fractions showed no further evidence for desorption. The flow was then stopped for a number of hours. Resuming the flow with a small amount of liquid then quickly removed additional amounts of DEHP that had been desorbed during the stopped-flow state. The operation was then returned to the stopped-flow condition. The last two steps—a pulse of flow to remove

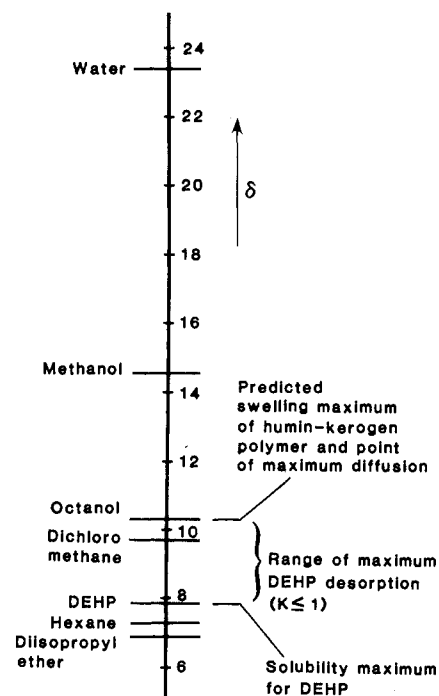


Fig. 1. Solubility parameters [from Burrell and Immergut (16)] are used to designate the conditions for optimal partition, humin-kerogen swelling, and solute solubility during liquid extraction of sediment.

desorbed solute, followed by stopped flow—were repeated until no further desorption could be detected.

The results of our first pulsed-flow experiments, shown in Fig. 3, indicate that the initially rapid desorption of DEHP from sediment is followed by substantially slower, diffusion-controlled desorption. More recent experiments (21) show the same pattern of diffusion-controlled desorption behavior in methanol. This finding of slow secondary diffusion can explain at least part of the lock-in effect as well as other evidence for incomplete desorption of lipophilic compounds from sediment or soil samples.

Secondary diffusion of uncharged lipophilic substances from sediment in the presence of hexane is consistent with the behavior expected of a partly collapsed gel network structure. The results seem to be analogous to evidence presented by Birr (22) for inaccessible gel network regions, which he proposed to explain impediments encountered during the Merrifield protein synthesis. Two brief tests were carried out to check this explanation. First, the modified sample of attapulgite was found to desorb its DEHP slowly during column elution with hexane. However, desorption by dichloromethane or methanol was rapid and complete. Similarly, column desorp-

tion tests on the modified PSDVB sample showed that only about 3 percent of the DEHP was readily removed by passing hexane through the column; further desorption occurred much more slowly. However, when the carrier was changed to pure tetrahydrofuran, the DEHP was desorbed rapidly. These results show that the behavior of the PSDVB gel, which is only slightly swollen by hexane but highly swollen by tetrahydrofuran (15), is similar to that of sediment during extraction under correspondingly varied conditions.

We find general agreement between the gel partition model and the hypothesized behavior of the humin-kerogen structure in sediment samples during extraction of the lipophilic solute DEHP. The model correctly predicts near-optimal extraction by dichloromethane and predicts conditions for gel contraction that are consistent with the finding of slow secondary diffusion in a nonoptimal liquid. The present experimental results show that partitioning (4) or adsorption (23) effects alone would tend to be irreversible unless the equilibrium condition is clearly demonstrated experimentally. In aqueous systems equilibrium may be particularly difficult to obtain.

In attempting to desorb lipophilic substances from sediment samples that are

finely divided, it is now clear that the humin-kerogen pore structure needs to be kept open by use of proper extractive conditions, including use of a suitable swelling-dissolving liquid that provides adequate diffusion rates. If the pore structure of the gel is not sufficiently open, which was evident with several liquids in this study, the time required for complete desorption may be much too long to be practical for conventional extractive technology.

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19. Two obstacles had to be overcome in order to elute water through wet sediment. A dilute solution of 0.03M $Mg(ClO_4)_2$ was added to the water to prevent peptization. Approximately 50 percent (by weight) sand particles (grain size, 0.5 to 0.9 mm) were added to prevent column compaction. We gratefully acknowledge the efforts of B. Petrocelli, who helped us find these elution conditions.
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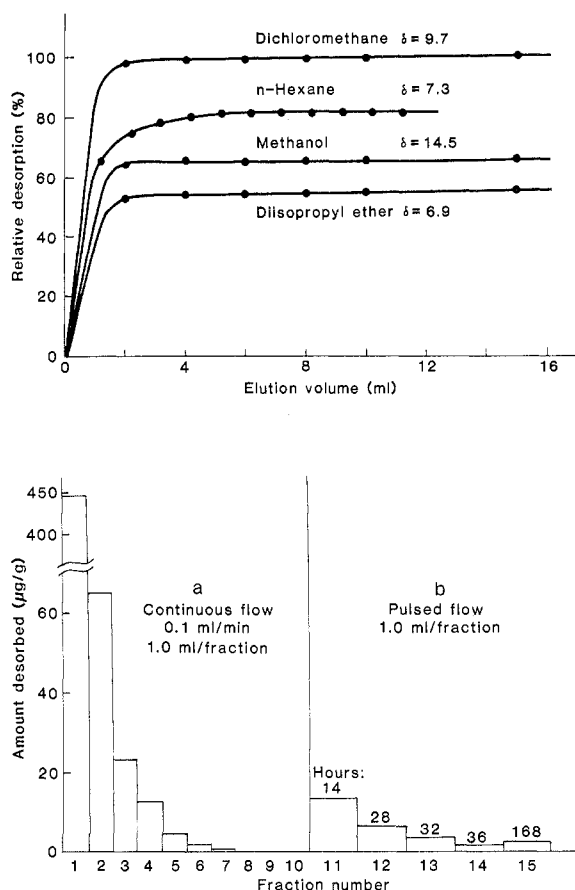


Fig. 2. Relative desorption of the lipophilic test solute DEHP for various liquids flowing at 0.2 ml/min (except hexane, at 0.1 ml/min) through a liquid chromatographic column ($24^\circ \pm 1^\circ\text{C}$) containing the sediment test sample. Previous experiments (17) showed that dichloromethane gives consistent DEHP extraction, which defines the apparent level of 100 percent desorption.

Fig. 3. Use of pulsed-flow column elution provides direct evidence for a secondary diffusion effect following initially rapid desorption of DEHP with hexane. The experiments in (a) involved continuous flow and those in (b) involved flow stoppage for the designated periods of time. After the stopped-flow period, the desorbed solute was easily removed from the test column.