# SORPTION OF HYDROPHOBIC COMPOUNDS BY SEDIMENTS, SOILS AND SUSPENDED SOLIDS—II

## SORBENT EVALUATION STUDIES

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**Abstract**—Concepts underlying the sorption of hydrophobic compounds and models for representation of observed equilibrium relationships were presented in Part I of this series. The earlier paper also summarized and evaluated major factors which affect the sorption of pollutants in natural environmental systems. This second part of the series presents a detailed summary and evaluation of the sorption of a particular class of hydrophobic pollutants, polychlorinated biphenyls (PCB), on a variety of different types of sediments, soils, suspended solids, and microorganisms. Equilibrium models described in Part I are used here to describe and analyze the PCB sorption data.

## INTRODUCTION

This series examines the influence of sorption reactions on the behavior of pollutants in environmental systems, in particular hydrophobic pollutants in aqueous systems. Complex slightly soluble organic compounds comprise many of the most indictable contaminants of aquatic environments. It is increasingly evident, moreover, that the transport and fate of such compounds in aquatic systems, as well as their partitioning to and from other compartments of the environment, depend markedly on sorptive interactions with non-aqueous phases; notably sediments and suspended solids.

Part I of the series (Voice and Weber, 1983) considered the theoretical and experimental evidence relating to the sorption of hydrophobic compounds in aquatic systems. The vast majority of the reports cited involved studies on other types of systems—most frequently soil/pesticide systems. Although such observations provide useful insights, any conclusions that are applied to dissimilar systems must be regarded as tentative until substantiated by direct experimental evidence.

Recent contributions by Smith *et al.* (1978); Karickhoff *et al.* (1979) and Means *et al.* (1980) have attempted to bridge this gap by conducting laboratory sorption studies with natural aquatic sediments and a number of hydrophobic solutes. These works have, for the most part, supported the supposition that the organic carbon content of the sediment and octanol–water partition coefficient of the solute are the most reliable indicators of sorption capacity.

The studies mentioned above have focused primarily on aquatic sediments and thus are somewhat limited to a range of sorbent characteristics typical of those found at the bottom boundary layer of most aquatic systems. The studies reported in this paper attempt to extend this data base by considering a full range of materials that can sorb hydrophobic pollutants. As this effort was primarily concerned with sorption reactions that may be important in the Laurentian Great Lakes, particular emphasis was given to evaluating suspended material characteristic of that found in these bodies of water and their tributaries.

### PILOT COMPOUND SELECTION

Revelation of the widespread contamination of aquatic environments by chlorinated hydrocarbons has provided an impetus for concern regarding the transport, fate and impact of these and other hydrophobic pollutants. Although a large number of such compounds have been released to the environment, few have generated the level of concern surrounding polychlorinated biphenyls (PCBs). The physical and chemical similarities of PCBs and the chlorinated hydrocarbon insecticides (e.g. DDT), coupled with their extensive utilization in a number of industrial applications, constitute the basis for this concern. Widespread environmental contamination by PCBs, their possible toxicological implications, their similarities to other compounds of environmental significance, and the availability of an extensive body of related literature led to the selection of a commer-

cial mixture of PCBs, Aroclor 1254[®], as the pilot compound class for this study.

The complex nature of Aroclor 1254 poses a number of problems. At least 69 different chlorobiphenyl isomers have been identified in the commercial mixture, and each can be expected to have slightly different physical and chemical characteristics. The aqueous solubility and octanol–water partition coefficient $(K_{ow})$ are probably the most important of these from the standpoint of sorption reactions. Solubility values reported in the literature for individual isomers range from $5.9\,\mathrm{mg\,l^{-1}}$ to $7.0\,\mathrm{ng\,l^{-1}}$ (Hutzinger *et al.*, 1974). Values for log $K_{ow}$ vary from 3.9 to 6.7 (Tulp & Hutzinger, 1979; Chiou *et al.*, 1977).

## SORBENT SELECTION

In pursuit of one of the primary goals of this study—the assessment of different natural materials able to function as sorbents of hydrophobic compounds—a number of clays, sediments, suspended solids and laboratory cultured microbial organisms were studied. These materials were selected to encompass the range of physical, chemical and biological characteristics of settleable materials commonly found in fresh water systems.

Three different clays were chosen to evaluate the role of inorganic materials in sorption processes and to compare physical sorption to partitioning reactions involving particle-associated organic matter. In light of the fact that physical sorption should be related predominantly to available surface area, two reference clays, kaolinite and montmorillonite, having markedly differently specific surface areas (10–20 and $100–110\,\mathrm{m^2 g^{-1}}$, respectively), were selected. A natural clay sample from the Rouge River (MI) drainage basin (designated Blue Clay) was also studied as a comparison.

Four different natural solids were studied to investigate the role of associated organic material. The Blue Clay and a Saginaw River (MI) sediment (designated Saginaw River Sediment 1), were stripped of all organic material and compared to the natural samples. A third sediment, Saginaw River 2, was studied extensively to investigate the role of humics, lipids, temperature and particle size, in addition to total organic carbon. The fourth sediment was a sand collected from Saginaw Bay (MI) and contained little associated organic material. The Saginaw River 2 and Saginaw Bay samples were collected from U.S. Environmental Protection Agency sampling stations designated 54 and 7, respectively, in these water bodies.

Three samples of suspended solids were studied: one from the Huron River near Ypsilanti, MI, and two from the Saginaw River. To assess the relative importance of solids contributed by sewage effluents, the Saginaw River samples were collected upstream from, and approximately one quarter mile downstream of, the Bay City, Michigan wastewater treat-

ment plant. All suspended solids samples were relatively high in organic content.

Finally, two cultures of microorganisms were grown in the laboratory for use in the sorption studies. Bacteria of the genus *Bacillus* were isolated from Saginaw River sediments and a mixed culture of algae was grown using Saginaw River water as inoculum. The genus *Chlorella* was found to dominate the culture, although traces of *Scenedesmus* and *Ankistrodesmus* were identified.

## SCOPE OF STUDY

The study was designed to evaluate the relative importance of various solids found in aquatic systems with respect to the sorption of hydrophobic pollutants. Because it has been shown previously that the organic content of a solid is of primary importance in this regard, an attempt was also made to further characterize this effect by selectively removing various organic fractions.

Both equilibrium and kinetic studies were conducted in all cases. Three models discussed and examined in detail in Part I of this series were used to quantify sorption relationships at equilibrium:

(i) The Freundlich model,

$$q_e = K_F C_e^{1/n} \qquad (1)$$

where $q_e$ is the amount sorbed $(\mu g\,g^{-1})$, $C_e$ is the equilibrium solution concentration $(\mu g\,l^{-1})$, and $K_F$ and $1/n$ are characteristic constants;

(ii) The Langmuir model,

$$q_e = \frac{Q^\circ b C_e}{1 + b C_e} \qquad (2)$$

where $Q^\circ$ is the "monolayer" sorption capacity and $b$ is the sorption coefficient; and,

(iii) The linear partitioning model,

$$q_e = \frac{K_p C_e}{1000} \qquad (3)$$

where $K_p$ is the partition coefficient and $q_e$ and $C_e$ are as previously defined.

## EXPERIMENTAL METHODS

The two reference clays, kaolinite and montmorillonite, were purchased from Wards Natural Science, Inc. and used as is. The remaining clay and all of the sediments were collected as grab samples, freeze-dried and stored in air-tight containers until used. It was determined that the freeze-drying procedure produced no significant changes in equilibrium capacity. The algae culture was grown by inoculating fresh water algal media (APHA, 1975) with Saginaw Bay water. The mixture was aerated continuously and illuminated for 12 h per day with Gro-Lux[®] lamps. Fresh cultures were prepared monthly using the old culture as inoculum. The bacteria were isolated from Saginaw River sediment by successive streaking onto nutrient agar. The culture was grown in lactose broth and stirred continuously in a dark, $20^\circ$C environment. Suspended solids samples were collected by filtering river water through a $0.45\text{-}\mu\mathrm{m}$ mem-

brane filter and repeatedly scraping the filter surface to recover solids. This procedure was carried out in the laboratory at 4°C to prevent sample deterioration.

In addition to studies on the solids as collected, purchased, or cultured, various procedures were employed to alter the characteristics of the solids. The effect on the sorption reaction was subsequently assessed. Complete removal of organic material was accomplished by hydrogen peroxide oxidation, while the lipid and humic fractions were selectively removed by benzene/methanol and sodium hydroxide extractions, respectively. Sorption by microorganisms was evaluated using both live and dead organisms. Bacteria were killed using silver nitrate and algae with copper sulfate. Death was confirmed by the absence of growth in fresh media inoculated with treated cultures.

Sorption equilibrium experiments for the bottom sediments and clays were performed in 1-l. Erlenmeyer flasks with ground-glass stoppers. Each flask, containing a known amount of solid material, was filled with 850 ml of Saginaw River water that had been passed through a 0.45-$\mu$m filter to remove suspended particulate matter. A slight headspace was left above the water surface to insure that agitation would be sufficiently turbulent to maintain particle suspension. Aroclor 1254 in an acetone carrier was then added to each flask to yield an initial PCB concentration of 30–40 $\mu$g l$^{-1}$. Each container was immediately stoppered and agitated by shaking for 24 h. After equilibration, two 12-ml aliquots were withdrawn and centrifuged for 30 min at 2600 rev min$^{-1}$, thus insuring virtually complete separation of liquid and solids. 10 ml of water were withdrawn from each sample and extracted with 2 ml of hexane in 6-dram screw-top vials with Teflon$^R$ liners. The flasks were emptied of the remaining water and 4 ml of hexane was added and swirled throughout to extract any Aroclor 1254 adsorbed onto the container walls.

The procedure employed for algae, bacteria and suspended solids was similar, although 150 ml Hypo-Vials$^R$ were used as reaction vessels. Each vial was filled with a known weight of solids, 125 ml of dilution water, spiked with PCB and shaken for 24 h. After equilibration, the vials were centrifuged and two 10-ml aliquots of the supernatant were extracted with hexane. All extracts were agitated for 5 min and stored at 4°C prior to analysis.

Sorption kinetic studies were conducted to determine rates of approach to equilibrium. The volatility of Aroclor 1254 necessitated the use of airtight, completely mixed batch (CMB) reactors. Each vessel was filled (2.6 l.) with water to eliminate headspace, and PCB in an acetone carrier was injected under the water surface. The solution was stirred for 15 min with a Teflon paddle to allow for mixing and sorption equilibration with glass reactor surfaces, after which the initial concentration was measured. After addition of the sorbent, stirring was held constant at 500 rev min$^{-1}$, a speed sufficient to maintain particle suspension. As 10-ml samples were removed at periodic intervals, the volume was displaced by glass plungers to prevent formation of a headspace. Samples were centrifuged and

extracted by the same procedure described for the equilibrium studies.

The hexane extracts were analyzed for Aroclor 1254 by electron-capture gas chromatography. A 6-ft long, 2-mm i.d. column packed with 3% OV-1 on 80/100 Gas Chrom Q$^R$ was found to provide good peak separation. The instrument was operated isothermally at a column temperature of 210°C using a nitrogen carrier.

The clays, sediments and suspended solids were analyzed for organic carbon content using a dry combustion technique.

## RESULTS AND DISCUSSION

Plots of the amount of PCB sorbed by the solid phase versus the amount remaining in solution at equilibrium reveal that most of the systems tested manifest reasonably linear phase-partitioning behavior at low solution concentrations. At higher solution concentrations, however, the sorptive partitioning is generally non-linear. Figure 1 shows typical Aroclor 1254 equilibrium sorption data exhibiting this type of behavior. The non-linear relationship observed at other than very low solution concentrations was found to accord with the Freundlich model. This is consistent with the findings of other studies reported in the soil-pesticides literature (Haque, 1975). The Freundlich model linearizes in logarithmic form, a fact which makes it particularly useful for analysis of sorption data that extend over large concentration ranges. As the present data vary over several orders of magnitude in both $q_e$ and $C_e$, the isotherm results are presented in log-log plots.

Figure 2 shows PCB isotherm data for the three clays: kaolinite, montmorillonite and the natural Blue Clay. As expected, the substantially higher specific surface area of montmorillonite relative to kaolinite (100–110 vs 10–20 m$^2$ g$^{-1}$) resulted in greater sorption of Aroclor 1254 by the former. The natural Blue Clay, however, which contains organic "impurities", is seen to have a far greater capacity than either of the two "pure" clays. To further investigate the importance of organic carbon, three materials, the Blue Clay and two Saginaw River sediments, were treated to remove associated organic matter by oxidation with hydrogen perioxide. The sorption isotherms for the organic-stripped solids are compared to these for the corresponding untreated natural materials in Fig. 3. Sorption capacity is obviously greatly reduced in all cases by the removal of organic material. This suggests that the findings of Lambert (1967) and others that organic carbon is one of the most important factors influencing sorption in soil/pesticide systems can be extended to the aquatic environment and further suggests that even trace amounts of organic material can overshadow the effects of large differences in surface area.

To gain further insight into the role of particle-associated organic material, several fractionations were performed on one of the Saginaw River sediments. Humic substances were removed by sodium hydroxide extraction and lipids were selectively re-
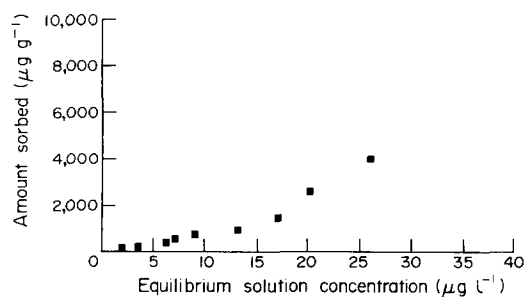


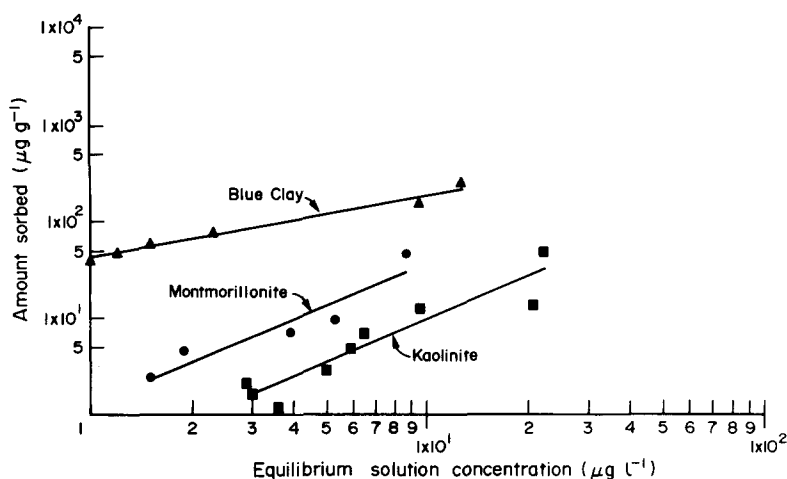Fig. 1. Sorption of Aroclor 1254 by Saginaw River sediment.

Fig. 2. Sorption of Aroclor 1254 by three clays.

moved by benzene/methanol (1:1 volume ratio) extraction. These treatments resulted in reductions in organic carbon content (24% for humics removal, 30% for lipids removal) and concurrent decreases in sorption capacity. It can be seen from Fig. 4 however, that the reductions effected by these two extractions were small relative to that of the hydrogen peroxide treatment, indicating that most of the associated organic material is in an insoluble form. Sorption data for the fraction of sediment smaller than 75 $\mu$m are also shown in Fig. 4. The increased capacity observed for the <75 $\mu$m size particles is in this case attributable to the increased organic carbon content of the smaller particles. The data suggest that the commonly observed effect of particle size on the sorption capacities of natural sediments may result primarily from the non-homogeneous physico-chemical nature of sediments, rather than from particle size *per se*.

Sorption data for the three suspended solids samples, shown in Fig. 5, indicate similar capacities for

the solids recovered from the Saginaw and Huron Rivers. The two samples from the Saginaw River, upstream and downstream of the Bay City sewage treatment facility, have similar organic carbon contents and nearly coincidental Freundlich isotherms. This may be due to the high solids content of the river at this point (30–40 ppm TSS) and the relatively low flow from the wastewater treatment plant ($\sim$15 cfs vs a river flow of $\sim$10,000 cfs) resulting in little net impact.

Sorption data for the live and dead cultured organisms are shown in Fig. 6. The algae appear to have a higher capacity than bacteria, and in both cases, live organisms sorbed slightly more than those that were treated. This suggests the possibility of active transport of sorbed compounds into viable cells, allowing additional surface sorption. However, the present study does not provide sufficient evidence to evaluate this hypothesis adequately.

Sorption experiments with one of the sorbents, the Saginaw River 2 sediment, were also conducted at
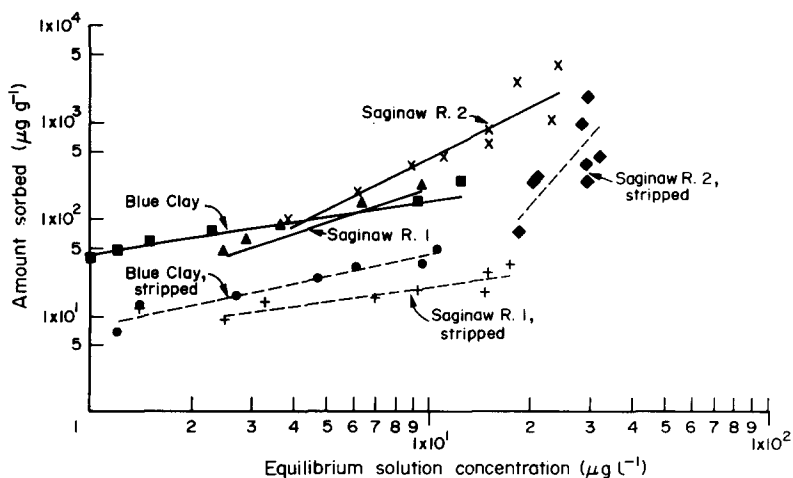


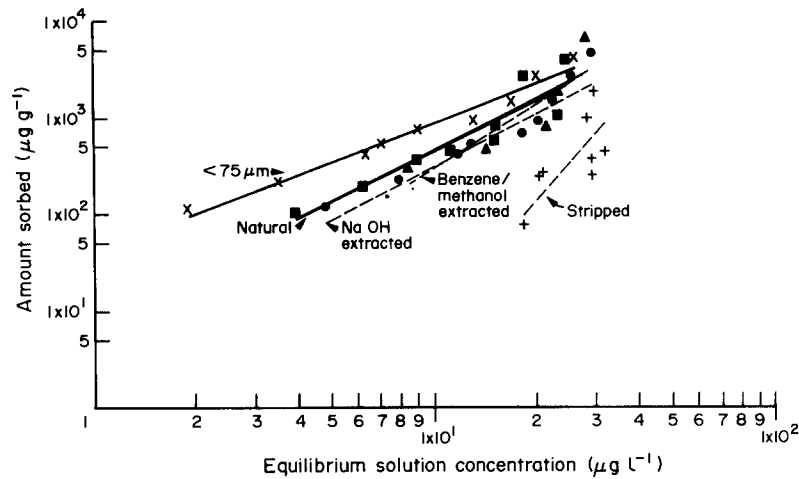Fig. 3. Sorption of Aroclor 1254 by natural and organics stripped ($H_2O_2$ oxidation) materials.

Fig. 4. Sorption of Aroclor 1254 by various fractions of Saginaw River sediment.

12°C and the data were compared to results obtained at the normal experimental temperature of ~22°C. This comparison, presented in Fig. 7, indicates that sorption of Aroclor 1254 decreases significantly at lower temperature.

Several of the isotherm studies have been replotted in Fig. 8 to illustrate the relative sorption capacities of various types of sorbents. It is evident from this figure that increased organic carbon generally results in increased sorption for solids with significant levels of associated organic material. There are, however, wide differences among sorbents having little associated organic material. It can therefore be assumed that in any real system containing a heterogeneous mixture of solids, hydrophobic pollutants will tend to accumulate in those materials with the highest organic content. This suggests that sorption to organics-laden solids can be thought of as a simple phase-partitioning reaction between highly polar (water) and non-polar (humin) phases. Relationships,

such as those developed by Karickhoff et al. (1979), which assume that sorption to organic material is analogous to octanol-water partitioning, may provide the possibility to predict partitioning a priori for such solids. In the absence of significant quantities of particle-associated organic material, sorption reactions may proceed via a number of other mechanisms for which similar predictive capabilities do not exist.

Table 1 shows the characteristic constants for the Langmuir, Freundlich, and linear-partitioning models, along with correlation coefficients obtained for each of the sorbents. The data are generally best described by the linear model over narrow ranges of concentration and by the Freundlich model where larger ranges of solution concentration are involved. The Langmuir model tends to fit the data poorly, particularly at high solution concentrations. An indication of the relative sorptive capacity of each solid is given by the values of the Freundlich constant, $K_F$, and the partition coefficient, $K_p$. Direct comparison
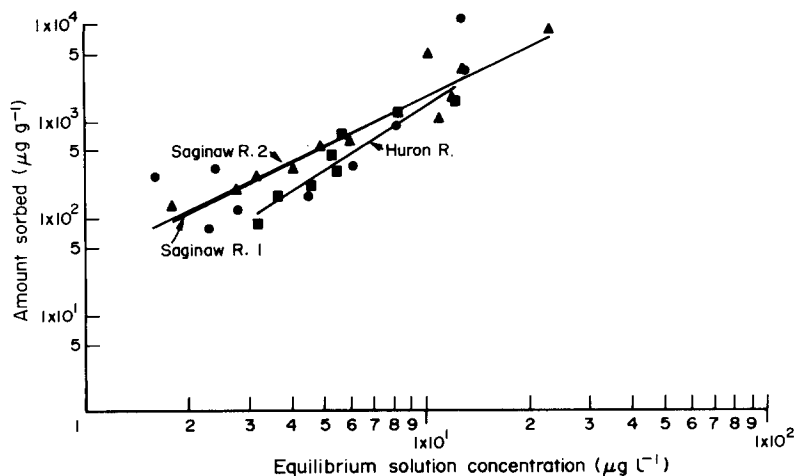


Fig. 5. Sorption of Aroclor 1254 by three suspended solids.
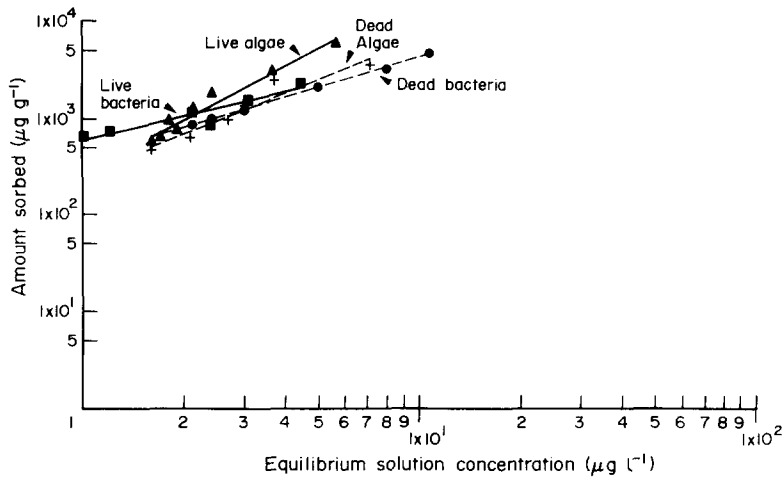
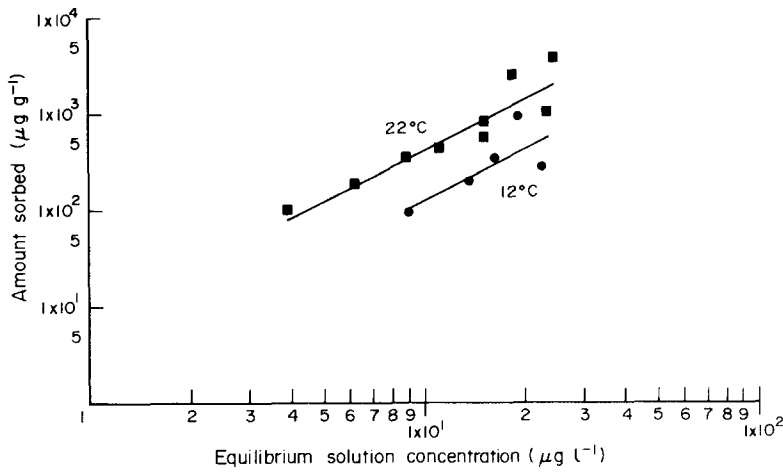Fig. 6. Sorption of Aroclor 1254 by live and dead microbial organisms.



Fig. 7. Sorption of Aroclor 1254 by Saginaw River sediment: effect of temperature.
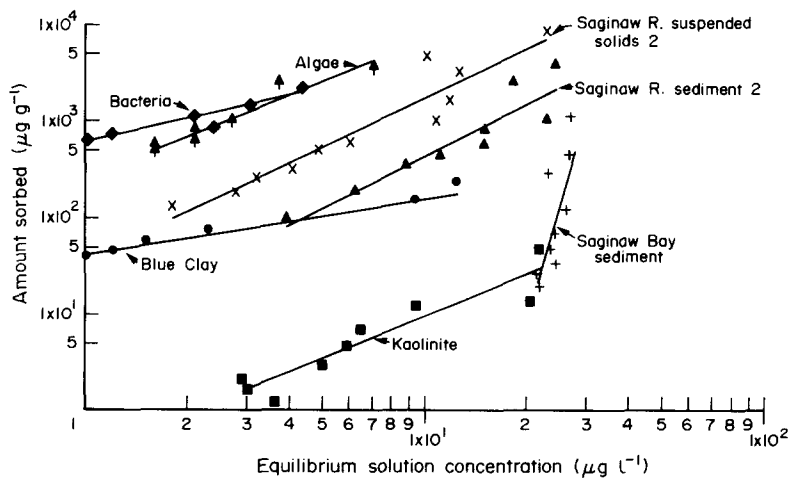


Fig. 8. Sorption of Aroclor 1254 by various sorbents.

Table 1. Isotherm model parameters for sorption of Aroclor 1254 by various solids*

| Sorbent | Langmuir | | | Freundlich | | | Linear | |
|---|---|---|---|---|---|---|---|---|
| | $Q$ | $B$ | corr. | $K_F$† | $1/n$ | corr. | $K_p$ | corr. |
| *Clays* | | | | | | | | |
| Kaolinite | −11.2 | −0.041 | 0.940 | 0.322 | 1.472 | 0.961 | 1686 | 0.888 |
| Montmorillonite | −31.6 | −0.052 | 0.983 | 1.333 | 1.436 | 0.987 | 5745 | 0.915 |
| Blue Clay, natural | 296.9 | 0.155 | 0.993 | 41.704 | 0.649 | 0.813 | 15,695 | 0.981 |
| Blue Clay, stripped | 103.4 | 0.071 | 0.972 | 7.753 | 0.739 | 0.939 | 3626 | 0.985 |
| *Sediments* | | | | | | | | |
| Saginaw R. 1, natural | −495.5 | −0.035 | 0.996 | 17.395 | 1.130 | 0.979 | 23,760 | 0.999 |
| Saginaw R. 1, stripped | 22.5 | 0.538 | 0.862 | 8.265 | 0.387 | 0.946 | 1152 | 0.957 |
| Saginaw R. 2, natural | −642.7 | −0.035 | 0.973 | 7.739 | 1.753 | 0.995 | 135,302 | 0.857 |
| Saginaw R. 2, NaOH ext. | −718.2 | −0.030 | 0.974 | 4.596 | 1.876 | 0.998 | 150,846 | 0.883 |
| Saginaw R. 2, Benz/MeOH ext. | −1245.3 | −0.021 | 0.969 | 1.861 | 2.196 | 0.997 | 243,669 | 0.813 |
| Saginaw R. 2, Stripped | −98.6 | −0.028 | 0.815 | 0.013 | 3.147 | 0.993 | 51,224 | 0.764 |
| Saginaw R. 2, 12 C | −248.8 | −0.032 | 0.950 | 2.151 | 1.777 | 0.996 | 31,859 | 0.844 |
| Saginaw R. 2, <75 µm | −2205.3 | −0.025 | 0.996 | 39.858 | 1.329 | 0.981 | 151,457 | 0.963 |
| Saginaw Bay | −7.1 | −0.036 | 0.790 | <0.001 | 12.448 | 0.967 | 115,381 | 0.624 |
| *Suspended Solids* | | | | | | | | |
| Huron R. | −207.7 | −0.107 | 0.910 | 8.813 | 2.205 | 0.995 | 175,440 | 0.949 |
| Saginaw R. 1 | 1050.4 | 0.078 | 0.818 | 33.915 | 1.733 | 0.962 | 608,728 | 0.771 |
| Saginaw R. 2 | −1316.9 | −0.050 | 0.985 | 36.836 | 1.674 | 0.979 | 372,804 | 0.912 |
| *Organisms* | | | | | | | | |
| Bacteria, live | 3178.3 | 0.247 | 0.981 | 605.114 | 0.786 | 0.851 | 464,372 | 0.992 |
| Bacteria, dead | −98887.2 | −0.004 | 0.998 | 420.972 | 0.998 | 0.953 | 421,753 | 0.999 |
| Algae, live | −1544.6 | −0.184 | 0.967 | 273.662 | 1.839 | 0.943 | 1,289,065 | 0.961 |
| Algae, dead | −2547.9 | −0.106 | 0.988 | 269.979 | 1.398 | 0.939 | 578,913 | 0.981 |

*All models evaluated using $C_c$ in $\mu g l^{-1}$ and $Q_c$ in $\mu g g^{-1}$.
†Intercept at $1.0 \mu g l^{-1}$.

of $K_F$ values indicates only the relative capacities at the intercept concentration, in this case $1.0 \mu g l^{-1}$. Differences in slopes will necessarily produce different relative capacities at other concentrations. The linear partition coefficient may, therefore, be a better indicator of relative capacity, but is still dependent on the liquid-phase concentration.

To better assess the phenomenon of linear partitioning, the isotherms were evaluated visually to determine their linear ranges, and new partition coefficients were determined for sorption at low solution concentrations. These results are shown in Table 2 along with organic carbon values. Generally, the partition coefficients are lower than those developed over the entire range of data and the linearity, as indicated by the correlation coefficients, is better. This result is expected, considering that most of the

isotherms exhibit a shape characteristic of the Freundlich model with $1/n > 1$ (see Part I), or manifest what is termed unfavorable adsorption (Weber, 1972). It is interesting to note, however, that the range over which sorption is linear varies radically among sorbents. It can be seen that the partition coefficient generally increases with increases in the organic carbon content of the sorbents, but the non-linearities involved prohibit development of a rigorous mathematical relationship.

Both of these effects—increasing partition coefficients with increasing solution concentrations and Freundlich $1/n$ values greater than 1—are also consistent with the "solids effect" noted by O'Connor and Connolly (1980) when consideration is given to the typical methods of performing isotherm experiments. These investigators noted that partition

Table 2. Linear partitioning of Aroclor 1254 onto various solids

| Sorbent | % Organic carbon | Low level linear | | | Solids effect* | | |
|---|---|---|---|---|---|---|---|
| | | $K_p$ | $C_c$max† | corr. | Slope | Intercept | corr. |
| *Clays* | | | | | | | |
| Montmorillonite | 0.11 | 1626 | 9.5 | 0.952 | −0.30 | 3.98 | 0.972 |
| Kaolinite | 0.00 | 1654 | 5.3 | 0.996 | −0.27 | 4.15 | 0.962 |
| Blue clay, natural | 1.82 | 26,408 | 2.3 | 0.996 | 0.37 | 3.59 | 0.991 |
| Blue clay, stripped | 0.47 | 3626 | 10.7 | 0.985 | 0.18 | 3.27 | 0.989 |
| *Sediments* | | | | | | | |
| Saginaw R. 1, natural | 3.45 | 23,760 | 9.6 | 0.999 | −0.09 | 4.52 | 0.988 |
| Saginaw R. 1, stripped | 1.05 | 1152 | 17.4 | 0.957 | 0.41 | 2.28 | 0.993 |
| Saginaw R. 2, natural | 2.61 | 53,543 | 15.2 | 0.982 | −0.41 | 5.40 | 0.928 |
| Saginaw R. 2, NaOH ext. | 1.98 | 150,686 | 29.2 | 0.883 | −0.42 | 5.39 | 0.928 |
| Saginaw R. 2, Benz/MeOH ext. | 1.84 | 35,734 | 21.4 | 0.999 | −0.54 | 5.62 | 0.921 |
| Saginaw R. 2, stripped | 0.67 | 102,841 | 29.2 | 0.635 | −0.16 | 4.43 | 0.930 |
| Saginaw R. 2, 12 C | | 31,859 | 22.6 | 0.844 | −0.39 | 4.88 | 0.950 |
| Saginaw R. 2, <75 µm | 3.51 | 76,759 | 13.2 | 0.997 | −0.22 | 5.28 | 0.937 |
| Saginaw Bay | 0.07 | 11,143 | 26.5 | 0.704 | −0.92 | 5.16 | 0.888 |
| *Suspended Solids* | | | | | | | |
| Huron R. | 9.25 | 116,338 | 5.5 | 0.956 | −0.47 | 5.58 | 0.936 |
| Saginaw R. 1 | 9.48 | 88,981 | 8.2 | 0.920 | −0.48 | 5.73 | 0.844 |
| Saginaw R. 2 | 8.30 | 117,693 | 6.1 | 0.990 | −0.37 | 5.70 | 0.891 |
| *Organisms* | | | | | | | |
| Bacteria, live | | 464,372 | 4.4 | 0.992 | 0.07 | 5.63 | 0.977 |
| Bacteria, dead | | 421,753 | 10.5 | 0.999 | −0.01 | 5.63 | 0.937 |
| Algae, live | | 1,289,065 | 5.6 | 0.961 | −0.39 | 6.18 | 0.931 |
| Algae, dead | | 578,913 | 7.1 | 0.981 | −0.22 | 5.85 | 0.935 |

*Linear regression of log $K_p$ vs log solids concentration $(mg l^{-1})$, intercept corresponds to log $K_p$ at $1.0 mg l^{-1}$ solids.
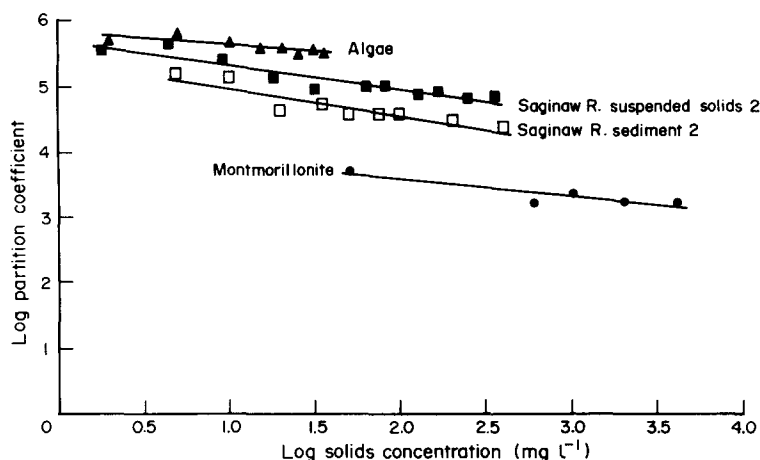†Highest liquid phase concentration $(\mu g l^{-1})$ used to develop $K_p$.

Fig. 9. Sorption of Aroclor 1254 by four sorbents: effect of solids concentration.

coefficients increased as the concentration of solids in the experimental system decreased. The most common method of performing isotherm studies is to add varying quantities of adsorbent to aliquots of a solution of the compound under investigation. The containers with the lowest quantities of solids adsorb the least solute and, hence, reach equilibrium with the highest residual aqueous-phase concentrations. A traditional isotherm plot of $q_e$ vs $C_e$ data generated in this manner can, therefore, be thought of as a number of "partition coefficients at a point" for decreasing (from left to right) solids concentrations. When the slope of a linear plot of such data increases as the liquid-phase concentration increases (as in the case of $1/n > 1$) the partitioning is characteristic of the solids effect noted by O'Connor and Connolly.

The sorption data from the present study were evaluated in this manner. Figure 9 is a plot of single-point partition coefficients as a function of the concentration of solids in the system for a number of the sorbents. Log values were used, since the relationship appears to linearize in this manner. The last three columns in Table 2 show the least-squares

relationship between log $K_p$ and log solids concentration (in $mg\,l^{-1}$) for each sorbent. The effect is significant and pronounced with all of the sorbents except the Blue Clay, Saginaw River 1 sediment and bacteria. Excluding these solids, the slope of the relationship is seen to vary from $-0.16$ to $-0.92$, with an average value of $-0.40$ and a standard deviation of $0.18$. This result implies that the partition coefficient increases an average of an order of magnitude for every two and one half orders of magnitude decrease in solids concentration. Since isotherm experiments are typically performed at solids concentrations two to four orders of magnitude above natural levels, extrapolation of laboratory-derived partition coefficients to natural systems without accounting for this effect can yield erroneous estimates of sorption capacity.

Rates of sorption of Aroclor 1254 were investigated for all of the sorbents studied. Figure 10 shows the time-concentration profiles for two solids, chosen to represent two extremes of sorption capacity. Equilibrium is seen to be reached rapidly in both cases. This phenomenon was observed for all of the
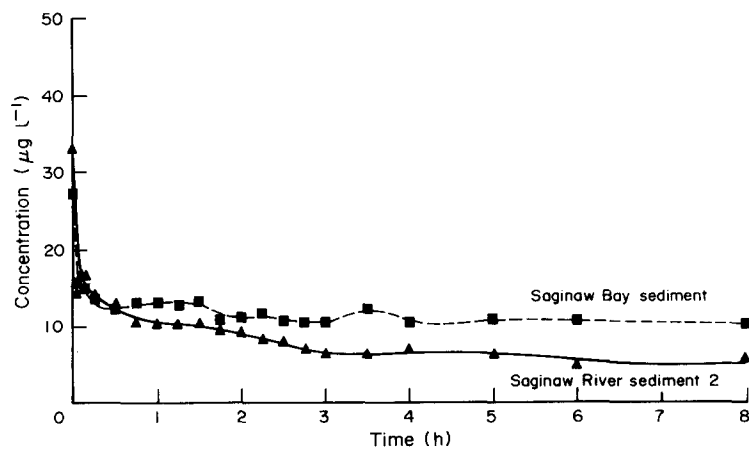


Fig. 10. Rate of sorption of Aroclor 1254 in a completely mixed batch reactor (CMBR) by two sorbents.
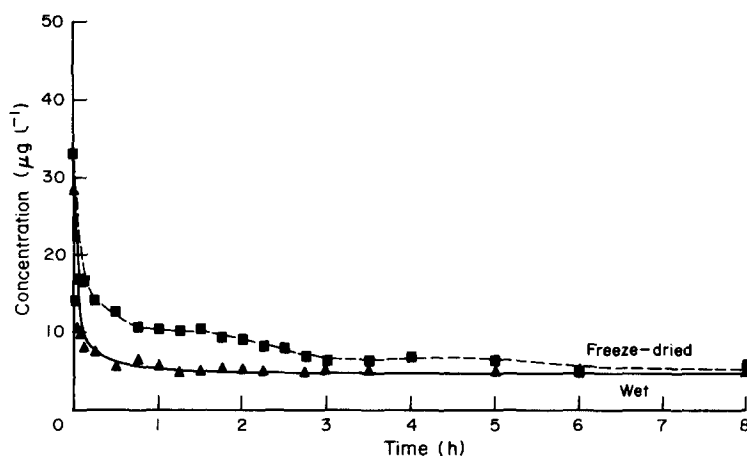
Fig. 11. Rate of sorption of Aroclor 1254 in a completely mixed batch reactor (CMBR) by Saginaw River sediment: effect of freeze-drying.

solids investigated. The slight "resonance" behavior or cyclical variation of the curve around the equilibrium value was also observed in all cases. It is speculated that this results from the competitive interactions of the various PCB isomers. Sorbed species rearrange as individual isomers sorb, desorb and displace each other in the process of reaching a minimum energy state.

The effect of the sample preparation procedure of freeze-drying can be seen in Fig. 11. Although the equilibrium value is the same in both cases, a slower rate of sorption is observed for the freeze-dried sediment. It was found that this difference could be eliminated by wetting the solid for 24 h in a small volume of water prior to study.

## CONCLUSIONS

The data presented in this paper directly expand the limited base of available information regarding sorptive interactions of pollutants with sediments and suspended solids in natural aquatic systems. Interpretation of these data vis-à-vis published data for other systems suggests that certain conclusions, particularly those drawn from pesticide/soil systems, can be extended to hydrophobic pollutants in aquatic environments.

Specifically, this work has shown that:

The organic carbon content of a solid appears to be the major factor in determining its sorptive capacity. Other properties of both the solid and the system in which it is dispersed, especially the concentration of a sorbing pollutant, are important.

Assumptions of linear partitioning, commonly made in the descriptive modeling of sorption reactions in aquatic systems, should be used with extreme caution, and only after substantiation for the specific sorbate/sorbent combination and concentration range in question.

The concentration of solids appears to affect linear partition coefficients in a manner consistent with the

Freundlich model. As the study was not designed to evaluate this phenomenon specifically, this must be considered only as an observation which requires further study for confirmation.

Sorption reactions between hydrophobic pollutants and sediments or suspended solids in aqueous systems are rapid and probably not rate-limited.

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