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## PARTITIONING RELATIONSHIPS FOR CHLORINATED ORGANICS BETWEEN WATER AND PARTICULATES IN THE ST. CLAIR, DETROIT AND NIAGARA RIVER

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## EXECUTIVE SUMMARY

The suspended sediment/water partition coefficients have been measured for 19 chlorinated organics in 25 samples from the St. Clair, Detroit and Niagara Rivers. An excellent linear correlation  $(r^{2}=0.87)$  between the organic-carbon corrected partition coefficient and the octanol/water partition coefficient was found (log  $K_{OC}=0.76$  log  $K_{OW}+1.66$ ). Using this equation plus another equation developed in this paper it was shown that the percentage of chemical in the "dissolved" and "particulate" phases in the study rivers could be estimated from the chemical  $K_{OW}$  to within a factor of 2. The paper also discusses the time required for equilibrium to be achieved between the "dissolved" and "particulate" phases, and the potential importance of biota such as algae in the partitioning process.

### MANAGEMENT PERSPECTIVE

This paper discusses the partitioning between the "dissolved" and "suspended sediment" components in samples from the St. Clair, Detroit and Niagara Rivers. Equations have been developed so that the percentage of organic contaminant in the "dissolved" and "suspended sediment" phases can be estimated to within a factor of 2. This information is essential for modelling the fate of organic contaminants in the Niagara and St. Clair/Detroit system. Relations de partage pour les composés organiques chlorés sur les matières particulaires, dans les rivières St. Clair, Détroit et Niagara.

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## RESUME POUR LA DIRECTION

Les coefficients de partage sédiments en suspension/eau ont été mesurés pour 19 composés organiques chlorés dans 25 échantillons des rivères St. Clair, Détroit et Niagara. On a obtenu une excellente corrélation linéaire ( $r^2$ = 0.87) entre le coefficient de partage corrigé organique-carboné, et le coefficient de partage octanol/eau (log K<sub>oč</sub>= 0.76 log K<sub>ow</sub>+ 1.66). À l'aide de cette équation et d'une autre, formulée dans cette communication, il a été possible de montrer que le pourcentage de produit chimique dans les phases "dissoutes" et "particulaires" des rivières étudiées pourrait être déterminé à partir du K<sub>ow</sub> chimique à un facteur de moins de 2 près. La communication examine également les temps requis pour atteindre l'équilibre entre les phases "dissoutes" et "particulaires", ainsi que le rôle des biocénoses, comme les algues, dans le processus de partage.

#### PERSPECTIVES DE GESTION

La présente communication examine le partage entre constituants "dissous" et "particulaires" dans des échantillons des rivières St. Clair, Détroit et Niagara. Des équations ont été formulées afin de déterminer le pourcentage de contaminants organiques dans les phases "dissoutes" et "particulaires" à un facteur de moins de 2 près. Cette information est indispensable pour la modélisation du comportement des contaminants organiques dans les systèmes hydrographiques Niagara et St. Clair/Détroit.

#### ABSTRACT

The suspended sediment/water partition coefficients have been measured for 19 chlorinated organics in 25 samples from the St. Clair, Detroit and Niagara Rivers. An excellent linear correlation  $(r^2=0.87)$ between the organic-carbon corrected partition coefficient and the octanol/water partition coefficient was found (log  $K_{OC}=0.76$  log  $K_{OW}+1.66$ ). Using this equation plus another equation developed in this paper it was shown that the percentage of chemical in the "dissolved" and "particulate" phases in the study rivers could be estimated from the chemical  $K_{OW}$  to within a factor of 2. The paper also discusses the time required for equilibrium to be achieved between the "dissolved" and "particulate" phases, and the potential importance of biota such as algae in the partitioning process.

# RESUME

Les coefficients de partage sédiments en suspension/eau ont été mesurés pour 19 composés organiques chlorés dans 25 échantillons des rivières St. Clair, Détroit et Niagara. On a obtenu une excellente corrélation linéaire  $(r^2 = 0.87)$ entre le coefficient de partage corrigé organique-carboné, et le coefficient de partage octanol/eau (log K<sub>oc</sub> = 0.76 log K<sub>ow</sub>+1.66). À l'aide de cette équation et d'une autre, formulée dans cette communication, il a été possible de montrer que le pourcentage de produit chimique dans les phases "dissoutes" et "particulaires" des rivières étudiées pourrait être déterminé à partir du K<sub>ow</sub> chimique à un facteur de moins de 2 près. La communication examine également les temps requis pour atteindre l'équilibre entre les phases "dissoutes" et "particulaires", ainsi que le rôle des biocénoses, comme les algues, dans le processus de partage.

#### INTRODUCTION

Suspended sediment/water partitioning information for contaminants in rivers and lakes is required to assess the bioavailability and ultimate fate of the chemical in an aquatic ecosystem. Chemicals in the "dissolved" form are readily available to biota, whereas, chemicals associated with suspended particulates may be unavailable to biota. The association of a chemical with suspended sediments may eventually lead to burial of the contaminant in bottom sediments.

Laboratory studies (Karickhoff <u>et al.</u> 1979; Means <u>et al.</u> 1980; Steen <u>et al.</u> 1978) have shown that organic carbon content of the solids plays an important role in the partitioning process likely because organic chemicals are sorbed into the organic coatings surrounding the particles. Thus the partition equation is usually written:

$$K_{oc} = \frac{K_{p}}{f_{oc}} = \frac{C_{s}}{C_{p} f_{oc}}$$
(1)

where  $K_{OC}$  is the organic carbon corrected partition coefficient,  $K_p$  the partition coefficient,  $f_{OC}$  the fraction organic carbon of the solids,  $C_g$  the concentration of chemical (ng/Kg) on the solids, and  $C_p$  the concentration (ng/L) of the chemical "dissolved" in the water phase. The partition coefficient has been demonstrated to change with suspended sediment concentration (O'Connor and Connolly 1980; Voice <u>et al.</u> 1983; Weber <u>et al.</u> 1983). Such changes in partition coefficient could be attributed to increases in the dissolved organic carbon (DOC) levels in solutions with high suspended solids (DOC has been shown to bind organic chemicals (Hassett and Anderson 1982; Carter and Suffet 1982)), or to increasing concentration of microparticles with increasing solids concentration (Gschwend and Wu 1985).

The sediment/water partition coefficient has been shown to positively correlated with a chemical's octanol/water partition coefficient,  $K_{OW}$  (Karickhoff 1981). Similar relationships have been shown between  $K_{OC}$  and a chemical's water solubility, the lower the chemical's solubility the higher  $K_{OC}$  (Karickhoff 1981; Chiou <u>et al</u>. 1983). Since  $K_{OW}$  and water solubility are strongly interrelated, they cannot be considered to be completely independent variables.

The investigations cited above were all laboratory studies. In this paper partition coefficients derived from field measurements in the St. Clair, Detroit and Niagara Rivers are reported. These coefficients will be correlated with octanol-water partition coefficients and compared to empirically-derived equations.

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## Materials/Methods

A total of 25 samples were collected from the upper and lower St. Clair and Detroit Rivers, and from the lower Niagara River and the river plume in Lake Ontario in the summer of 1984 and 1985. Water was pumped from a 1 meter depth using a submersible pump which fed directly into a Westphalia continuous-flow centrifuge (9500 RPM). The centrifuged water was then collected in a 200 L stainless-steel aqueous phase liquid-liquid extractor (APLE). A surrogate spike containing 1,3-dibromobenzene; 1,3,5-tribromobenzene; 1,2,4,5-tetrabromobenzene; 2,3,5,6-tetrachlorobiphenyl and octachloronaphthalene was added to the drum after it was half-filled. The addition of the surrogate chemicals, which were not present in the study rivers, enabled us to calculate chemical recoveries for each sample. After the sample was loaded, 8L of high purity dichloromethane (DCM) was added to the drum and the sample was extracted for 30 min. Detailed laboratory and field testing showed that the extraction efficiency of the APLE for the study chemicals and surrogates was in the 50-70% range (Oliver and Nicol 1986).

The 5 - 6 L of DCM recovered from the extractor was evaporated to 25 mL in a mantel-heated flask equipped with a 12-ball Snyder condenser. Final concentration to 1 mL was made in a water-bathheated smaller flask with a Kuderna-Danish condenser. The suspended sediments were soxhlet extracted overnight with an acetone/hexane mixture. After back extraction with water to remove the acetone, the

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extract was concentrated to 1 mL by the above procedure. The extract was cleaned up on a minicolumn packed with 2 cm  $Na_2SO_4/4$  cm 40% H<sub>2</sub>SO<sub>4</sub> in silica gel/2 cm florisil. Final gas chromatographic analysis was performed using dual capillary columns (SE54 and OV17) with electron capture detectors. Further method details and recovery efficiencies of the procedures has been previously reported (Oliver and Nicol 1982).

The following 19 chemicals were chosen for detailed study from among the approximately 100 analyzed because of their predominance in the samples: 1,2,4-trichlorobenzene (1,2,4-TCB); 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB); pentachlorobenzene (QCB); hexachlorobenzene (HCB); hexachloroethane (HCE); hexachlorobutadiene (HCBD); octachloro-(p-chlorophenyl) styrene (OCS): 2,2-bis - 1,1-dichloroethylene (pp'-DDE); 2,2',5-trichlorobiphenyl (PCB18); 2,4',5-trichlorobiphenyl (PCB31): 2,2',5,5'-tetrachlorobiphenyl (PCB52); 2,3',4',5-tetrachlorobiphenyl (PCB70); 2,2',3,5',6-pentachlorobiphenyl (PCB95); 2,2', 4,5,5'-pentachlorobiphenyl (PCB101); 2,3,3',4',6-pentachlorobiphenyl (PCB110); 2,2',3,4,4',5'-hexachlorobiphenyl (PCB138); 2,2',4,4',5,5'hexachlorobiphenyl 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB153); (PCB180); 2,2',3,3',4,4',5,5'-octachlorobiphenyl (PCB194).

#### **RESULTS AND DISCUSSION**

The concentration of suspended sediments in the St. Clair, Detroit and Niagara Rivers was quite low and fairly consistent for a

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given sampling station. The range of concentration observed was 0.6 to 14.4 mg/L with a mean and standard deviation, SD, of  $4.4\pm2.7$  mg/L. In the St. Clair/Detroit system the suspended sediment concentrations were lowest at the head of the St. Clair River and increased gradually downstream. The organic carbon content of the suspended solids ranged from 7-13% with a mean of about 10%. The dissolved organic carbon, DOC, in all three rivers was about 2 mg/L.

Figure 1 shows the observed log  $K_{OC}$  for hexachlorobenzene for the 25 individual samples from the rivers. There does not seem to be any change in log  $K_{OC}$  with changing suspended solids concentration in contrast to other studies (O'Connor and Connolly 1980; Voice <u>et</u> <u>al</u>. 1983; Weber <u>et al</u>. 1983). This is probably due to the small range of suspended solids concentrations in the samples. The log  $K_{OC}$ 's for HCB ranged from 5.2 to 6.7 with a mean ±SD of 6.1±0.3.

It is interesting that four St. Clair River samples appear to be considerably above the normal range of data scatter while one Niagara River sample appears to be well below the scatter. These results may provide information on the time required to reach chemical equilibrium between the "dissolved" and "particulates" fractions. The four St. Clair River samples were collected at Port Lambton which is about 35 km and 10 hours travel time for the water below the major chemial sources at Sarnia. Much of the contaminants enter the St. Clair River in the particuate phase ("puddles" of waste material have been found in the river (Environment Canada and Ontario Ministry of the Environment 1986)) and may not have had sufficient time to reach

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equilibrium with the "dissolved" phase by the time the water reaches Port Lambton. Even higher partition coefficients have been observed in samples collected in industrial plumes near Sarnia (Oliver and Kaiser 1986). The low value observed in the Niagara River was for a sample collected just before the river reached Lake Ontario about 4-8 hours residence time below the major chemical sources. The other Niagara River samples were collected in the Niagara River plume more than 6-8 hours later. In the Niagara River, it appears that waste material is entering the river in the "dissolved" form and equilibrium has not been reached by the time the water reaches Lake Ontario. Similar observations were made for several other contaminants. These results seem to indicate that the time required for suspended sediment/water equilibrium to be established is probably of the order of 12 to 24 hours.

The log  $K_{OC}$  data for the samples are tabulated in Table 1. A fairly wide range of  $K_{OC}$ 's was observed for the 25 individual samples probably due to analytical difficulties for some samples where data were close to detection limits, and to the kinetic factors mentioned earlier. The standard deviations from the mean are about 0.3 to 0.4 log units or about a factor of two. This is reasonably good considering the diversity of sample locations and the wide concentration ranges encountered.

Figure 2 shows a graph of log  $K_{OC}$  versus log  $K_{OW}$ . The plot indicates a strong linear correlation between the parameters with the least squares equation:

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$$\log K_{\rm oc} = 0.76 \log K_{\rm ow} + 1.66$$
 (2)

This equation is somewhat different than the laboratory-derived equation of Karickhoff 1981:

 $\log K_{oc} = 0.989 \log K_{ow} - 0.35$  (3)

The field data are higher than predicted by Karickhoff's equation by a factor of 13 at log  $K_{OW}$  4 and by a factor of 3 at log  $K_{OW}$  7. To develop his equation Karickhoff studied the adsorption of 47 chemicals (only 12 of which were chlorinated) on resuspended bottom sediments at sediment concentrations of 1000 mg/L. Subsequent studies have shown that Koc decreases with increasing suspended sediment concentration (O'Connor and Connolly 1980; Voice et al. 1983; Weber et al. 1983). Thus part of the discrepancy between our equation and Karickhoff's is probably due to differences in the suspended sediment concentrations in the two studies. But this effect should result in a parallel shift of our line upward when compared to Karickhoff's, in other words, in a line with similar slope but with a higher intercept. In fact our equation has a lower slope which leads to an increasing discrepancy between Koc's from the two equations for chemicals with lower Kow's. These dissimilarities may simply be due to the fact that different to develop empirical chemicals üsed the two were

relationships. Also Karickhoff used bottom sediments in which the organic carbon should be "stabilized", whereas, in this study suspended sediments contain living organic matter. In any case, empirical equation 2 should be useful in predicting the behaviour of chlorinated chemicals in the study rivers.

An estimate of the percentage of chemicals in the "dissolved" and "particulate" fraction in the samples can be calculated by rearranging equation 1 and developing the appropriate expressions.

$$C_{S} = C_{D} K_{oc} f_{oc}$$
(4)  
$$C_{T} = C_{D} + C_{S} [SS]$$

where  $C_{\rm T}$  is the total concentration (ng/L) in the whole water sample and [SS] in the suspended sediment concentration in Kg/L (10<sup>-6</sup> times the suspended sediment concentration in mg/L).

$$\frac{FRACTION}{DISSOLVED} = \frac{C_D}{C_D + C_S [SS]} = \frac{C_D}{C_D + C_D K_{oc} f_{oc}}$$
(6)  

$$\frac{PERCENT}{DISSOLVED} = \frac{100}{1 + K_{oc} f_{oc} [SS]} = \frac{100}{1 + K_p [SS]}$$
(7)

Assuming the  $f_{oc}$  for the samples is 0.1, then it is possible to construct the diagram in Figure 3 which shows the percentage of chemical in the "dissolved" fraction for chemicals with various log

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 $K_{oc}$ 's.  $K_p$  measurements could also be used for this purpose. Even for chemicals with high  $K_{oc}$ 's, a significant fraction of the chemicals is found in the "dissolved" form in the study rivers because of the low suspended solids concentrations (4.4 mg/L). Equations 2 and 7 can be used to calculate the phase distribution of a variety of compounds in the rivers from the chemical's octanol-water partition coefficient.

In an effort to estimate the importance of the biotic component the suspended solids, the six Niagara River samples were of prefiltered through a stainless-steel 50 µm sieve prior to entering the centrifuge. The sieve retained of the larger algae and other small biota such as zooplankton. This material, which ranged from 1.7 to 7.8% (mean 3.8±2.2%) of the suspended solids, was assumed to have an organic carbon content of 50%. Log Roc's for this component are shown in column 4 of Table 1. The algae Koc's for the chlorinated hydrocarbons, excluding the PCB's, are very similar to those of the suspended sediments. However, the algae Koc's for the PCB's are one order of magnitude higher than those of the suspended sediments. This appears to indicate that bioconcentration processes in addition to simple partitioning is occurring for the PCB's. Although the algae fraction represented only 3.8 weight % of the suspended solids fraction; on average 25% of the PCB's in the whole water sample were found in this fraction.

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As mentioned earlier several recent studies have shown that dissolved organic carbon can bind hydrophobic organics (Hassett and Anderson 1982; Carter and Suffet 1982). A schematic diagram of the processes affecting partitioning in natural waters is shown in Figure 4. This figure illustrates that different partitioning relationships will probably be found in waterbodies in different trophic states and/or with different DOC's. Thus, although K<sub>ow</sub> is a useful parameter for predicting partitioning between the "dissolved" and "particualte" phases in natural waters for diverse chemicals, the equations derived will likely be site specific.

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Compound	log K <sub>OC</sub> Suspended Sędiments (n=25)		log K <sub>oc</sub> Algae >50 μm (n=6)	
	Range	Mean	Mean	log K <sub>ow</sub>
1,2,4-TCB	4.3-5.9	5.1±0.4	5.1	4.0 <sup>a</sup>
1,2,3,4-TeCB	4.1-6.0	5.2±0.4	4.5	4.5 <sup>b</sup>
QCB	4.9-6.2	5.8±0.4	5.7	4.9 <sup>c</sup>
нсв	5.2-6.7	6.1±0.3	5.8	5.5ª
HCE	2.7-5.2	3.8±0.8	-	3.6 <sup>b</sup>
HCBD	4.6-6.0	5.3±0.3	4.9	4.8 <sup>c</sup>
OCS	5.9-7.3	6.6±0.3	6.3	6.2 <sup>d</sup>
pp'DDE	5.1-6.7	6.2±0.3	6.5	5.7e
PCB18	5.1-6.3	5.5±0.3	7.0	5.6f
PCB31	5.5-6.3	5.9±0.2	6.8	5.6f
PCB52	5.0-6.4	5.9±0.4	7.0	5.9f
PCB70	5.6-6.8	6.3±0.3	7.2	5.9 <sup>f</sup>
PCB95	5.3-6.8	6.1±0.4	7.4	6.2 <sup>f</sup>
PCB101	5.1-6.7	6.2±0.5	7.2	6.2 <sup>f</sup>
PCB110	5.6-6.8	6.4±0.4	7.7	6.2 <sup>f</sup>
PCB138	5.8-7.3	6.6±0.4	7.6	6.5 <sup>f</sup>
PCB153	6.1-7.2	6.6±0.3	7.2	6.5 <sup>f</sup>
PCB180	6.2-7.4	6.9±0.4	7.3	6.7 <sup>f</sup>
PCB194	6.5-7.1	6.8±0.3	7.8	6.9 <sup>f</sup>
Total PCB's	5.3-6.4	6.1±0.3	7.0	-

Table 1 Organic carbon corrected partition coefficients, K<sub>OC</sub>, for samples from the St. Clair, Detroit and Niagara Rivers and octanol/water partition coefficients, K<sub>OW</sub>, for the study chemicals.

<sup>a</sup>Data from Chiou <u>et</u> <u>al</u>. (1982). <sup>b</sup>Data from Könemann <u>et</u> <u>al</u>. (1979). <sup>c</sup>Data from Banerjee <u>et</u> <u>al</u>. (1980). <sup>d</sup>Data from Veith <u>et</u> <u>al</u>. (1979). <sup>e</sup>Data from O'Brien (1974). <sup>f</sup>Calculated by the method of Kaiser (1983).



- Fig. 1 Log K<sub>oc</sub> versus suspended sediment concentration for 25 individual samples from the St. Clair, Detroit and Niagara Rivers.
- Fig. 2 Log Roc versus Row for study chemicals.
- Fig. 3 The percentage of chemical "dissolved" at various suspended sediment concentrations.
- Fig. 4 Schematic diagram for chemical partitioning in natural waters.

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