Environment Canada
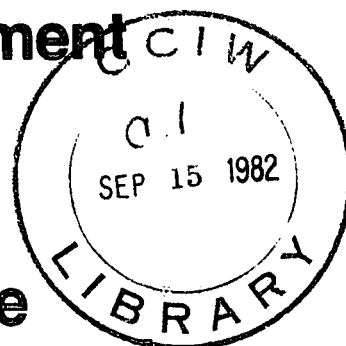
Environnement Canada

National Water Research Institute

Institut National de Recherche sur les Eaux

NWRI Unpublished Manuscript

BIS (TRI-N-BUTYLTIN) OXIDE (TBTO) IN WATER
HYDROLYSIS AND VOLATILIZATION

R. JAMES MAGUIRE AND ELIZABETH J. HALE

Environmental Contaminants Division

BIS (TRI-N-BUTYLTIN) OXIDE (TBTO) IN WATER:
HYDROLYSIS AND VOLATILIZATION

R. JAMES MAGUIRE AND ELIZABETH J. HALE

Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Department of the Environment
Burlington, Ontario, Canada L7R 4A6

SEPTEMBER 1982

ABSTRACT

Concentrations of 18 chlorinated hydrocarbons were deter-
mined in samples of surface microlayer, subsurface water and suspended
solids which were collected at five stations along the length of the
Niagara River in July, 1981. In 45% of the cases in which a compound
had a measurable concentration in either the surface microlayer or
subsurface water, or both, there was significant enrichment in surface
microlayer concentration relative to subsurface water concentration;
heptachlor epoxide, α-endosulfan and total PCB were concentrated by
factors of up to at least 225. The significance of high surface
microlayer concentrations with regard to loadings of chlorinated
hydrocarbons to Lake Ontario from the Niagara River could not be
assessed. A mass balance showed only that the amounts of the above
three compounds in the surface microlayer may be significant; however,
the mass balance did show that there was far more α- and γ-BHC, diel-
drin and total PCB dissolved in water than adsorbed to suspended
solids, which would necessitate a revision of loading estimates based
solely on concentrations in suspended solids.

INTRODUCTION

The nature and chemical and biological significance of sur-
face water microlayers are matters which have received increasing
attention over the last 15 years (for reviews, cf. Parker and Barsom
1970; MacIntyre 1974; Liss 1975). The thickness of the surface micro-
layer is operationally defined by the type of collector used (Garrett
1965; Harvey 1966; Harvey and Burzell 1972; Baier, 1972; Hatcher and
Parker 1975); values up to 2×10^{-4} m are common. Several articles
have demonstrated that surface microlayers can concentrate contami-
nants. The term "enrichment factor" (EF) has been used in this con-
nection, and is defined as:

$$EF = \frac{\text{Concentration in surface microlayer}}{\text{Concentration in subsurface water}} - 1 \qquad (1)$$

EF values of 0 to 10^4 have been reported for metals in ocean and lake
water (Piotrowicz et al. 1972; Szekielda et al. 1972; Andren et al.
1975) and values around 2 have been reported for chlorinated hydro-
carbons in ocean water (Seba and Corcoran 1969). Pollution of the
Niagara River has been noted by the International Joint Commission
(1981) and is the focus of a significant amount of surveillance and

research by the Department of the Environment; this work attempted to determine if there were significant concentrations of chlorinated hydrocarbons in the surface microlayer of the Niagara River, and to compare these concentrations with those in subsurface water and suspended solids.

EXPERIMENTAL METHODS

Samples of surface microlayer, subsurface water and suspended solids were collected at five locations (cf. Figure 1) along the length of the Niagara River. There was no sediment at these five stations.

Surface microlayer samples of volume approximately 100 mL were collected with a glass plate sampler (Harvey and Burzell 1972). Subsurface water samples (1 L) were collected at a depth of 1 to 2 m. Suspended solids samples were collected with a Westfalia continuous flow separator (Kuntz et al. 1981) from the same depth. Table 1 shows the station depths and suspended solids concentrations. All three kinds of samples were analyzed for 18 chlorinated hydrocarbons by

electron capture gas chromatography (Water Quality Branch 1981). The limit of detection of these compounds is 0.0001 µg L^{-1} in water and 0.001 mg kg^{-1} in suspended solids (except for PCB, for which the limits are 0.001 µg L^{-1} and 0.01 mg kg^{-1}, respectively), but the concentrations at which the compounds could be detected with confidence were 5 X the detection limit in each case. Accordingly, since replicate samples were not analyzed in this study, we ignored concentration values less than 0.0005 µg L^{-1} (0.005 µg L^{-1} for PCB) in water, and less than 0.005 mg kg^{-1} (0.05 mg kg^{-1} for PCB) in suspended solids, except in cases in which ratios of concentrations or amounts were calculated (cf. below).

RESULTS AND DISCUSSION

Table 2 shows concentrations of 13 chlorinated hydrocarbons in the surface microlayer, subsurface water and suspended solids at the five stations. Heptachlor epoxide, aldrin, γ-chlordane, o,p'-DDT and p,p'-TDE were not detected in any "compartment" at any station.

In general, concentrations of chlorinated hydrocarbons in the surface microlayer and subsurface water were below limits of

detection; an exception is heptachlor epoxide which was observed at all five stations in the surface microlayer, but in no subsurface water sample and in only one suspended solids sample. In addition, α-endosulfan and PCB were observed in the surface microlayer at two stations each.

In many cases, concentrations in the suspended solids fraction were also below detection limits. In those cases in which there were measurable concentrations in the suspended solids, results were similar to those observed for 1979-1980 by Warry and Chan (1981).

Table 3 shows surface microlayer:subsurface water enrichment factors (cf. equation 1) for the chlorinated hydrocarbons at the five stations in the Niagara River. There was significant enrichment in 9 of the 20 cases in which a compound had a measurable concentration in either the surface microlayer or subsurface water, or both; heptachlor epoxide showed enrichment at all five stations, α-endosulfan at the only two stations at which it was observed, and total PCB at two of the three stations at which it was observed in water. The tendency of a compound to accumulate is not simply directly related to its octanol-water partition coefficient; for example, dieldrin (log

K_{ow} = 5.5 - 6.2) does not accumulate in the surface microlayer while

α-endosulfan (log K_{ow} = 3.5) and heptachlor epoxide (log K_{ow} =

5.4) do accumulate.

Concentrations of pollutants are occasionally so high in the

surface microlayer that the microlayer contains significant amounts of

pollutant relative to subsurface water (Pellenbarg and Church 1979;

Maguire et al. 1982). In an effort to determine if high concentra-

tions of chlorinated hydrocarbons in the surface microlayer made any

difference to estimates of loadings to Lake Ontario from the Niagara

River, we estimated ratios of amounts of the compounds in various

compartments. This was done by:

i) considering a sample of water of length, width and depth

A, B and C m, respectively, upon which rests a

microlayer D m thick;

ii) supposing that the concentration of the relevant

compound is X μg L^{-1} in the surface microlayer, Y μg L^{-1}

in the subsurface water, and Z μg g^{-1} in suspended

solids; and

iii) assuming that Y, Z and ρ, the concentration of suspended

solids in subsurface water (g L^{-1}), are invariant with

depth.

With the data in Tables 1 and 2, and with D = 6 × 10^{-5} m

(determined at several locations), the following ratios were calcula-

ted:

$$\frac{\text{Amount in surface microlayer}}{\text{Amount in subsurface water}} \; = \; R \; = \; \frac{XD}{YC} \qquad (2)$$

$$\frac{\text{Amount in surface microlayer}}{\text{Amount in suspended solids}} \; = \; R' \; = \; \frac{XD}{Z\rho C} \qquad (3)$$

$$\frac{\text{Amount in subsurface water}}{\text{Amount in suspended solids}} \; = \; R'' \; = \; \frac{Y}{Z\rho} \qquad (4)$$

Values of R, R' and R" for the chlorinated hydrocarbons are shown in

Table 4 for each of the five stations.

The data for R show only that the ratio of the amount in the

surface microlayer to the amount in subsurface water may be signifi-

cant for heptachlor epoxide at all five stations, α-endosulfan at two

stations and PCB at one station. Further work with much larger sub-surface water samples should resolve this ambiguity.

The data for R' show that the ratio of amount in surface microlayer to amount in suspended solids is significant for heptachlor epoxide at stations 19.3, 20.5 and 37.7, and may be significant at the other two stations.

The data for R" show that the amount of α- and γ-BHC, PCB and dieldrin in subsurface water far outweigh their amounts in suspended solids. This observation has important implications for the calculation of loadings of some chlorinated hydrocarbons to Lake Ontario from the Niagara River. For example, Warry and Chan (1981) calculated the loading of PCB to Lake Ontario from the Niagara River to be 950 kg year^{-1} in 1979 to 1980, based solely on concentrations of PCB in suspended solids at station 1.5 (Niagara-on-the-Lake). Using their flow data and our concentration data at station 1.5, we calculate PCB loading in 1981 to be 166 kg year^{-1} from suspended solids and 7700 kg year^{-1} from subsurface water, or 7534 kg year^{-1} from the "dissolved" state. This large excess may be truly dissolved or adsorbed to particles too small to be retained in the continuous flow separator.

ACKNOWLEDGEMENT

REFERENCES

Ali, S. 1978. Degradation and environmental fate of endosulfan
isomers and endosulfan sulfate in mouse, insect and labora-
tory model ecosystem, PhD Thesis, Univ. Illinois, 101 pp.

Andren, A.W., Elzerman, A.W. and Armstrong, D.L. 1975. Chemical and
physical aspects of surface organic microlayers in fresh-
water lakes. In _Proc. First Specialty Symp. Atmosph._
Contrib. Chemistry Lake Waters, Intern. Assoc. Great Lakes
Res., pp. 101-113.

Baier, R.E. 1972. Organic films on natural waters: their retrieval,
identification and modes of elimination. _J. Geophys. Res._
77: 5062-5075.

Briggs, G.G. 1981. Theoretical and experimental relationships
between soil adsorption, octanol-water partition coeffi-
cients, water solubilities, bioconcentration factors, and
the parachor. _J. Agric. Food Chem._ 29: 1050-1059.

Garrett, W.D. 1965. Collection of slick-forming materials from the sea surface. Limnol. Oceanogr. 10: 602-605.

Harvey, G.W. 1966. Microlayer collection from the sea surface: a new method and initial results. Limnol. Oceanogr. 11: 608-613.

Harvey, G.W. and Burzell, L.A. 1972. A simple microlayer method for small samples. Limnol. Oceanogr. 17: 156-157.

Hatcher, R.F. and Parker, B.C. 1975. Laboratory comparisons of four surface microlayer samplers. Limnol. Oceanogr. 19: 162-165.

International Joint Commission. 1981. Special report under the 1978 Great Lakes Water Quality Agreement on pollution in the Niagara River. Windsor, Ontario, January 20, 10 pp.

Kenaga , E.E. 1980. Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties. Environ. Sci. Technol. 14: 553-556.

Kuntz, K., Chan, C.H., Clignett, A.H. and Boucher, R. 1982. Water quality sampling methods at Niagara-on-the-Lake. Report of Inland Waters Directorate, Ontario Region, Dept. of the Environment, Canada Centre for Inland Waters, Burlington, Ontario, Canada L7R 4A6, March, 15 pp.

Kurihara, N., Uchida, M., Fujita, T. and Nakajima, M. 1973. Studies on BHC isomers and related compounds. V. Some physiochemical properties of BHC isomers. Pestic. Biochem. Physiol. 2: 383-390.

Liss, P.S. 1975. Chemistry in the sea surface microlayer. In Chemical Oceanogr., Riley, J.P. and Skirrow, G. (eds.) pp. 193-243. New York: Acad. Press.

Macek, K.J., Buxton, K.S., Derr, S.K., Dean, J.W. and Sauter, A. 1976. Chronic toxicity of lindane to selected aquatic invertebrates and fishes. U.S. Environmental Protection Agency, Ecol. Res. Ser., EPA-600/3-76-099, Washington, DC, U.S.A., 50 pp.

MacIntyre, F. 1974. The top millimeter of the ocean. Scientif. Amer. 230: 62-77.

Maguire, R.J., Chau, Y.K., Bengert, G.A., Hale, E.J., Wong, P.T.S. and Kramar, O. 1982. Occurrence of organotin compounds in Ontario lakes and rivers. Environ. Sci. Technol. in press.

Neely, W.B., Branson, D.R. and Blau, G.E. 1974. The use of the partition coefficient to measure the bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115.

O'Brien, R.D. 1974. Nonenzymic effects of pesticides on membranes. In Environmental Dynamics of Pesticides, Haque, R. and Freed, V.H. (eds.), pp. 331-342. New York: Plenum Press.

Parker, B. and Barsom, G. 1970. Biological and chemical significance of surface microlayers in aquatic ecosystems. Bio. Science 20: 87-93.

Pellenbarg, R.E. and Church, T.M. 1979. The estuarine surface microlayer and trace metal cycling in a salt marsh. Science 203: 1010-1012.

Piotrowicz, S.R., Ray, B.J., Hoffman, G.L. and Duce, R.A. 1972. Trace metal enrichment in the sea-surface microlayer. J. Geophys. Res. 77: 5243-5254.

Sanborn, J.R., Metcalf, R.L., Bruce, W.N. and Lu, P.-Y. 1976. The fate of chlordane and toxaphene in a terrestrial-aquatic model ecosystem. Environ. Entomol. 5: 533-538.

Seba, D.B. and Corcoran, E.F. 1969. Surface slicks as concentrators of pesticides in the marine environment. Pestic. Monitor. J. 3: 190-193.

Szekielda, K.-H., Kupferman, S.L., Klemas, V. and Polis, D.F. 1972. Element enrichment in organic films and foam associated with aquatic frontal systems. J. Geophys. Res. 77: 5278-5282.

Veith, G.D., DeFoe, D.L. and Bergstedt, B.V. 1979a. Measuring and estimating the bioconcentration factors of chemicals in fish. J. Fish. Res. Board Can. 36: 1040-1048.

Veith, G.D., Austin, N.M. and Morris, R.T. 1979b. A rapid method for estimating log P for organic chemicals. Water Res. 13: 43-47.

Warry, N.D. and Chan, C.H. 1981. Organic contaminants in the suspended sediments of the Niagara River. J. Great Lakes Res. 7: 394-403.

Water Quality Branch. 1981. Analytical Methods Manual, Inland Waters Directorate, Dept. of the Environment, Ottawa, Ontario, Canada K1A OE7.

FIGURE LEGEND

Figure 1. Sampling Locations in the Niagara River.

LAKE ONTARIO

●
1.5

* SCA

```
0   2   4   6   8
|---|---|---|---|
    kilometres
```

* BLOODY RUN CREEK

6.8 ●

* HYDE PARK

N.F. TREATMENT
* PLANT

GILL CREEK
HOOKER CHEMICAL

* * ← LOVE CANAL
* * ← 102nd STREET SITE

● 19.3

20.5 ●

↑
N

● NO SEDIMENTS

* WASTE DISPOSAL SITES

● 37.7

LAKE ERIE
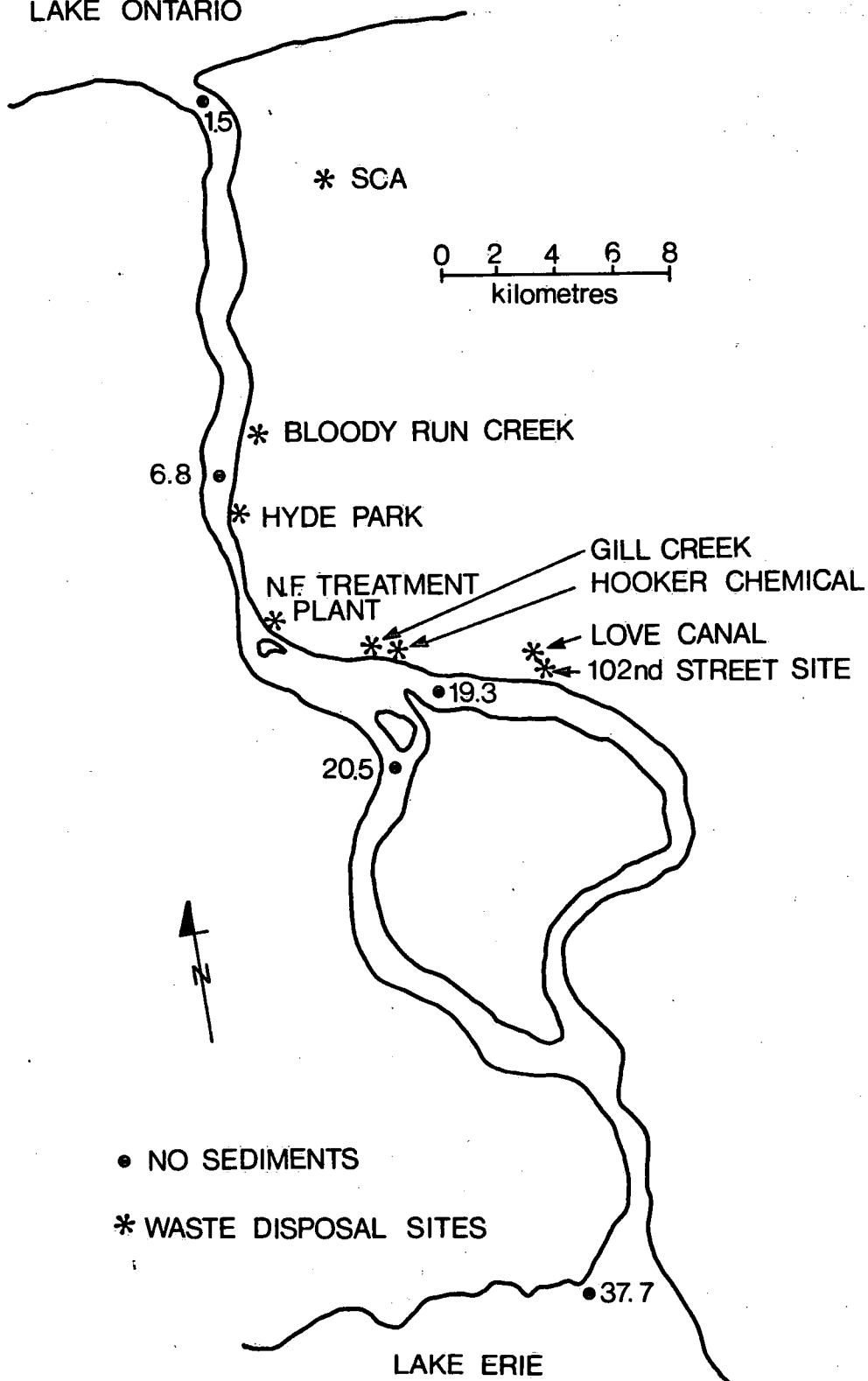
TABLE 1. Station Depths and Suspended Solids Concentrations, July 1981

Station	Depth m	Volume of Water Centrifuged L	Dry Weight of Solids g	Concentration mg L^{-1}
1.5	16.8	17640	71	4.0
6.8	12.2	14580	54	3.7
19.3	3.7	17280	48	2.8
20.5	3.7	16200	30	1.8
37.7	7.6	17723	21	1.2

TABLE 2. Concentrations* of Chlorinated Hydrocarbons in Three Compartments at Five Stations in the Niagara River, July 1981

Compound	1.5			6.8			19.3			20.5			37.7		
	SM	SW	SS	SM	SW	SS	SM	SW	SS	SM	SW	SS	SM	SW	SS
α-BHC	0	0	0	0	0.0070	0	0	0.0051	0	0	0.0062	0	0	0.0051	0
γ-BHC	0	0.0009	0	0	0.0005	0	0	0	0	0	0	0	0	0.0007	0
Hexachlorobenzene	0	0	0.018	0	0	0.036	0	0	0	0	0	0	0	0	0
Endrin	0	0	0	0	0	0	0	0	0.007	0	0	0	0	0	0
Dieldrin	0	0	0	0	0.0009	0.006	0	0.0005	0.005	0	0	0.016	0	0	0.018
Heptachlor Epoxide	0.0167	0	0	0.0182	0	0	0.0226	0	0	0.0139	0	0	0.0145	0	0
α-Chlordane	0	0	0	0	0	0	0	0	0.006	0	0	0	0	0	0.011
α-Endosulfan	0	0	0	0	0	0.014	0.0067	0	0.007	0.0204	0	0.025	0	0	0
β-Endosulfan	0	0	0	0	0	0	0	0	0	0	0	0.021	0	0	0
Methoxychlor	0	0	0	0	0.0010	0.015	0	0	0	0	0	0	0	0	0
p,p'-DDE	0	0	0.008	0	0	0.014	0	0	0.027	0	0	0.006	0	0	0.025
DDT	0	0	0.032	0	0	0	0	0	0	0	0	0	0	0	0
PCB (Total)	0.057	0.039	0.21	0.033	0	0.31	0	0	0	0	0.011	0	0	0	0

* Concentrations in water are $\mu g\ L^{-1}$; in suspended solids, $mg\ kg^{-1}$.
 SM - surface microlayer; SW - subsurface water; SS - suspended solids.

TABLE 3. Surface Microlayer: Subsurface Water Enrichment Factors for Chlorinated Hydrocarbons in the Niagara River[a]

Compound	log K_{OW}[b]	EF				
		1.5	6.8	19.3	20.5	37.7
α–BHC	3.81[c]	–	0	0	0	0
γ–BHC	3.72[c], 3.85[d], 3.89[e]	0	0	–	–	0
Hexachlorobenzene	5.23[e,f], 5.44[g], 6.18[h]	–	–	–	–	–
Endrin	4.56[f]	–	–	–	–	–
Dieldrin	5.48[i], 6.2[g]	–	0	0	–	–
Heptachlor Epoxide	5.40[e]	$> 1.66 \times 10^2$	$> 1.81 \times 10^2$	$> 2.25 \times 10^2$	$> 1.38 \times 10^2$	$> 1.44 \times 10^2$
α–Chlordane	2.78[j]	–	–	–	–	–
α–Endosulfan	3.55[k]	–	–	$> 6.6 \times 10^1$	$> 2.03 \times 10^2$	–
β–Endosulfan	3.62[k]	–	–	–	–	–
Methoxychlor	4.20[h], 4.30[e]	–	0	–	–	–
p,p'–DDE	5.69[e], 5.69[l]	–	–	–	–	–
DDT	5.75[e], 6.19[h]	–	–	–	–	–
PCB (Total)	5.6–6.9[e,h]	0.46	$> 3.2 \times 10^1$	–	0	–

a = Blanks signify that a compound was found in neither the surface microlayer nor subsurface water. A zero or ">" sign indicates that there was a measurable concentration in one compartment and that the concentration in the other compartment was assumed to be 0.0001 μg L^{-1} (0.001 μg L^{-1} for PCB).

b = K_{OW} is the octanol–water partition coefficient.

c = Kurihara et al. 1973.

d = Macek et al. 1976.

e = Veith et al. 1979a.

f = Neely et al. 1974.

g = Briggs 1981.

h = Veith et al. 1979b.

i = Kenaga 1980.

j = Sanborn et al. 1976.

k = Ali 1978.

l = O'Brien 1974.

TABLE 4. Ratios* of Amounts of Chlorinated Hydrocarbons in Three Compartments at Five Stations in the Niagara River, July 1981

Compound	1.5			6.8			19.3			20.5			37.7		
	R	R'	R"	R	R'	R"	R	R'	R"	R	R'	R"	R	R'	R"
α-BHC	–	–	–	$<7.03\times10^{-8}$	–	$>1.89\times10^3$	$<3.21\times10^{-7}$	–	$>1.83\times10^3$	$<2.64\times10^{-7}$	–	$>3.35\times10^3$	$<1.54\times10^{-7}$	–	$>4.32\times10^3$
γ-BHC	$<3.98\times10^{-7}$	–	$>2.24\times10^2$	$<9.84\times10^{-7}$	–	$>1.35\times10^2$	–	–	–	–	–	–	$<1.12\times10^{-6}$	–	$>5.93\times10^2$
Hexachlorobenzene	–	$<4.95\times10^{-6}$	<1.38	–	$<3.69\times10^{-6}$	$<7.51\times10^{-1}$	–	–	–	–	–	–	–	–	–
Endrin	–	–	–	–	–	–	–	$<8.42\times10^{-5}$	<5.14	–	–	–	–	–	–
Dieldrin	–	–	–	$<5.47\times10^{-7}$	$<2.22\times10^{-5}$	4.05×10^1	$<3.28\times10^{-6}$	$<1.18\times10^{-4}$	3.60×10^1	–	$<5.54\times10^{-5}$	3.38	–	$<3.71\times10^{-5}$	<4.71
Heptachlor Epoxide	$>5.98\times10^{-4}$	$>1.49\times10^{-2}$	–	$>8.96\times10^{-4}$	$>2.42\times10^{-2}$	–	$>3.70\times10^{-3}$	$>1.33\times10^{-1}$	–	$>2.28\times10^{-3}$	$>1.23\times10^{-1}$	–	$>1.14\times10^{-3}$	$>9.67\times10^{-2}$	–
α-Chlordane	–	–	–	–	–	–	–	$<9.83\times10^{-5}$	<5.99	–	–	–	–	$<6.07\times10^{-5}$	<7.70
α-Endosulfan	–	–	–	–	$<9.50\times10^{-6}$	<1.93	$>1.10\times10^{-3}$	5.64×10^{-3}	<5.14	$>3.34\times10^{-3}$	7.23×10^{-3}	<2.16	–	–	–
β-Endosulfan	–	–	–	–	–	–	–	–	–	–	$<4.22\times10^{-5}$	<2.57	–	–	–
Methoxychlor	–	–	–	$<4.92\times10^{-7}$	$<8.87\times10^{-6}$	1.80×10^1	–	–	–	–	–	–	–	–	–
p,p'-DDE	–	$<1.11\times10^{-5}$	<3.11	–	$<9.50\times10^{-6}$	<1.93	–	$<2.18\times10^{-5}$	<1.33	–	$<1.48\times10^{-4}$	<9.01	–	$<2.67\times10^{-5}$	<3.39
DDT	–	$<2.78\times10^{-6}$	$<7.77\times10^{-1}$	–	–	–	–	–	–	–	–	–	–	–	–
PCB (Total)	5.23×10^{-6}	2.42×10^{-4}	4.62×10^1	$>1.62\times10^{-4}$	1.42×10^{-4}	$<8.72\times10^{-8}$	–	–	–	$<1.49\times10^{-6}$	–	$>5.94\times10^2$	–	–	–

* Ratios R, R' and R" are defined in equations 2 to 4. Blanks signify that a compound was observed in neither compartment of the ratio in question. A ">" or "<" sign indicates that there was a measurable concentration in one compartment and that the concentration in the other compartment was assumed to be 0.0001 µg L^{-1} for water or 0.001 mg kg^{-1} for suspended solids (except for PCB for which the relevant figures are 0.001µg L^{-1} and 0.01 mg kg^{-1}, respectively).

15903