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**SURFACE WATER MICROLAYERS AS RESERVOIRS
OF ENVIRONMENTAL CONTAMINANTS**

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ABSTRACT

The surface microlayer of natural waters sometimes contains significant amounts of pollutants relative to the amounts in the whole depth of underlying water. An observation on PCBs in surface microlayers is discussed, as are data on organotins in the lower Great Lakes basin. The possible importance of the surface microlayer as a reservoir of lipophilic pollutants has profound implications for water quality modeling and monitoring programs.

INTRODUCTION

The nature and chemical and biological significance of surface water microlayers are matters which are receiving increasing attention over the last fifteen years (for reviews, cf. Parker and Barsom 1970; MacIntyre 1974; Liss 1975). The surface microlayer is composed of, at least, long chain fatty acids, fatty alcohols and fatty acid esters (MacIntyre 1974). The thickness of the surface microlayer is operationally defined by the type of collector used (Garrett 1965; Harvey 1966; Harvey and Burzell 1972; Baier 1972; Hatcher and Parker 1974); values ranging up to 2×10^{-4} m are common. The operationally defined surface microlayer is thus much thicker than the physical chemist's monolayer.

Several articles have demonstrated that surface microlayers are capable of concentrating contaminants. The term "enrichment factor" (EF) has been used in this connection, and is defined as

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

EF values between 0 and 10^4 have been reported for metals in ocean and lake water (Piotrowicz et al. 1975; Szekiolda et al. 1972; Andren et al. 1975). EF values between 2 and 10^7 have been reported for chlorinated hydrocarbons in ocean water and lake water (Seba and Corcoran 1969; Ofstad et al. 1979). Freshwater foam is also capable of concentrating metals relative to subsurface water; corresponding values of EF have been

reported between 3.8 and 2.4×10^3 (Pojasek and Zajicek 1978; Eisenreich et al. 1978).

Although the presence of pollutants in high concentrations in the surface microlayer is of obvious importance (i) to surface-dwelling biota, and (ii) in considerations of air-water exchange, little attention has been given to the possibility that the surface microlayer may also contain significant amounts of pollutant relative to subsurface water. To our knowledge, only one article has explicitly addressed this point; Pellenbarg and Church (1979) found that the aqueous surface microlayer in a Delaware salt marsh contained an average of 10% of the copper, 19% of the zinc and 23% of the iron relative to the combined amounts in the subsurface water and seston.

The purpose of this article is to illustrate the potential importance of the carrying capacity of the surface microlayer (i) with a few simple calculations, and (ii) with some observations of our own in organotins in the lower Great Lakes basin.

DISCUSSION

Consider a sample of water of length A m, width B m and depth C m, upon which rests a microlayer D m thick. Suppose that the concentration of the compound of interest is $X \mu\text{g l}^{-1}$ in the surface microlayer and $Y \mu\text{g l}^{-1}$ in the subsurface water; furthermore, Y is assumed to be invariant with depth. The ratio (R) of the amount in the surface microlayer to the amount in the subsurface water is

$$R = \frac{10^3 X ABD}{10^3 Y ABC} = \frac{XD}{YC} \quad (2)$$

As stated above, the thickness of the surface microlayer is operationally defined. Since we used a glass plate sampler in the work described below we estimate $D = 6 \times 10^{-5} \text{ m}$ (Harvey and Burzell 1972; Winchester and Duce 1977). Equation 2 then becomes

$$R = \left(\frac{X}{Y}\right) \left(\frac{6 \times 10^{-5}}{C}\right) \quad (3)$$

At what combination of subsurface water depths and concentration ratios does the amount of pollutant in the surface microlayer become significant with respect to the amount in the subsurface water? If significance is defined for convenience as the 6% level, then the amounts in the surface microlayer become significant compared to the amounts in subsurface water of depths 1, 10 and 100 m when X/Y is 10^3 , 10^4 and 10^5 , respectively. Ofstad et al. (1979) found X/Y values of 10^6 - 10^7 for PCBs in Norwegian waters. Equation 3 shows that when X/Y equals 10^6 , there is 60% as much PCB in the surface microlayer as in the whole depth of subsurface water even when the water is 100 m deep.

A less dramatic example of the carrying capacity of the surface microlayer is afforded by our research on butyltins, part of which is described here. Samples of surface microlayer (by glass plate - Harvey and Burzell 1972) and whole subsurface water were collected in glass

containers from several locations around the lower Great Lakes. The samples were preserved, extracted and analyzed for the butyltins Bu_3Sn^+ , $\text{Bu}_2\text{Sn}^{2+}$, BuSn^{3+} and inorganic Sn^{4+} according to a method developed earlier (Maguire and Huneault 1981). The results are shown in Table 1. In no case was there a significant amount of Sn^{4+} in the surface microlayer, but in 10 of the 19 butyltin analyses shown the amount of organotin in the surface microlayer exceeded 5% of the amount in the subsurface water. The highest amounts were for dibutyltin in Whitby and Belleville harbours, >33% and >24%, respectively.

Table 1 also shows that in many cases the carrying capacity of the surface microlayer for organotins is insignificant. This may be due to the variable nature of the surface microlayer; physical factors such as wind, waves and turbulence in rivers, and chemical factors such as the presence of substantial local sources (both natural and anthropogenic) of surface-active materials, must surely play important parts. The concentration of a pollutant in a surface microlayer in a particular location will probably display significant fluctuation compared with its concentration in subsurface water on a daily basis or even an hourly basis.

It is reasonable to assume that the surface to subsurface weight (or concentration) ratio for a particular pollutant is related in some way to its lipophilicity, as expressed, for example, by its octanol/water partition coefficient. The octanol/water partition coefficients of Bu_3Sn^+ , $\text{Bu}_2\text{Sn}^{2+}$ and BuSn^{3+} are all less than 1.5×10^3 (Wong et al. 1981). It is thus possible that the common organochlorine pollutants,

which have partition coefficients orders of magnitude higher, may concentrate to a much greater extent in the surface microlayer. In a similar fashion, metals, as opposed to the organic and organometallic compounds discussed here, may concentrate through association with soluble or particulate material which is at least partially soluble in the surface microlayer.

The results of this work suggest that the surface microlayer may be an important, and hitherto neglected, reservoir of pollutants compared to subsurface water. It may be that loadings of highly lipophilic pollutants to the Great Lakes have been underestimated. Despite the daunting prospect of sampling a highly variable microlayer to determine a time-averaged concentration, researchers engaged in determining loadings of pollutants and mass balances in aquatic "compartments" should consider the possible importance of the surface microlayer.

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TABLE 1. Ratio of amount of butyltins* and Sn⁴⁺ in surface microlayer to amount in subsurface water.

Location**	R _{Bu₃Sn⁺}	R _{Bu₂Sn²⁺}	R _{Sn⁴⁺}
St. Clair River-1	>0.07	>0.12	8.4x10 ⁻⁴
St. Clair River-2	>0.02	>0.08	6.0x10 ⁻³
St. Clair River-3	n.d.	>0.08	5.5x10 ⁻⁵
Lake St. Clair-1	>0.01	>0.08	8.0x10 ⁻⁴
Lake St. Clair-2	5.1x10 ⁻⁴	5.0x10 ⁻⁴	3.3x10 ⁻⁵
Thames River	n.d.	n.d.	6.6x10 ⁻⁵
Port Dover	>1.4x10 ⁻⁴	>0.07	>3.0x10 ⁻³
Port Maitland	n.d.	n.d.	n.d.
Toronto	n.d.	>0.07	>7.0x10 ⁻⁴
Whitby	>3.0x10 ⁻⁴	>0.33	>2.0x10 ⁻³
Belleville	>0.07	>0.24	>2.0x10 ⁻³
Kingston	n.d.	>0.01	8.2x10 ⁻⁴
St. Lawrence River-1	>6.0x10 ⁻³	>0.03	>1.0x10 ⁻³
St. Lawrence River-2	n.d.	n.d.	>3.0x10 ⁻⁴

* BuSn³⁺ not found in any water sample; the minimum detectable amount of each species was 0.01 µg l⁻¹; n.d. = not determined; ">" indicates that a particular species was detected in the surface microlayer but not in the subsurface water.

** Precise locations available on request.

