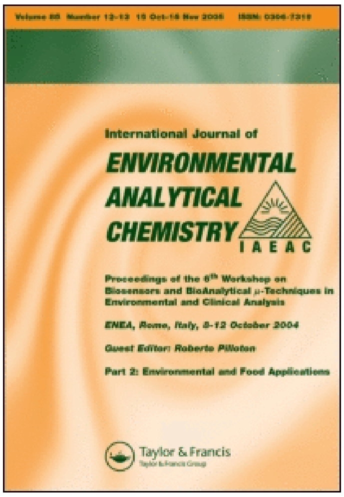

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R. James Maguire[a]
[a] Department of the Environment, Process Research Division, National Water Research Institute, Burlington, Ontario, Canada

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LETTER TO THE EDITOR

Pollutants in Aquatic Surface Microlayers: A Cautionary Note

R. JAMES MAGUIRE

Process Research Division, National Water Research Institute, Department of the Environment, Burlington, Ontario, Canada L7R 4A6

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Sir: The surface microlayer of natural water, which is covered by a fatty film of, at least, long-chain fatty acids, fatty alcohols and fatty acid esters, is thought to be important in the aquatic environmental distribution of hydrophobic pollutants. It has been shown that organic matter is concentrated in surface slicks,[1–5] and that the kinetics of some reactions may differ between the surface microlayer and bulk solution.[6] Although the presence of pollutants in high concentrations in the surface microlayer of natural waters is of obvious importance to surface-dwelling biota, and for the process of volatilization, it should be borne in mind that in the consideration of mass balance of pollutants in aquatic ecosystems, it is important to know the sizes of the various environmental "compartments" so that the total *amounts* of pollutants in the various compartments are known. This is part of a normalizing process which corrects the distortion involved in reporting concentrations of pollutants in aquatic compartments of widely varying sizes. It may be that, due to differences in the volumes of the surface microlayer and the subsurface water, a high surface:subsurface concentration ratio is accompanied by a much lower (or even inverted) mass ratio. The extreme ratios of 10^6–10^7 observed recently by Ofstad *et al.*[5] for polychlorinated biphenyls (PCBs) in Norwegian waters probably reflect situations in which the amount of PCBs in the surface microlayer is still larger than the amount in subsurface water; however there are cases in which a rather lower concentration ratio can lead to a situation in which the mass of pollutants in the surface microlayer is insignificant compared with that in the subsurface water. Our experience, described below, affords a good example of this point.

Fenitrothion [*O,O*-dimethyl-*O*-(*p*-nitro-*m*-tolyl)phosphorothionate] was used in the period 1969–1978 in New Brunswick, Canada, for control of the spruce budworm (*Choristoneura fumiferana* [Clemens]) in the province's forests. Millions of hectares were sprayed annually with 150–300 g active ingredient per hectare. The routes and rates of environmental distribution and transformation were, and still are, subjects of a great deal of interest.[7,8] We collected samples of surface water, subsurface water, suspended solids and sediment from a small pond (est. area $4.46 \times 10^2 m^2$; est. mean depth 0.3 m) in a spruce-fir forest in New Brunswick before and after the spraying of a fenitrothion formulation for spruce budworm control, and the samples were analyzed for fenitrothion and its degradation and transformation products.

The surface microlayer, which is operationally defined by the type of collector used, was sampled with a 20 cm × 20 cm glass plate, fitted with a handle. The plate was gently lowered into the water and then withdrawn vertically over a period of 5 s. The water adhering to both sides of the plate ($\sim$5 ml) was scraped into a beaker with a neoprene scraper. This procedure was carried out 20 times for each sample, and the surface water sample was extracted within two hours of collection. The thickness of the surface microlayer was estimated to be about 60 μm.[9,10] Subsurface water samples were obtained by lowering a stoppered 1 l glass bottle below the surface of the water, filling the bottle and replacing the stopper before removing the bottle from the water; the samples were extracted within two hours of collection. All extracts were analyzed by electron capture gas chromatography.

In the surface microlayer, the fenitrothion concentration declined from 1.5 mg l^{-1} 40 min. after the spraying to 2 μg l^{-1} 49 hr later. In the subsurface water, the fenitrothion concentration declined from 15 μg l^{-1} 40 min. after the spraying to 0.1 μg l^{-1} 49 hr later. The concentration in the surface microlayer at $t = 40$ min was thus 10^2 that in the subsurface water; at $t = 49$ hr, the factor was 20. However, the estimated volume of the surface microlayer over the area of the pond was 28 l, compared with the estimated volume of subsurface water of 1.36×10^5 l. Thus at $t = 40$ min there were 42 mg of fenitrothion in the surface microlayer compared to 2.04×10^3 mg in the subsurface water. Hence the surface microlayer contained only about 2% of the fenitrothion that the subsurface water contained; this figure was reduced to 0.4% at $t = 49$ hr.

The assumption implicit in these calculations was that the fenitrothion concentration in subsurface water was uniform throughout the depth of the water column, a reasonable assumption given the shallow depth of the pond. The assumption will probably not hold for larger bodies of water unless they are well mixed so that sampling should be done as a function of depth, and the results integrated over the whole depth.

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