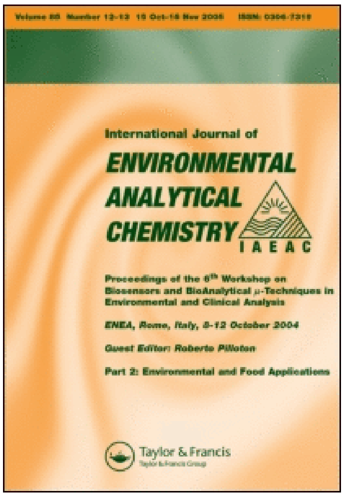

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Chlorinated Organic Compounds in the Fatty Surface Film on Water†

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KEY WORDS: Chlorinated organics, water, surface films, gas chromatography profiles.

The content of chemically persistent (i.e. sulphuric acid resistant) chlorinated hydrocarbons in the fatty surface film on water is investigated. The sampling method is based on adsorption of the surface film to teflon sheets, and analysis was performed using a gas chromatograph with an electron capture detector (GC/ECD). The results are obtained as gas chromatographic profiles.

When comparing chromatographic profiles of surface film and corresponding water samples a significant difference between the two is observed.

The results indicate that the atmosphere is the main source for chlorinated organic pollutants in the surface, while enrichment of these compounds from the water seems to be of minor importance.

Only small differences are observed when comparing pollution profiles of surface samples taken at different times at the same locality.

The most predominant chlorinated organic pollutants in all the surface film samples are found to be PCB. It is estimated that the concentration of PCB in the surface film is 10^6–10^7 times higher than in the water underneath.

INTRODUCTION

The persistent chlorinated hydrocarbons like polychlorinated biphenyls (PCB), hexachlorobenzene (HCB) and DDT with its metabolites are well known pollutants. These compounds are widespread in the environment and numerous analyses have shown their presence in water, air, sediments and biological material. Because of their persistence and lipophilic character they exhibit strong bioaccumulation.

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The distribution of these chlorinated micropollutants has been studied extensively and much effort has been given to understand the mechanisms for their transport in the environment. Knowledge about the transport of the chlorinated hydrocarbons or other similar pollutants like PAH, phtalates and petroleum hydrocarbons between the air and water phase can be obtained by studying the occurence of these pollutants at the interface between air and water.

It is well known that the water surface is covered by a fatty film. The components of the surface film has been shown to be lipids, mainly long chain fatty acids, fatty alcohols and fatty acid esters. These components which result mainly from the biological activity in the water, will be enriched on the water surface due to their hydrofobic and surface active character[1,2]. Duce *et al.*[3] has estimated the fatty film to consist of about 5 molecular layers, while Larsson *et al.*[2] has estimated the amount of lipid in surface samples to vary between 0, 3 and 20 mg/m^2.

The aim of this study was to investigate the content of persistent chlorinated hydrocarbons in this fatty surface film in order to get a better understanding of how they are transported in the environment. To achieve this, samples of the fatty film were taken at different localities representing both water- and air-polluted as well as fairly unpolluted areas in Norway. By comparing the different surface samples and also by comparing with corresponding ordinary water samples it is possible to estimate the relative importance of water and air as the source for pollutants in the surface film.

Furthermore, the possibility of using surface film analyses for surveillance of the deposition of air pollutants was tried. In doing this, surface samples were collected regularly at one site to look for time-dependent variations in the composition and amounts of pollutants in the film.

SAMPLING

Several methods for sampling of the fatty surface film have been developed. Among these is a rather simple technique described by Larsson[2] based on adsorption of the film to teflon sheets. Development of our sampling equipment has been based on this principle.

The teflon sheets we used for adsorbing the surface film are 20 cm × 5 cm × 5 mm each, and they are perforated with conical holes to avoid air bubbles between the sheets and the surface film during sampling. Before use the sheets were washed three times with acetone in an ultrasonic bath, rinsed with distilled water and dried at 200°C. This treatment has been shown to give sufficiently clean sheets. Four teflon sheets kept together in a stainless steel device are used for one sampling. This device is constructed in such a way that the sheets can easily be replaced with a pincet. The sampling is performed by dipping the device with the teflon sheets carefully onto the water surface and keeping it there for a few seconds. The teflon sheets are stored and transported in glass containers prewashed with acetone and heated to 500°C.

At each sampling site 2–5 samples were taken. Samples were taken of sea water surfaces from polluted areas like the Frierfjord and the Oslofjord at Tofte. Samples of fresh water surfaces were taken from unpolluted lakes in Hedal, Tovdal and Gulsvik in Southern Norway and from a drinking water supply, lake Østernvann, near Oslo.

The Frierfjord and the Oslofjord at Tofte are polluted due to industrial effluents containing non-polar chlorinated organic compounds. The lakes in southern Norway are situated in an area influenced by the precipitation of air transported pollutants from Middle Europe and Great Britain. The drinking water source near Oslo is totally devoid of any form of effluents from local sources and this site was therefore chosen for studying possible variations in the deposition of pollutants from the atmosphere and also to study the influence of the urban air. The surface samples for this purpose were collected with two and three weeks intervals during the summer period.

Water samples were simultaneously collected at half a metres depth in 5 l glass bottles prewashed with acetone and rinsed with distilled water.

ANALYTICAL PROCEDURE

All solvents used for the analysis were distilled in an all glass apparatus. The distilled water was extracted with cyclohexane to remove traces of organic impurities. All glass equipment was washed with acetone and heated to 550°C before use.

For the analysis of persistent chlorinated hydrocarbons in the surface samples the following procedure was used:

Cyclohexane (100 ml) was added to the four teflon sheets in the container and extraction was carried out for two hours. The cyclohexane extract was transferred to a separating funnel, washed three times with distilled water, dried with sodium sulphate and concentrated by evaporation at 120°C to about 3 ml. The concentrate was pipetted into a centrifuge tube and shaken with concentrated sulphuric acid to get rid of the non-persistent compounds. After 1 hour contact time the sample was centrifuged, and the cyclohexane phase was pipetted into another centrifuge tube. The extract was further concentrated in a heating block at 50°C under a gentle stream of N_2 to a final volume of about 0.2 ml.

The water samples were extracted with cyclohexane (200 ml) in the glass bottles by vigorously stirring for 2 hours with a magnetic stirrer. The cyclohexane phase was transferred to a separating funnel and further treated in the same way as described for the surface samples.

The samples were analysed by using a gas chromatograph equipped with an electron capture detector. The gas chromatographic conditions are given in Table II. During the first investigations packed columns were used. Later we also utilized a gas chromatograph system with a glass capillary column which gives a superior resolution of the chromatogram.

Calculation of PCB-values given in Table 2 is, to be consistent, based on the packed column chromatograms. The chromatograms shown in Figures 1–5 are, however, all obtained with the glass capillary system.

RESULTS AND COMMENTS

The results are obtained as gas chromatograms with a pattern of peaks, a "pollution profile", which is characteristic for each sample. The profiles for some selected samples are shown in Figures 1–5. By comparing the chromatographic profiles of corresponding surface film and water samples one can detect possible differences in the composition of the chlorinated compounds. In Table II quantitative data on the content of PCB in the surface layer and water samples is given.

The sample from the drinking water source near Oslo shown in Figure 1 demonstrates that the surface film mainly contains PCB but also a certain amount of hexachlorobenzene. The PCB-peaks which are marked with an asterisk in the chromatograms have been identified by comparing with peaks in Aroclor 1254 and Clophen A60 standards. The water sample contains mainly the same components as the surface sample and in addition a few unknown ones. The internal proportions of the components are, however, slightly different in the two samples.

The samples from the inland of Norway shown in Figure 2 give a somewhat different picture. The surface film still contains mainly PCB, but in addition several unknown components can be observed. The corresponding water samples contain the same components but the relative abundance of these differs greatly from the surface samples. These lakes are not polluted by any local sources, but they are situated in an area where precipitation of air transported pollutants from middle Europe and Great Britain is noticeable[4]. The surface sample in Figure 2 gives a good indication of the influence of these air-deposited pollutants.

The Frierfjord is an example of an area which is heavily polluted by

TABLE I
Analytical conditions

Gas chromatograph	Hewlett Packard 5730A with ECD	Perkin Elmer 3920 with ECD
Column	50 m × 0.35 mm i.d. glass capillary	2 m × 1/8′ i.d. packed, stainless steel
Stationary phase	SE-54	SE-30
Column temperature programme	100°C, 3°C/min, 250°C	130°C, 8°C/min, 230°C
Carrier gas	Helium, 1 kg/cm^2	Argon with 5% methane, 20 ml/min
Detector make-up gas	Argon with 5% methane, 50 ml/min	Argon with 5% methane, 20 ml/min
Detector temperature	300°C	275°C
Injector temperature	250°C	250°C
Remarks	splitless injection at room temperature	

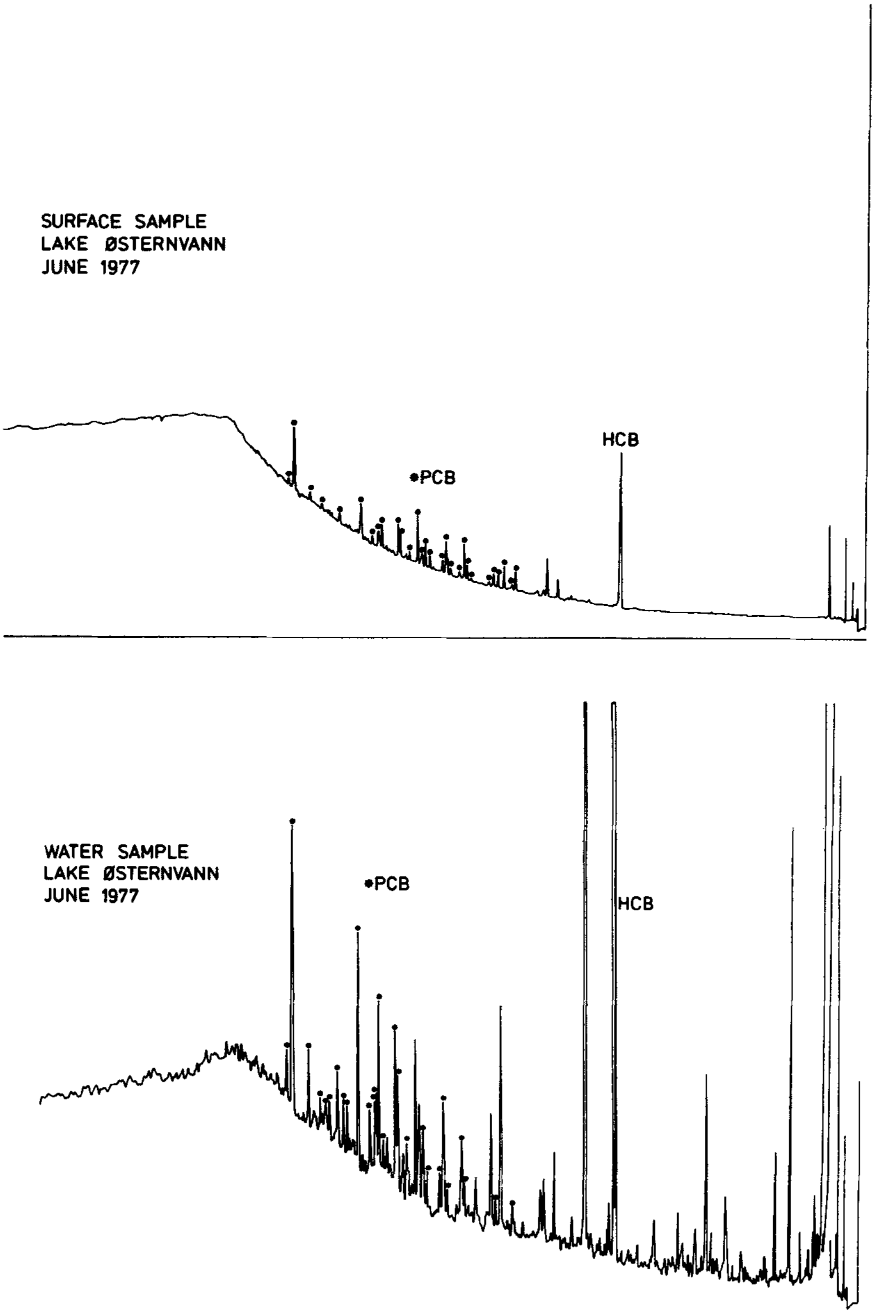
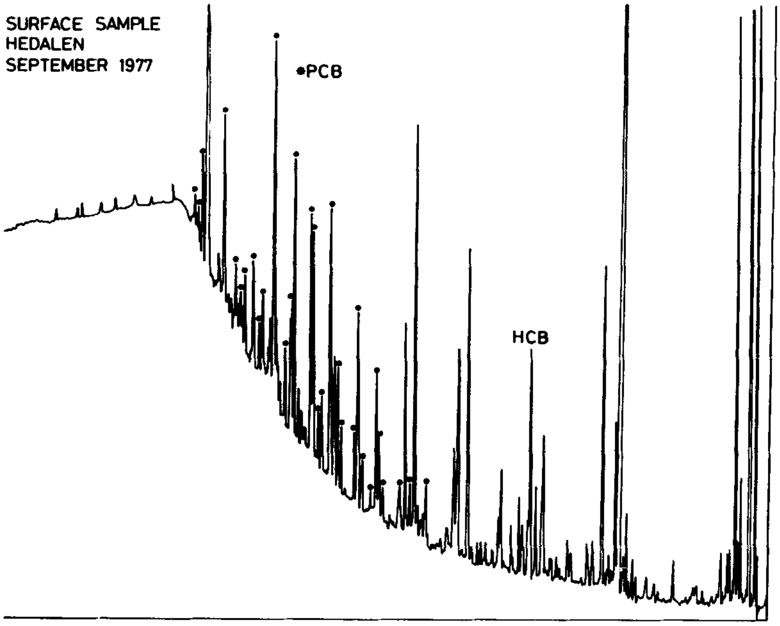


FIGURE 1 Surface film and water samples from lake Østernvann near Oslo, June 1977.



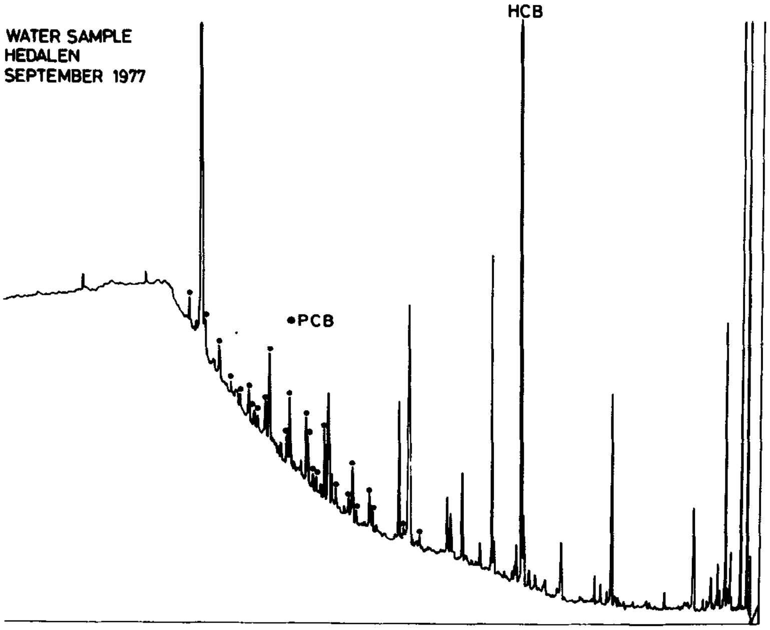


FIGURE 2 Surface film and water samples from Hedalen, Southern Norway, September 1977.

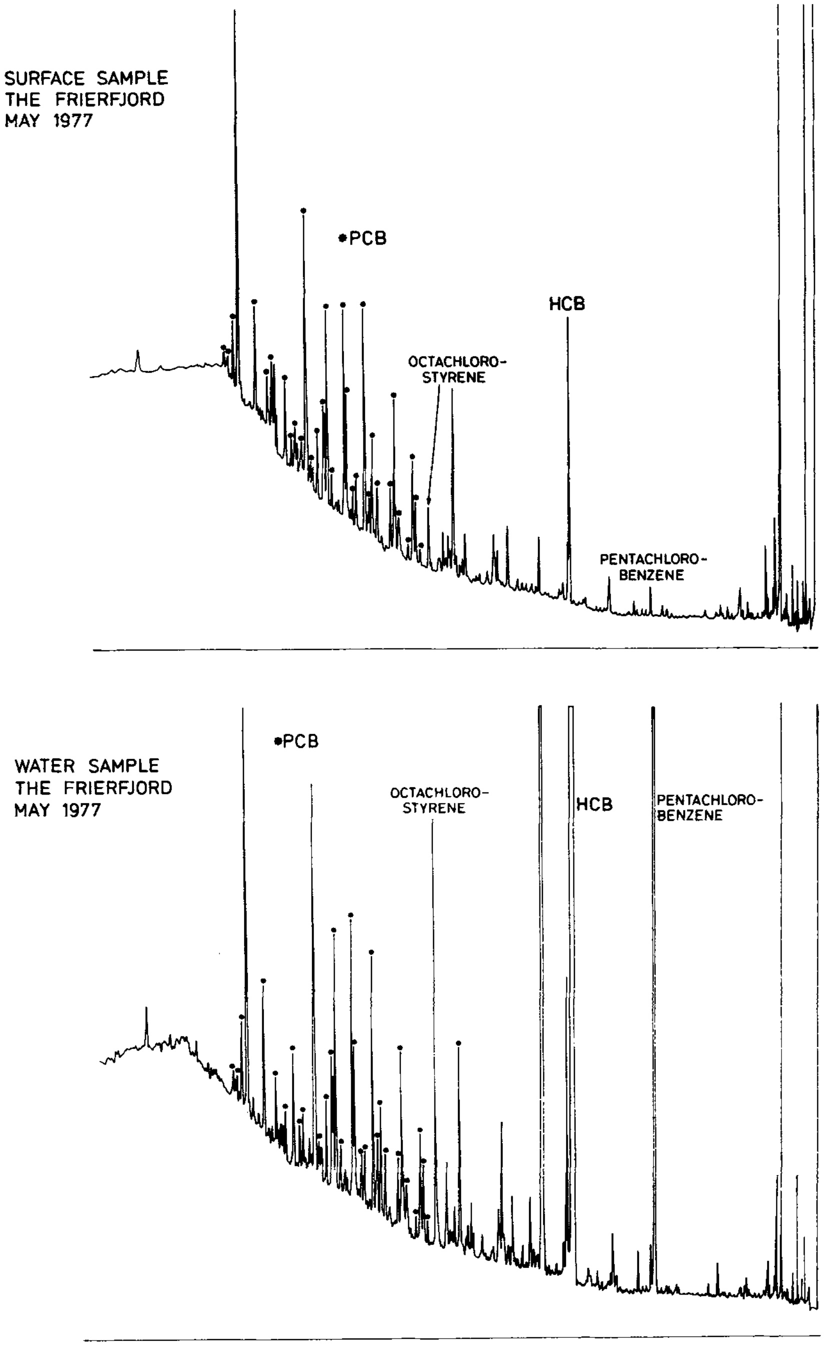
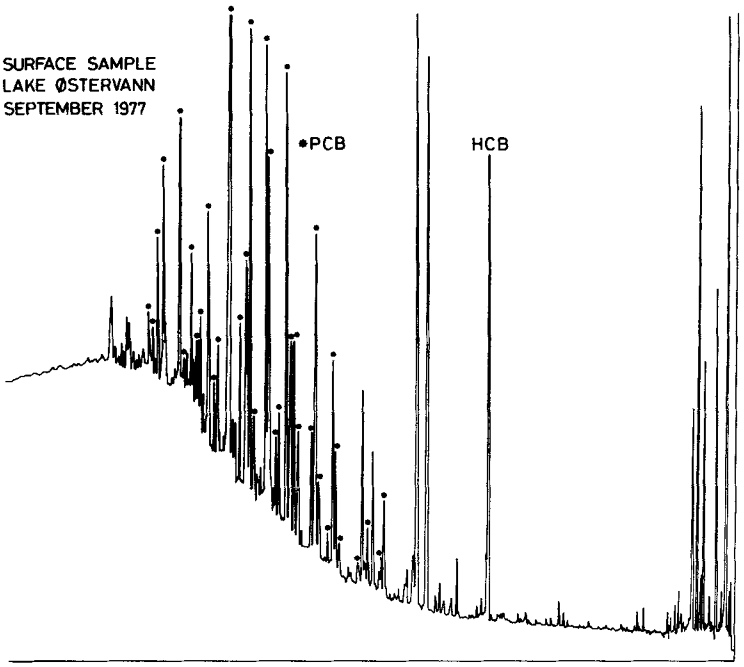


FIGURE 3 Surface film and water samples from the Frierfjord, Southern Norway, May 1977.



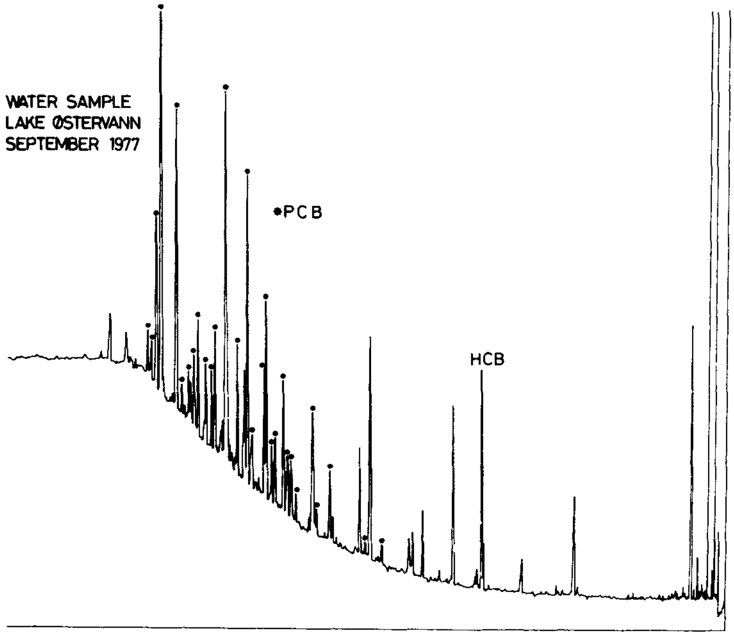


FIGURE 4 Surface film and water samples from lake Østernvann near Oslo, September 1977.

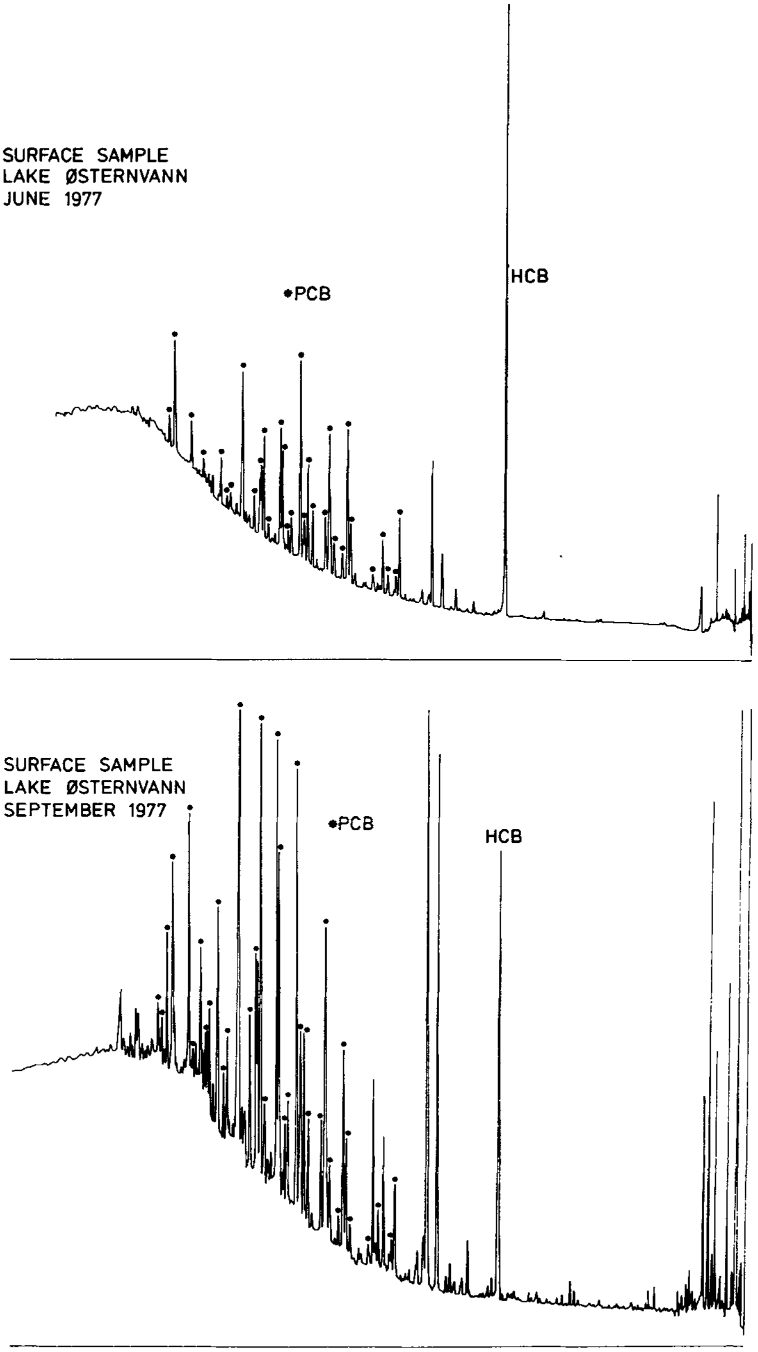


FIGURE 5 Surface film samples from lake Østernvann June 1977 and September 1977.

persistent chlorinated hydrocarbons[5, 6]. These pollutants originate from an industrial effluent. Among the most predominant compounds are pentachlorobenzene, hexachlorobenzene and octachlorostyrene, and the water samples from this area show substantial amounts of these components, Figure 3.

The corresponding surface samples contain mainly PCB and only to a small extent the typical effluent components. An exception is hexachlorobenzene which is, in addition, a general pollutant like PCB. Hence, the surface area will also be supplied with this pollutant from sources other than the industrial effluent. These samples from the Frierfjord area clearly indicate that the typical effluent components,—even though they are persistent and fat soluble,—are not concentrated to the same extent as PCB in the surface film.

TABLE II
PCB in surface and water samples

Locality	Date	PCB (ng/l) in surface sample	PCB (ng/l) in water sample
Tovdal, S. Norway	July 1976	19, 17, 15	10
Tovdal, S. Norway	May 1977	6, 2	7
Gulsvik, S. Norway	July 1976	18, 14, 24	27
Hedal, S. Norway	Sept. 1977	5, 4, 6	1
Lake Østernvann, Oslo area	June 1977	6, 10. 13	3
Lake Østernvann, Oslo area	June 1977	2, 5	1
Lake Østernvann, Oslo area	July 1977	13, 8	1
Lake Østernvann, Oslo area	Aug. 1977	15, 9, 19	3
Lake Østernvann, Oslo area	Sept. 1977	14, 6	—
The Oslofjord at Tofte	Dec. 1976	12, 10, 21	<10
The Frierfjord, S. Norway	May 1977	2, 5, 2	4
The Frierfjord, S. Norway	May 1977	6, 4, 8	6

The results obtained from surface samples from the Oslofjord at Tofte, an area which is polluted by effluents from a pulp mill, also indicate that enrichment of such effluent components in the surface film is less important than could be expected.

It is well known that PCB is a global pollutant which can be transported over long distances in the atmosphere[7, 8]. All the results presented here indicate that the pollutants found in the surface film on water are mainly supplied from the atmosphere while transport of pollutants from the water masses underneath seems to be of minor importance.

In Figure 4 is shown a sample from lake Østernvann that was collected about three months after the one presented in Figure 1. This surface sample also contain mainly PCB, but by comparing the two surface samples, Figure 5, one can see that the profiles differ slightly. A similar variation can be observed when comparing pollution profiles of all the surface samples that were collected in this way during the summer period. The differences between these profiles are, however, fairly small.

Generally, by observing changes in the pollution profile of the surface film in this way it should be possible to detect variations in the deposition of pollutants from the atmosphere.

The amounts of PCB in surface samples and the concentrations of PCB in the water underneath are given in Table II for some selected samples. When using this particular sampling method it is not possible to measure the amount of surface film sampled. It is however, possible to estimate this amount from data given by Duce[3] and Larsson[2]. By assuming 10 mg lipids/m^2 surface area the concentration level of PCB in the surface film can be estimated to vary typically between 5 and 50 ppm. Similar values published by Duce and Larsson are ~60 ppm and 14 to 39 ppm. By comparing these results with the concentrations in the corresponding water samples it is found that the PCB level in the surface film is 10^6 to 10^7 times higher than in the water masses underneath.

In this connection the importance of avoiding the surface film during water sampling should be pointed out. According to our results, including 1 m^2 of surface film in a 5 l water sample would correspond to an additional PCB-concentration of 10 ng/l in the sample. This additional PCB would in many cases lead to erroneous results.

In the Frierfjord samples the concentration levels of the effluent pollutants octachlorostyrene and pentachlorobenzene in the surface are compared to the water concentrations in the same way as previously described for PCB. The corresponding ratios are however an order of magnitude of 5–100 times lower than those observed for PCB. This again indicates that atmospheric deposition of pollutants onto the surface is more important than enrichment of pollutants from the water in determining the surface "pollution profile".

References

1. W. D. Garrett, *Deep-Sea Res.* **14**, 221 (1967).
2. K. Larsson, G. Odham, and A. Sødergren, *Marine Chemistry* **2**, 49 (1974).
3. R. A. Duce, J. A. Quinn, C. E. Olney, S. R. Piotrowicz, B. J. Ray, and T. L. Wade, *Science* **176**, 114, 161 (1972).
4. G. Lunde, J. Gether, N. Gjøs, and M. B. Støbet Lande, *Atmos. Environ.* **11**, 1007 (1977).

5. G. Lunde, and E. Baumann Ofstad, *Z. Anal. Chem.* **282,** 395 (1976).
6. E. Baumann Ofstad, G. Lunde, K. Martinsen, and B. Rygg, submitted to *Sci. Tot. Environ.* March 1978.
7. V. E. McClure, *Envir. Sci. & Techn.* **10,** 1223 (1976).
8. A. Sødergren, *Pesticides.* Proceedings IUPAC 3. Int. Congress on Pesticide Chemistry. Helsinki 3–9 July 1974. Coulston, Frederick and Fridhelm Korte (Ed.) Stuttgart, West Germany.