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Chlorinated hydrocarbons in seawater of the German Bight and the Western Baltic

by

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Introduction

The analysis of chlorinated hydrocarbons in fishes is well documented. A number of laboratories routinely analyse fishes and shellfish within the framework of national monitoring activities. The analysis of chlorinated hydrocarbons in seawater, however, is not as common. This is partly due to the difficulties arising from sampling and analysing samples which contain, for instance, less than 10^{-9}g of a single compound in 1 l of water. German legislation requests the monitoring of pollutants in seawater. This is the task of the Deutsches Hydrographisches Institut in Hamburg.

We started our work in late 1971, and developed suitable sampling techniques for the different water layers, as well as a fairly quick and gentle method for the analyses of some pesticides and the PCB group.

Sampling techniques

We investigated different surface layers. The samples are taken in front of the bow of the slowly moving ship, in order to obtain water which is not contaminated by the ship.

Sampling of the micrometre layer is carried out with a stainless steel screen, which is mounted in a wooden frame. The screen can be operated from on board the ship. After having touched the surface, the screen is extracted on board in the special container by rinsing it with suitable solvents (STADLER and SCHOMAKER, 1977).

The millimetre layer is collected with a funnel-type sampler made of stainless steel. It is stabilized by a ring-type floating device. While sinking slowly through the sea surface it samples 1 l of the surface layer, which corresponds to a 3.5 mm layer. A ball valve automatically shuts the sampler. The water is extracted on board (STADLER and SCHOMAKER, 1975).

The metre layer collection method was our original one. It is carried out simply with a stainless steel bucket. 10 l water samples are collected and extracted in special

3 l two-necked glass bottles by shaking on a mechanical shaker for half an hour. After 2 h, the extract is decanted by a special separation device, which is constructed to simplify the procedure and to avoid contamination with further glassware (STADLER and ZIEBARTH, 1975, 1976).

For the collection of sub-surface samples, we constructed two types of samplers, which pass through the sea surface in a closed position and which are opened at any desired depth down to 240 and 500 m respectively. This is to avoid contamination of the sample with the surface film, which is known to be an accumulator for chlorinated hydrocarbons and other pollutants.

The 20 l stainless steel sampler has the advantage of high stability, which is useful under rough weather conditions (STADLER and SCHOMAKER, 1976).

The 10 l spherical glass sampler has some big advantages: in particular, it can be cleaned very easily and the sample can be extracted within the sphere. A decantation device similar to that used for the 3 l bottles facilitates separation of the extract (STADLER and SCHOMAKER, 1977).

Analytical procedure

In our land-based laboratory, the extracts are dried, concentrated to 2 ml, and sprayed - with a band sprayer - onto thin layer plates. On both edges of the plate, a standard is running in a sufficiently high concentration to give spots under UV when sprayed with $AgNO_3/H_2O_2$/2-phenoxiethanol.

This is in order to find the separated substances in the different zones in a reproducible way. Four zones are cut off and eluted separately in special elutors.

The eluates are concentrated to 0.2 ml and analysed and identified by multi-column gas chromatography using packed columns.

Results

The concentrations of the different pollutants are for

the µm layer from 7 to 300 ng/m^2;
the mm layer from 0.6 to 162 ng/l;
the m layer from 0.06 to 20 ng/l;
the 1-10 m layer from 0.06 to 14 ng/l;
the >10 m layer from 0.06 to 13 ng/l.

The following nine substances have been detected: lindane, α-BHC, δ-BHC, dieldrin, p.p'-DDE, p.p'-DDD, β-BHC p.p'-DDT, and PCB.

As a preliminary result of our recent investigations we found some unexpected relationships:

- no correlation between the amount of visible particulate matter and organochlorine concentrations (OCC);
- no correlation between land distance and OCC;
- no correlation between rain and OCC in the surface layer;
- only slight decrease of OCC with depth (STADLER, in press).

Conclusion

After a preliminary phase of introduction of methods for sampling and analytical procedures, we are now in a position to monitor organochlorine pesticides and PCBs on a routine basis.

The analytical method was intercalibrated in a national intercalibration exercise with success.

The intercalibration of the sampling device, however, is much more complex. This could be seen during a Canadian/German Intercalibration Experiment in October last year, and during the Baltic Intercalibration Workshop in Kiel in March this year. Both exercises showed clearly the need for sufficient time for the preparation of the experiments, and for the experiments themselves, in order to obtain valuable results.

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