

## Organohalogen Pesticides in the North Sea and Baltic Sea

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### Introduction

Organohalogen substances like Trifluralin, Endosulfan I and II, Chlorpyrifosmethyl and –ethyl are used as active agents in a wide variety of pesticidal applications.<sup>1,2,3</sup> Via the hydrological cycle these contaminants can be released into the aquatic environment and finally reach the oceans.<sup>4</sup> The substances mainly Endosulfan I and Chlorpyrifos-ethyl are very toxic. The half-lives of the compounds in water or sediment vary between two weeks and one year, depending on the soil type, climate or other conditions. Most of the substances show a significant liability to bioaccumulate. For this reason they are under review as priority substances under the European Commission's Water Framework Directive process, and/or on the OSPAR list of candidate substances, comprising hazardous chemicals in the marine environment.<sup>5,6</sup> There is only few information about concentrations of Chlorpyrifos-ethyl in the North Sea, whereas nothing is known about the levels of the other substances in the North and Baltic Sea.<sup>7</sup> This study aimed at developing methods to determine concentrations of Trifluralin, Chlorpyrifos-methyl, Chlorpyrifos-ethyl, Endosulfan I and II in seawater and sediment samples from the German Bight and Baltic Sea.

### Materials and Methods

**Samples.** During four monitoring surveys into the German Bight (January 2004, July 2004, January 2005) and the Baltic Sea (June 2004) seawater and sediment samples were collected. Seawater samples were taken using a 10L glass sampler and extracted by solid phase extraction (SPE) at sea.<sup>8</sup> Sediment samples were taken using a box corer and stored in aluminium containers at  $-20^{\circ}\text{C}$ .<sup>9</sup> The schemes for the analytical procedures are shown in figure 1.

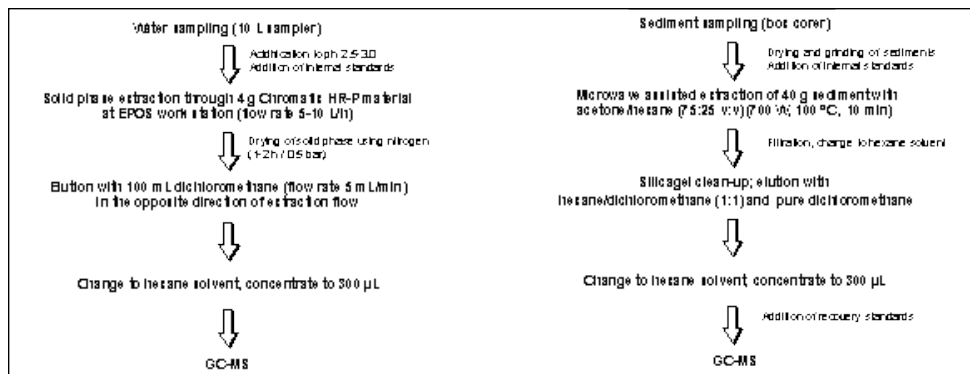


Figure 1 Scheme for the analysis of seawater and sediment samples.

**Solid phase extraction of water samples.** Before SPE the samples were acidified to pH 2.5-3.0 (25% hydrochloric acid, p. a.).  $D_{14}$ -Trifluralin,  $D_{10}$ -Chlorpyrifos-ethyl and  $D_4$ -Endosulfan I (Dr. Ehrendorfer GmbH) were added as internal standards. The seawater was pumped through a column filled with 2 g Chromafix HR-P resin (Macherey and Nagel) at a custom made extraction system. The loaded columns were dried and stored in the dark at  $8^{\circ}\text{C}$  until elution. All target substances were eluted with dichloromethane. After solvent change to hexane the extracts were analysed by GC-MS.

**Microwave assisted extraction of sediment samples.** Before analysis the sediments were dried and ground.  $D_{14}$ -Trifluralin,  $D_{10}$ -Chlorpyrifos-ethyl and  $D_4$ -Endosulfan I were added as internal standards. To remove sulphur the sediment was mixed up with activated copper powder. Hot extraction was accomplished in a microwave oven (10

min; 100°C) using acetone/hexane (75/25 v/v) as solvent. After cooling the solution was separated from the sediment by filtration. After solvent change to hexane the extracts were cleaned up on silica gel (silica gel 60, Merck; heated for 2 h at 150°C, deactivated with 6% w/w water). Elution was done with hexane/dichloromethane (50/50 v/v) and pure dichloromethane. The solvent of both fractions was changed to hexane and D<sub>6</sub>-Chlorpyrifos-methyl was added as recovery standard. The first fraction contains all target compounds.

**Analysis.** Seawater and sediment extracts were analysed by GC-MS (Trace MS, Thermo Electron) with negative chemical ionisation (NCI).<sup>10</sup> In comparison to GC-MS with electron impact ionisation (EI) the NCI technique produces less fragmentation and yields for all compounds of this investigation a higher response and better selectivity.

For method validation limits of quantification (LoQ) and recovery rates of the target compounds were determined. In seawater samples the recovery rates of the analytes varied between 72-90%, in sediment samples between 65-110 %. Blank values were carefully controlled, no blank values were observed above the LoQ.

## Results and Discussion

**Watersamples.** Figure 1 shows the concentrations of Trifluralin, Endosulfan I and II, Chlorpyrifosmethyl and –ethyl in water samples collected in 2004 in the Baltic Sea and the German Bight. The levels of these compounds in winter-surveys (January 2004 and 2005, German Bight) are similar to the concentrations in summer (data not shown) with the exception of Trifluralin (s.b., figure 2). Thus the levels of Chlorpyrifos and Endosulfan do not show seasonal fluctuations. In all seawater samples from the German Bight the concentrations of Endosulfan II and Chlorpyrifos-methyl are beneath the limit of quantification. The ubiquitarily measurable low concentrations (lower pg/L range) of Endosulfan I and Chlorpyrifos-ethyl can be best explained by a chronic pollution without near-by acute sources.

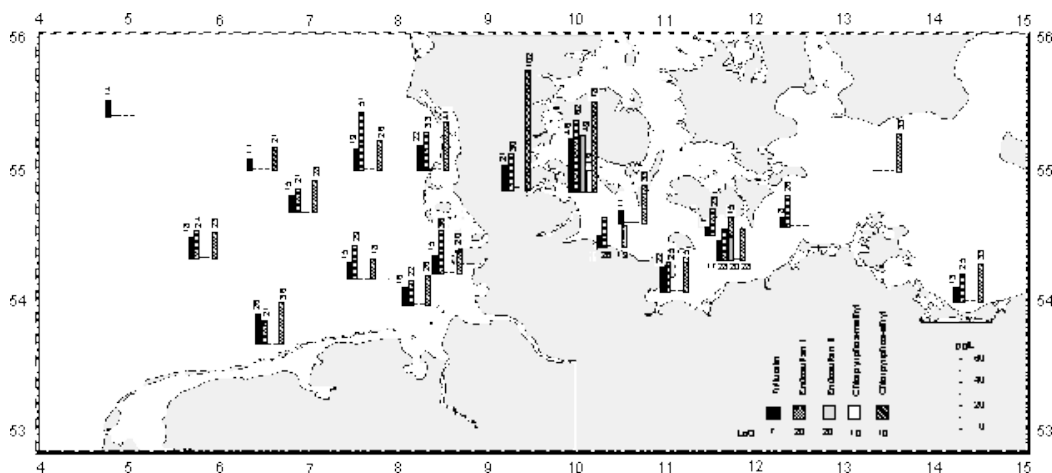


Figure 2 Concentrations of Trifluralin, Chlorpyrifos-methyl, Chlorpyrifos-ethyl, Endosulfan I and II in seawater [pg/L] from the German Bight (July 2004) and Baltic Sea (June 2004).

In general the concentrations of the target compounds in the Baltic Sea are similar to that of the North Sea except for the concentrations in the Flensburger Bight. Here the levels of all substances are significantly increased. In the same area (Eckernförder Bight) the sediment samples showed elevated concentrations of Endosulfan I and II too (figure 3). This result indicates a slight pollution of this area by the targeted compounds caused by e. g. intensive agriculture along the coast. In addition the mass transfer caused by currents is slow in this area because of narrow fjords and bights.

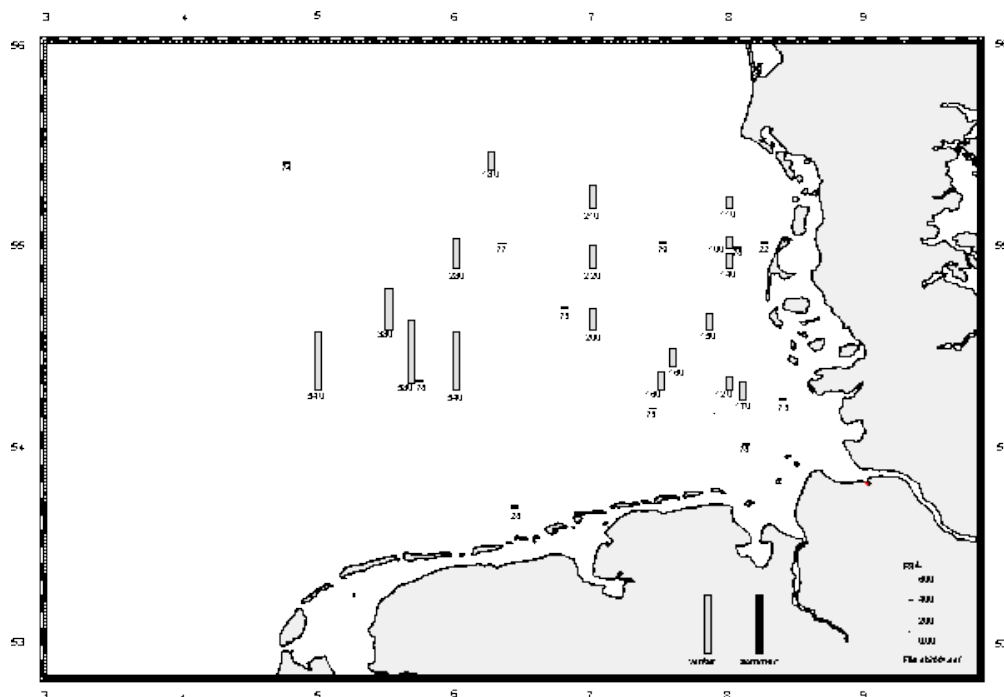


Figure 3 Concentrations of Trifluralin (summer and winter) in seawater samples from the German Bight (January 2004, July 2004, January 2005); LoQ: 7 pg/L.

The results of three sampling cruises into the German Bight (January 2004, July 2004, January 2005) showed that during winter season ten times higher concentrations of Trifluralin were observed than in summer (winter: 100-580 pg/L, summer: 11-22 pg/L; figure 2). This seasonal dependence can be explained by the use of this compound as herbicide for pre-sowing or pre-emergence treatment of grasses and dicotyledonous weeds in autumn.<sup>1</sup> Considerable amounts of Trifluralin were washed out by rain water and transported into the North Sea via rivers or atmospheric deposition. In the mouth of the river Elbe, generally the main source of pollution for the German Bight, the levels are in winter higher than in summer, as well. However, in comparison to winter levels of the open sea (100-580 pg/L) the levels of the Elbe estuary (120-170 pg/L) are relatively low. Thus, the main load of Trifluralin in the German Bight is probably "imported" by the main current from the west. The seasonal variability of Trifluralin concentrations indicate an annually arising new contamination input.

**Sediment samples.** In sediment samples of the German Bight Trifluralin and Chlorpyrifos-ethyl were detected in the lower pg/g range (figure 3). The levels of Endosulfan I and II and Chlorpyrifos-methyl were always beneath the limit of quantification. In the Baltic Sea Trifluralin was identified in all sediment samples - at low concentrations. Endosulfan I and II were found only at one station at the west coast (Eckernförder Bight) showing slightly elevated concentrations of 196 pg/g and 86 pg/g

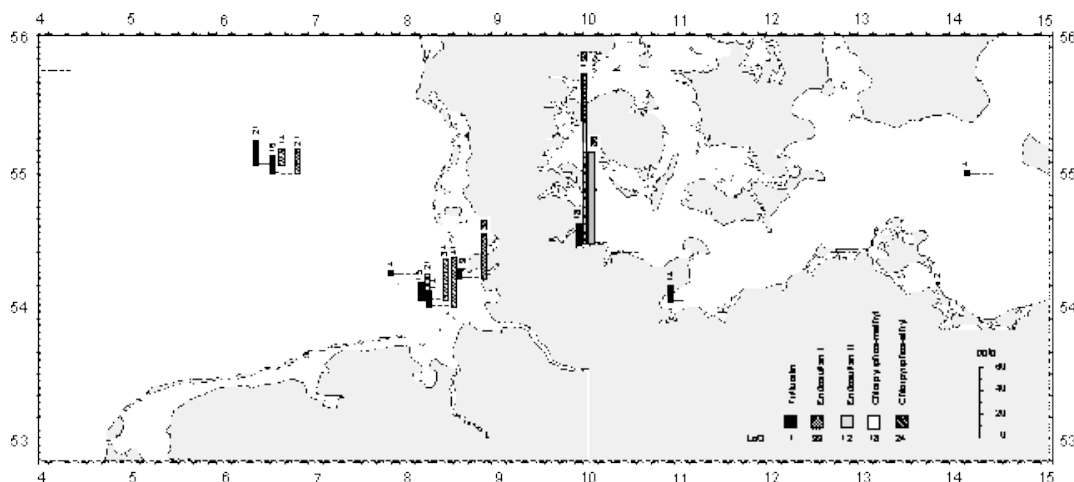


Figure 4 Concentrations (pg/g dw) of Trifluralin, Chlorpyrifos-methyl, Chlorpyrifos-ethyl, Endosulfan I and II in sediment samples from the German Bight and Baltic Sea (June 2004, July 2004).

**Conclusion:** Trifluralin, Endosulfan and Chlorpyrifos-ethyl have been detected at low concentrations in water and sediment samples from the North Sea and Baltic Sea and thus indicate a certain level of persistence in the marine environment. The observed concentrations (10 to 100 pg/L) are higher than the routinely monitored PCBs and DDT-metabolites (< 5 pg/L) but lower than the HCH isomers (80 to 400 pg/L). For a final comprehensive assessment, concentrations in biota have to be considered as well; therefore, the presented procedure is presently further developed for the analysis of fish tissue.

#### Acknowledgements

This study is supported by the German Environmental Agency, Berlin (FKZ 200 25 22402).

#### References

1. OSPAR Background Document on Trifluralin, OSPAR Commission 2004
2. OSPAR Background Document on Endosulfan, OSPAR Commission 2002
3. Extoxnet (1993), Pesticide Information Profile on Chlorpyrifos Oregon State University, <http://extoxnet.orst.edu/pips/chlorpyr.htm>
4. Chernyak S. M., Clifford P. R. and McConnel, L. L. (1996) *Marine Pollution Bull.* 32 (5): 410-419.
5. European Commission's Water Framework Directive, Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, OJ EC No. L 327
6. OSPAR List of Chemicals for Priority Action (Update 2004), OSPAR Commission
7. Horth H. and Richards R. (2002) Review of monitoring and occurrence of Chlorpyrifos in the marine environment in Europe, final report, WRcRef: UC 6009, Dow AgroSciences: 1-20
8. Theobald N., Lange W., Rave A., Pohle U. and Koennecke P. (1990) *Dt. hydrogr. Z.* 43: 311-322.
9. Nies H., Albrecht H., Rechenberg V., Goroncy I., Dahlgaard H., Weiß D. and Bruegmann L. (1990) *Dt. hydrogr. Zt.* 43: 27-53.
10. Liapis K. S., Miliadis G. E. and Tsiropoulos N. G. (2000) *Bull Environ Contam Toxicol.* 65: 811-817.