

On the presence of hepta- and hexachlorostyrenes in addition to octachlorostyrene in fish samples from the river Elbe

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Introduction:

Biota, e.g., fish samples are often extracted with organic solvents, cleaned up and analysed for standard pollutants like HCHs, PCBs, chlorobenzenes, DDT and the respective metabolites. Although the clean ups are supposed to be rather selective a lot of the resulting peaks in a gas chromatogram, detected with an electron capture detector (ECD) remain unknown and unanalysed. During a study on PCB concentrations in fish samples mass spectral verification in full scan modus was applied which revealed some chlorine clusters that were not easily explained. In the following interpretation the spectra obtained from the so far „unknown“ compounds were found to be similar to the well known pollutant octachlorostyrene (OCS), except for the fact that they were lacking one respectively two chlorine atoms; thus they were identified as hepta- and hexachlorostyrenes.

Chlorostyrenes have been identified in the past in biota samples from the Great Lakes¹⁻³ and from the Frierfjorden in Norway^{4,5} as well as other ecosystems. The emission of penta-, hexa-(HxCS) and heptachlorostyrenes (HCS), in addition to OCS, has been traced to electrolytic processes including the production of magnesium with graphite electrodes. In Germany only OCS and in rare cases heptachlorostyrenes were identified in environmental samples⁶⁻⁸.

In this study we show the presence of hexa-, hepta- and octachlorostyrene in fish samples in the river Elbe from the Czech border downstream to the estuary.

Experimental:

Fish samples (bream, *abramis brama*) were taken at the diverse stations. Liver and muscle samples of these fishes were homogenised with anhydrous Na₂SO₄ (1:5), extracted with *n*-hexane (residue grade) and successively cleaned up with alumina, H₂SO₄, silica and gel permeation chromatography.

The resulting extracts were analysed with capillary gas chromatography on a Carlo Erba 8000 GC equipped with a CP-Sil 5/C 18 CB column (100 m x 0.32 mm, 0.1 µm film, Chrompack) and a ⁶³Ni electron capture detector with carrier gas hydrogen at 160 kPa.

The identification was performed with an Magnum ion trap mass spectrometer. The respective gas chromatograph was equipped with a DB5-MS (30 m x 0.25 mm, 0.25 µm film) with helium at 70 kPa as carrier gas.

TOXA (po)

A mixture containing three heptachlorostyrenes was synthesised from OCS with NaH in *n*-heptane, while αH -heptachlorostyrene was obtained from OCS with Zn and aqueous hydrochloric acid in dioxane⁹.

Results and discussion:

Three heptachlorostyrenes, showing the same mass spectra were found in fish samples from the river Elbe (hereafter denominated HCS1, HCS2, and HCS3, respectively). These compounds were identical with those synthesised from OCS with NaH. Though one of the respective compounds (HCS3) supplies the same gas chromatographic and mass spectrometric data as the synthesised αH -heptachlorostyrene the exact identification of the respective isomers is not yet possible. In figure 1 a mass spectrum of the most abundant heptachlorostyrene (HCS1) obtained from a fish sample is shown.

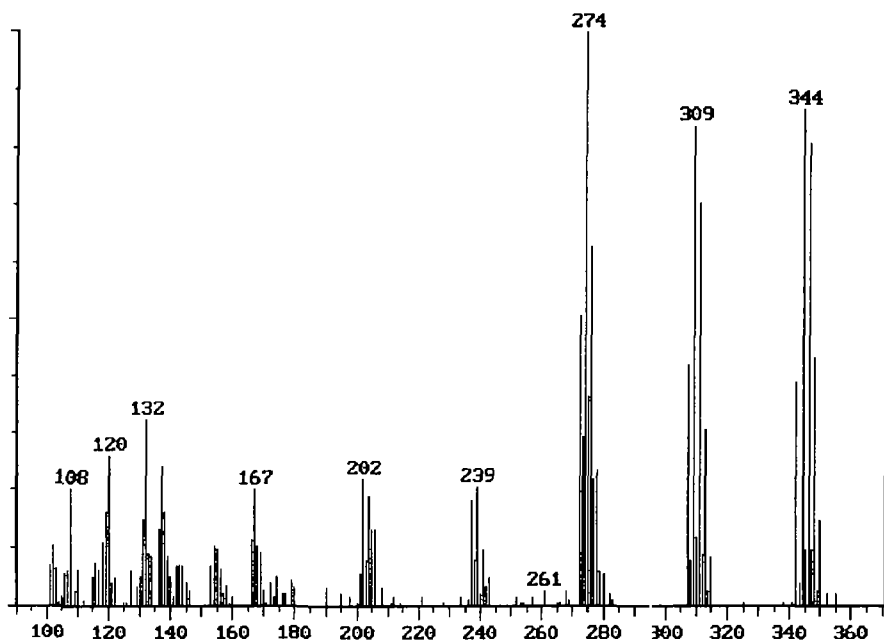


figure 1 Spectrum of heptachlorostyrene (HCS1) [MG=342] obtained from a fish sample (liver) from the river Elbe

The concentrations as obtained by comparing the respective areas for the analytical ion chromatograms (i.e. 344 and 274 m/z for heptachlorostyrenes, 380 and 308 m/z for OCS respectively) of heptachlorostyrenes were in the same order of magnitude as the concentrations of octachlorostyrene. Integrals of the respective ion chromatograms and the respective retention times are depicted in table 1.

At least three hexachlorostyrenes were identified by their mass spectra, though no standard compounds were available (compare figure 2). The concentrations of the HxCS are generally lower than those of HCS and OCS (table 1).

table 1) Relative integrals and retention times of the most abundant chlorostyrenes from a fish sample (liver) from the river Elbe near the Czech border

compound	integral	analytical ion [m/z]	retention time [scan nr]
HxCS2	10	275	1990
HxCS3	1	275	2020
HCS1	100	274	2230
HCS2	10	274	2240
HCS3	10	274	2343
OCS	650	308	2555

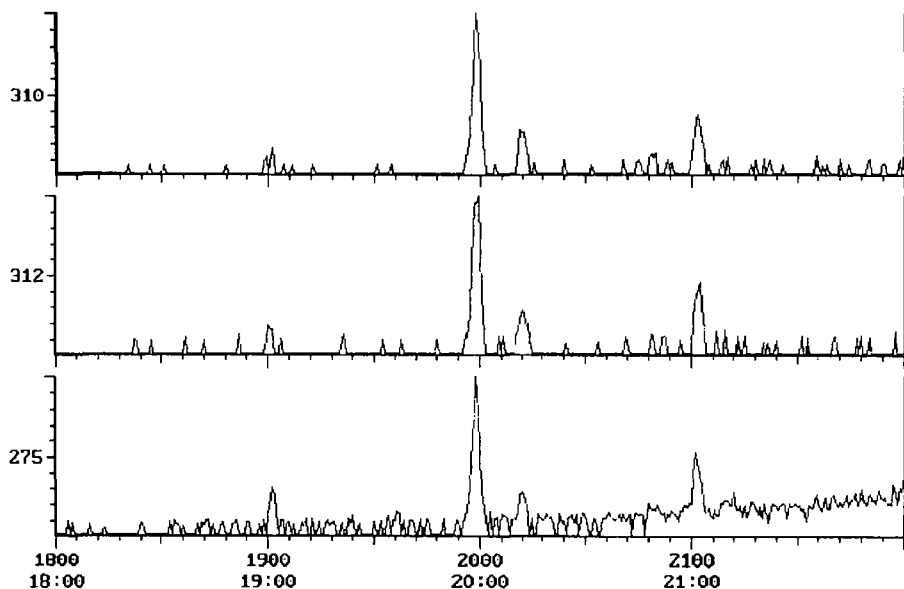


figure 2 Ion chromatograms ($m/z=310, 312, 275$) of the most abundant ions of hexachlorostyrenes (HxCS) [MG=308] obtained from a fish sample (liver) from the river Elbe.

Concentrations were calculated using the synthesised compounds for identification and OCS for a calibration with GC-ECD (figure 3). The concentrations in liver samples were high in the upper part of the river Elbe near the Czech border and in the vicinity of the city of Dresden, further downstream they are declining, until the river Mulde enters the Elbe near Barby. In the samples downstream from the mouth of the Mulde the pattern has changed, as the concentration ratio HCS1 referred to OCS is clearly elevated.

All chlorostyrene derivatives were still detectable in fish (bream, muscle sample) from the river Elbe estuary, though the concentrations referred to fresh weight (fw) changed to 8.8 ng/g (HCS1) and 9.3 ng/g (OCS). On the other hand no OCS and HCS was found in lake Belau which is located in central Schleswig-Holstein in an agricultural area and receives its water from small springs.

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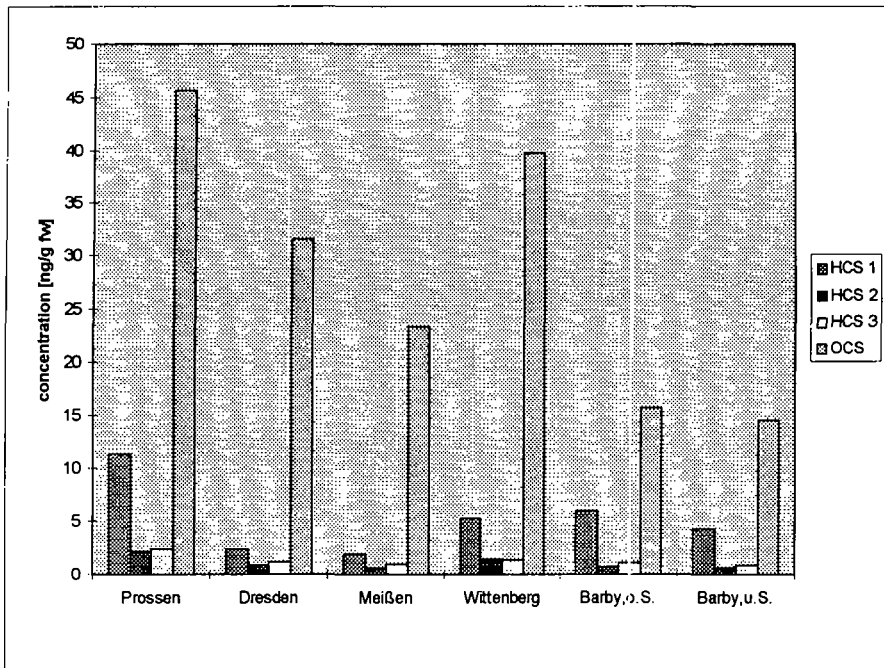


figure 3 Concentrations (referred to fresh weight) of octachlorostyrene (OCS) and heptachlorostyrenes (HCS1-3) in fish samples (liver) obtained from the river Elbe

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