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Ocean Incineration of Toxic Wastes: a Footprint in North Sea Sediments

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In an investigation of organochlorine levels in sediments from the North Sea, most organochlorine pesticides as well as polychlorinated biphenyls (PCB) showed highest sediment contamination levels close to the German, Dutch, and British coasts that decreased towards the open sea, but elevated hexachlorobenzene (HCB) concentrations were found in the sediments of the international ocean combustion area in the centre of the southern North Sea and were accompanied by exceptionally high levels of octachlorostyrene (OCS). It is suggested that both HCB and OCS enter the North Sea ecosystem as products of incomplete combustion from ocean incineration.

Ocean incineration of hazardous wastes has been conducted in the North Sea since 1969. Between 1980 and 1985, the annual amount of combusted wastes has been about 100 000 t yr⁻¹ (UBA, 1985; Anon., 1987). In spite of the high effort necessary to ship the waste to the incineration site (centre point located at 54°17.5'N/03°45'E, radius 15 nm), ocean combustion became cost-competitive with waste incineration on land due to one big legal advantage; at sea, no measures have to be taken in order to retain the large amounts of hydrochloric acid produced during waste combustion (Fig. 1). This is particularly important for certain highly chlorinated wastes that lead to corrosion problems in the scrubbers used on land (Sutter & Noll, 1987). Furthermore, the combustion vessels lack additional techniques like secondary combustion chambers designed to reduce the amounts of undestroyed organic matter emitted with the stack gases.

For all these reasons, critics have claimed for years that ocean incineration is by far inferior to waste combustion on land (Zurer, 1985). They also point out the fact that at open sea it is much more difficult to monitor the emissions of products of incomplete combustion, than on land.

While numerous studies on the destruction efficiency of the combustion vessels have been carried out so far (Nassos, 1987), no reports of actual monitoring of emitted organic substances in the marine ecosystem are

known. In the present study, sampling stations from the ocean combustion area in the southern North Sea were included in the sediment investigation programme.

Materials and methods

Sampling

Surface sediment samples were taken with a van Veen grab sampler on several cruises on RV *Anton Dohrn* and RV *Valdivia* between December 1984 and May 1987 (Fig. 3, 4).

Sediment samples were stored in hexane rinsed metal boxes and frozen at -20°C.

Sample preparation

In the laboratory, samples were thawed and dried at 40°C. Depending on the type of sediment, between 50 and 200 g were extracted with hexane/acetone (41:59 v/v) in a Soxhlet apparatus. Sulphur was removed with tetrabutylammoniumsulphite reagent following the procedure of Jensen *et al.* (1977). The extracts were concentrated to 100–1000 µl.

All steps were checked for recovery rates and blank values before quantitation was carried out. Solvents were residue analysis grade and were pre-distilled if necessary. The overall recoveries were between 95 and 102% for each component. Detection limits were at 2 pg g⁻¹ dry wt for HCB and 5 pg g⁻¹ d.w. for OCS and the PCB congeners, respectively.

Quantitative Analysis

The organochlorine concentrations in the extracts were determined by capillary gas chromatography on two 25 m columns of different polarity (SE 54 and OV 1701) using an on-column injection system and electron capture detection. Quantitation was carried out by the external standard method. A compound was considered to be identified only if the results from both columns differed by less than 20%. In other cases, after inspection of chromatograms, either the lower value was assumed to be correct, or the compound in question was considered as not determined in this sample.

Quantitation of PCBs has been the topic of lengthy

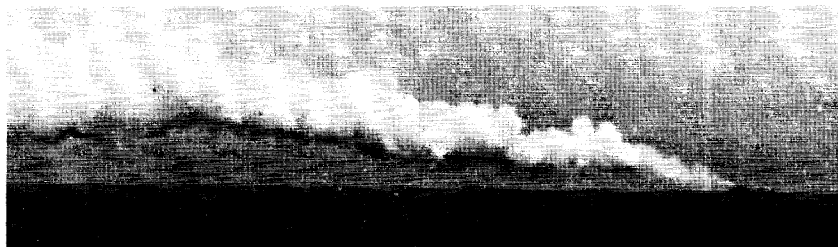


Fig. 1 Exhaust plume of combustion vessel *Vulcanus II* operating in the southern North Sea on 15 May, 1987. The stack emissions consist of mainly HCl, CO₂, and H₂O, plus minor contributions of other organic and inorganic species.

discussions because it is generally not possible to measure each one of the 209 possible congeners. Several methods have been suggested, most of which involve the separate quantitation of selected PCB isomers (Duinker *et al.*, 1980). In this work, the three most prominent PCB peaks that were present in all of the samples analysed, i.e. congeners 138, 153, and 180, have been summed up to give one numerical value for PCB concentration at each station.

Total organic carbon (TOC) content of sediments was determined by the method of Espitalié *et al.* (1984) on an Oil Show Analyzer (Delsi Instruments).

Results

Typical chromatograms of the non-polar fraction of sediment extracts, containing HCB, OCS, and PCB, are presented in Fig. 2 a–d. Chromatographic conditions were: 25 m SE 54, chemically cross-linked, cold on-column injection (60°C), ⁶³Ni-ECD, T-programme 60–135°C, 30°C min⁻¹; 135–220°C, 4°C min⁻¹; 220–270°C, 10°C min⁻¹.

Quantitatively, the chromatograms display different characteristic patterns of non-polar organochlorine pollutants in the four regions of investigation, namely: 1. high levels of PCB and pesticides, significantly lower but clearly detectable amounts of OCS in the German Bight (a); 2. low organochlorine levels on the Dogger Bank (b); 3. high HCB levels, medium concentrations of PCB and a variety of unknown ECD-active substances, and traces of OCS near the mouth of the Humber river (c); 4. large peaks of HCB and OCS, significantly lower PCB and pesticide concentrations in the ocean combustion area (d).

For quantitative evaluation, a correction has to be made with respect to the adsorption capacity for non-polar organic substances of the different types of sediments. The two approaches commonly used include standardization of organochlorine concentrations in total sediment for either a defined grain size fraction or total organic carbon (TOC) content of the sediment (Boon *et al.*, 1985). After thorough studies of the advantages of either method (Lohse, 1988), standardization for TOC content of sediments was chosen for comparison of analytical data from different sea areas. TOC standardization has not been calculated for samples with an organic carbon content smaller than 0.03% of the dry sediment.

Figure 3 shows the distribution map of HCB in total sediment (a) and the TOC standardized pattern (b). The

corresponding PCB patterns can be seen from Fig. 4a and 4b, respectively.

Figures 3b and 4b demonstrate that TOC standardized distributions of HCB and PCB in the southern North Sea show similar patterns, with the main exception that PCB concentrations in the ocean combustion area are close to the baseline pollution level (at about 50 ng g⁻¹ TOC), while HCB concentrations in this area lie clearly above the HCB baseline value of about 10 ng g⁻¹ TOC.

The pesticide data obtained during this investigation are reported elsewhere (Lohse, 1987).

Discussion

The significance of the riverine contributions to the total organochlorine burden of the North Sea is a well accepted fact that has been established by numerous investigations (e.g. RIWA, 1986; ARGE Elbe, 1987; Weber & Ernst, 1983; Boon *et al.*, 1985). However, the occurrence of HCB and OCS polluted sediments in the ocean combustion area certainly requires an explanation. So far, no proof can be given that HCB and OCS are actually released with the stack gases of the combustion vessels, but there are numerous hints in the scientific literature that support this assumption.

First, both HCB and OCS are known to be products of waste combustion (Ballschmiter *et al.*, 1983). It has even been shown that, in contrast to other organochlorine compounds, the formation of HCB is favoured by increasing combustion temperature (Ahling & Lindskog, 1982). Since ocean combustion is conducted at temperatures above 1120°C (Rühl, 1985), HCB formation could clearly be favoured (Fig. 5).

HCB and OCS formation becomes even more likely if one considers that the wastes presently combusted in the North Sea are rather inhomogeneous. They contain a variety of impurities and highly varying amounts of organochlorines that lower their combustion quality (Sutter & Noll, 1987). Therefore, under 'real-world' conditions there may be a lot more products of incomplete combustion than can be observed in test burns with pure substances as reported by Nassos (1987).

Once it is accepted that HCB and OCS may be formed during ocean combustion, there is still a need to discuss why these substances should be found in the sediments right at the incineration site, instead of being distributed over wider areas by wind and currents. In this context, the observation is important that, under certain weather conditions, the stack gases are pressed down to

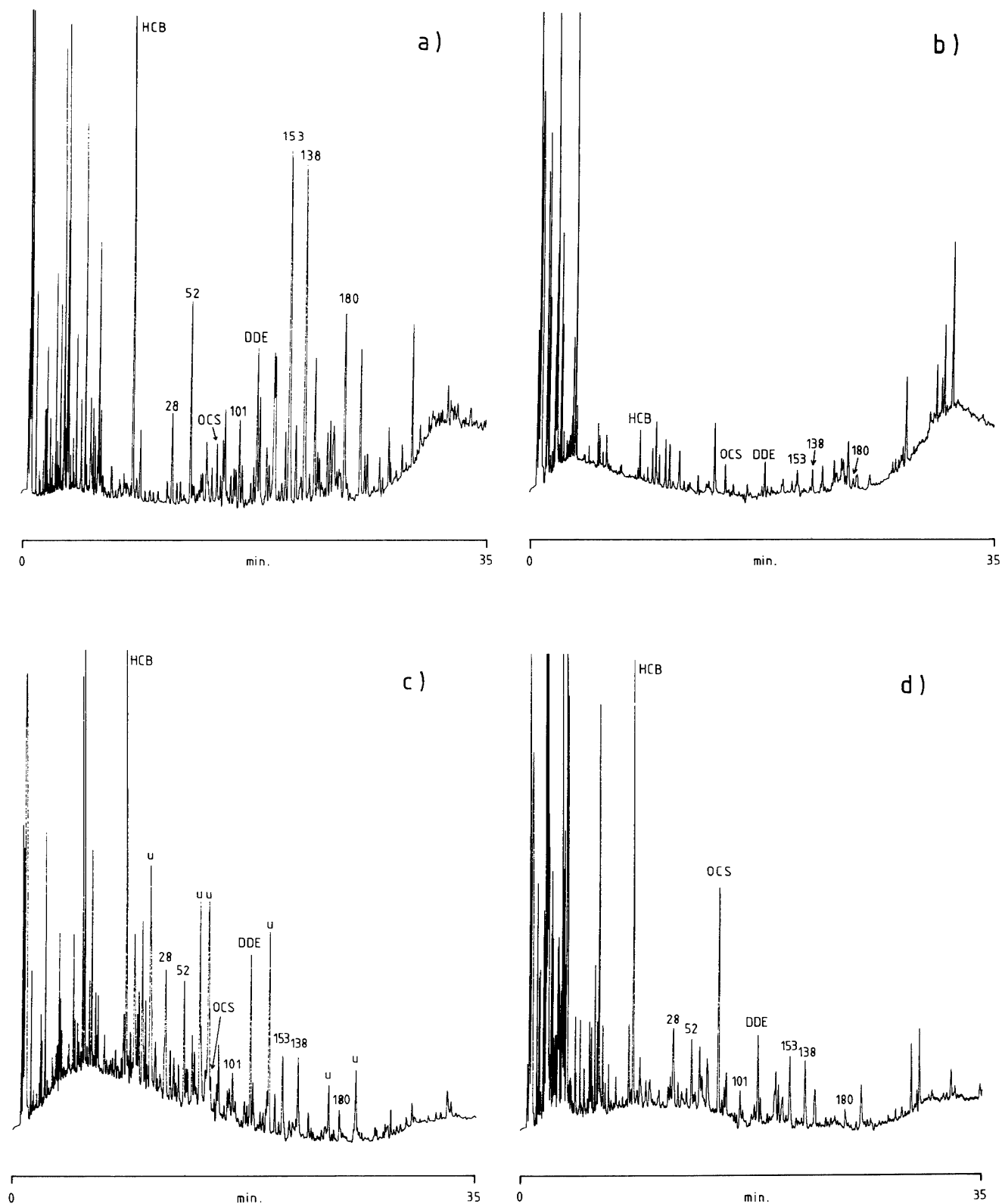


Fig. 2 Gas chromatograms of non-polar fractions of sediment extracts from a. the German Bight, b. the south-west end of the Dogger Bank, c. the British coast, and d. the international ocean combustion area (see Figs 3 and 4 for exact locations).

the water surface immediately behind the combustion vessel (Fig. 6). Thus, the less volatile organochlorines such as HCB and OCS can be rapidly transferred to the water column, where they are scavenged by sinking particles that carry them to the sediment. Rapid adsorption of non-polar organochlorine compounds onto particles is favoured as a consequence of their octanol/

water-partition coefficients that are about $\lg K_{OW}=5.5$ (Chiou, 1985). The importance of sinking biogenic particles, primarily faecal pellets, for removal of pollutants from surface waters has been emphasized in a review by Olsen *et al.* (1982) and can also be seen from the seasonal cycle of PCB deposition rates in the Baltic Sea (Osterroth & Smetacek, 1980).

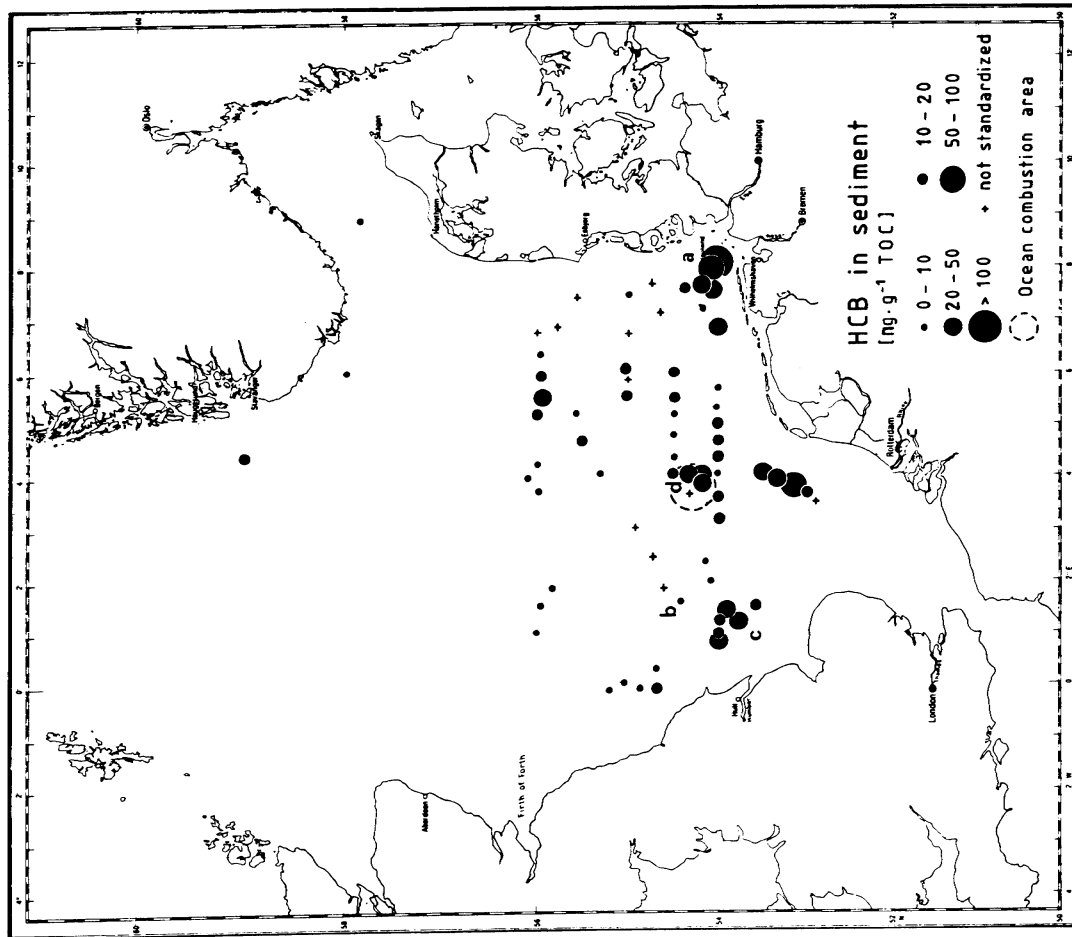


Fig. 3b TOC standardized HCB distribution (ng g^{-1} TOC).

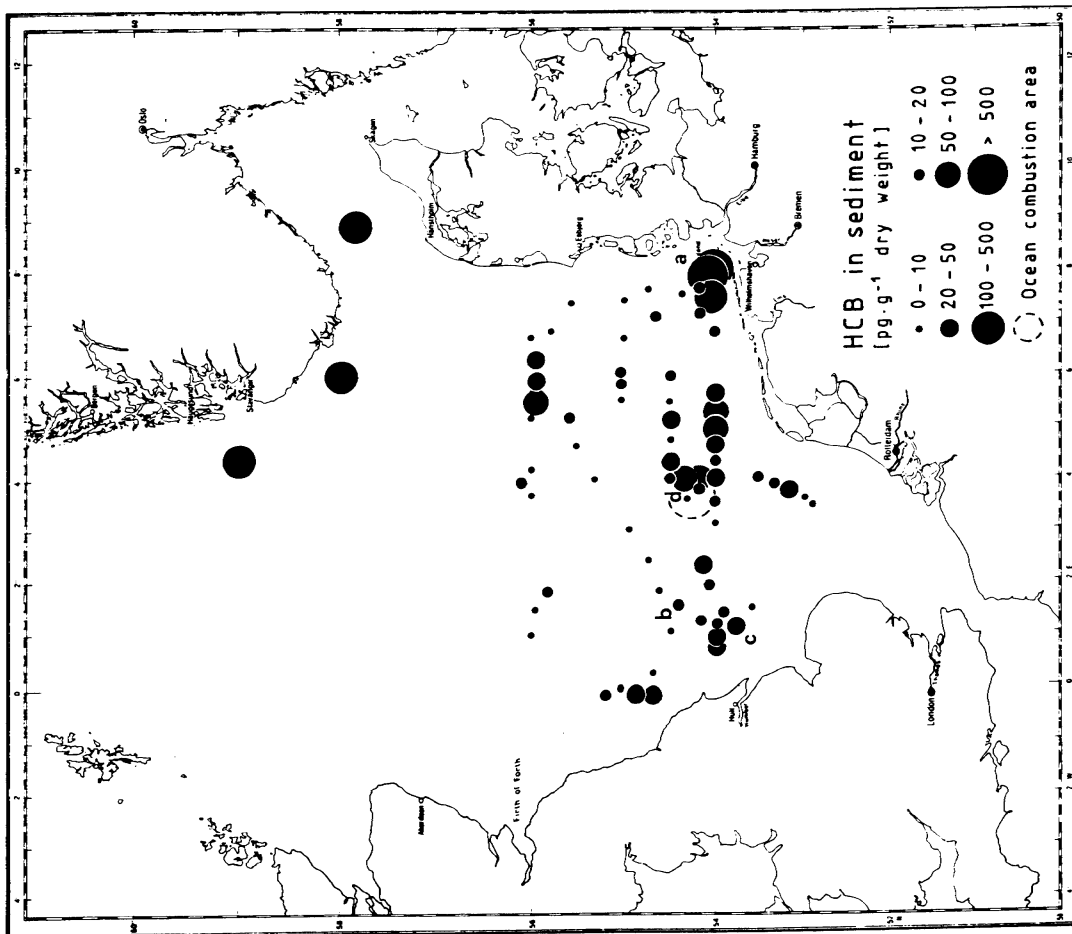


Fig. 3a Distribution of hexachlorobenzene in North Sea sediments (pg g^{-1} d.w.). Locations a-d. refer to gas chromatograms presented in Fig. 2.

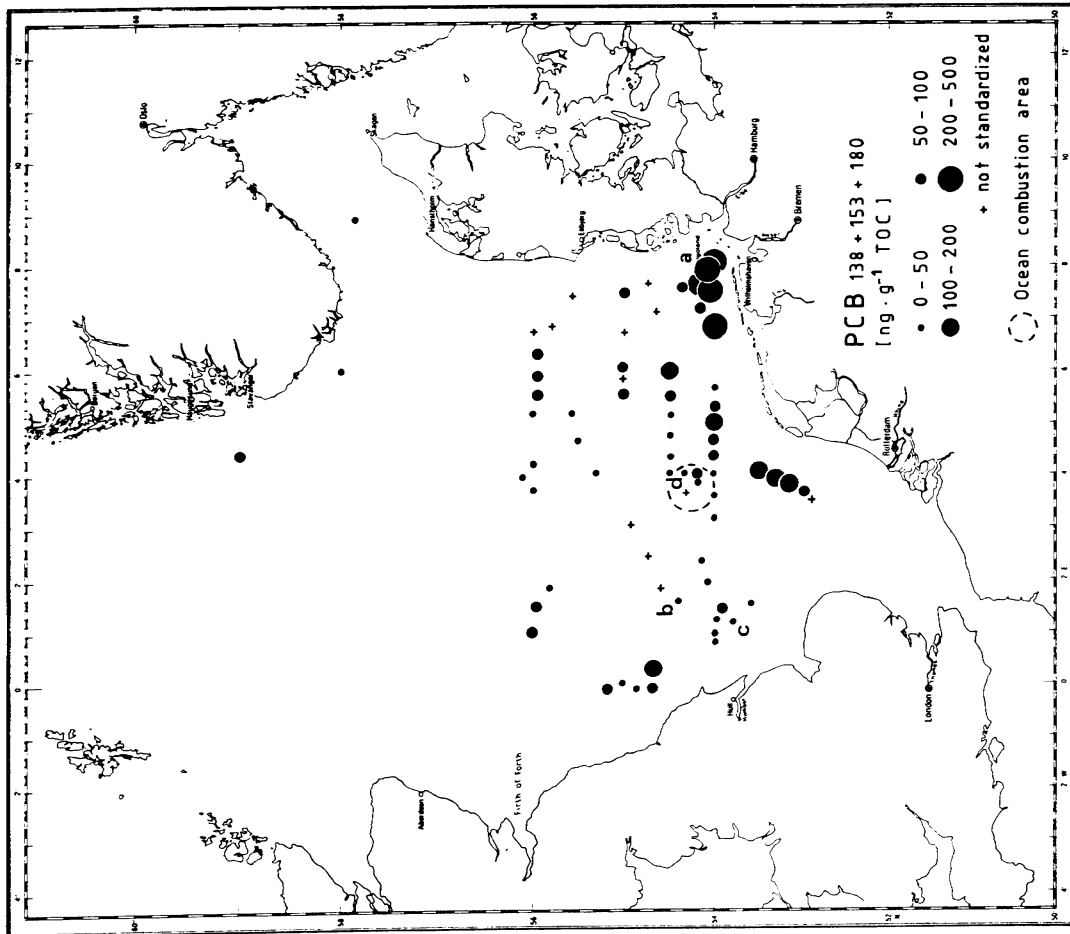


Fig. 4b TOC standardized PCB distribution ($\text{ng} \cdot \text{g}^{-1} \text{TOC}$).

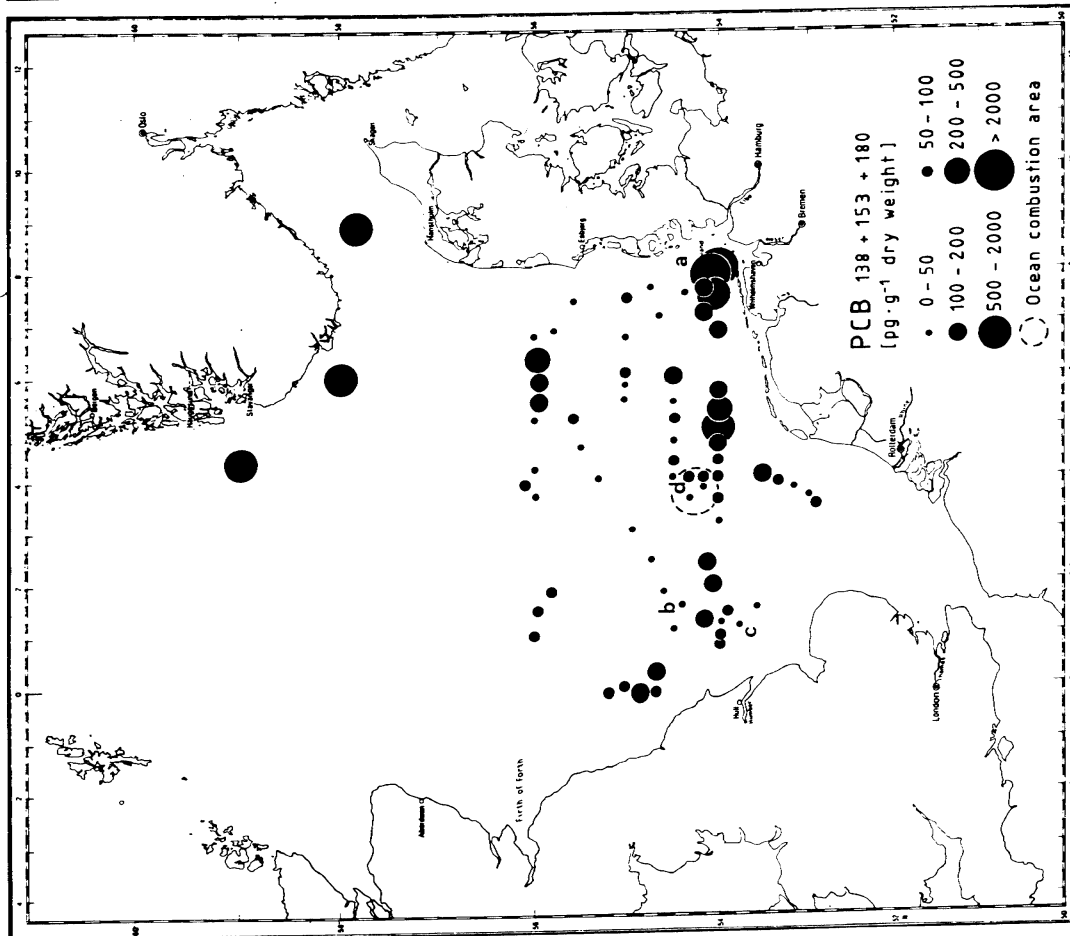


Fig. 4a Distribution of polychlorinated biphenyls in North Sea sediments ($\text{pg} \cdot \text{g}^{-1} \text{d.w.}$).

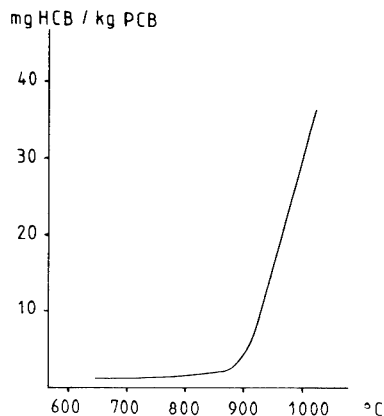


Fig. 5 HCB formation during combustion of PCB as a function of temperature (redrawn from Ahling & Lindsog, 1982).

Conclusions

The organochlorine distributions in North Sea sediments reported here feature the astonishing fact that elevated pollution levels of two known products of incomplete combustion, i.e. HCB and OCS, were found in the international ocean combustion area. Concentrations of other anthropogenic chemicals like PCB and organochlorine pesticides, which are known not to be products of incomplete combustion, were near the baseline level in the ocean combustion area. Thus it appears that HCB and OCS, and possibly other substances not covered in this investigation, are emitted from combustion vessels and are rapidly transferred to the sediment, thus adding to the organochlorine burden of the North Sea.

In the light of this study, the declared will of the participants of the Second International Conference on the Protection of the North Sea to abandon ocean combustion by 31 December 1994 (Ministerial Declaration, 1987) is certainly a step in the right direction. In my opinion, an attempt should be made to terminate this method of waste disposal at an even earlier date.

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Fig. 6 Ocean combustion vessel *Vulcanus II* at work (15 May 1987). The stack gases are touching the sea surface right behind the ship.

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