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Gas chromatographic determination of halogenated organic compounds in water and sediment in the Skagerrak

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ABSTRACT

Biogenic and anthropogenic volatile halocarbons and chlorinated phenolic compounds were monitored in the Skagerrak. Measurements were made both in water and in sediment by means of gas chromatography with electron-capture detection. The results show that the load of biogenic halocarbons exceeds that of the anthropogenic halocarbons and that the iodinated compounds show a more marked seasonal trend than the brominated compounds. Additionally, it was established that waters of different origins have exclusive sets of biogenic halocarbons. Pentachlorophenol is widely distributed throughout the Skagerrak. It is transported in its dissociated form. The concentration level of other chlorinated phenolics is less than 1 ng/l. However, it could be demonstrated that there is an accumulation of chlorinated phenolics in sediments in the deeper parts of the Skagerrak.

INTRODUCTION

Investigations of the distribution of halogenated organic compounds in a relatively large area in the marine environment are still rare, mainly owing to the difficulty of analysing large number of samples with low concentrations of analytes under complex hydrological conditions. In distribution studies the analytical procedure should ideally be simple, require small amounts of samples and be able to determine as many components as possible. Preconcentration is always necessary, as the concentrations are low and derivatization prior to analysis is needed for some compounds. Gas chromatography with electron-capture detection, with its high separation efficiency, speed of analysis and low detection limits, is by far the most commonly used technique for halogenated substances. In the coastal waters of Sweden and in the North Sea, only a few investigations have been made of individual compounds in the water phase [1–5]. However, for sediments several investigations have been made [2,6,7,8].

Marine organisms have the capability to form halogenated organic compounds. Hence, the halogenated organic compounds in sea water have both a biogenic and an anthropogenic origin. Of the naturally produced compounds, the volatile compounds are the most commonly investigated [9,10]. However, many substances are both biogenic and anthropogenic. For example, substances usually associated with the chlorination of water such as chloroform, bromoform and dibromomethane are also formed naturally [11]. In this investigation we focused on two groups of environmentally interesting compounds, volatile halocarbons and chlorinated phenolic compounds. The analytical techniques available permit the determination of these compounds in a vast number of samples. Consequently, we can study the dispersion of these compounds in sea water.

The volatile halocarbons are known to influence the atmospheric ozone. Several investigations have

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dealt with the distribution of halocarbons in sea water and the atmosphere, mainly the chlorofluoro-hydrocarbons (CFCs) and tetrachloromethane [12–14]. The naturally produced volatile halocarbons consist of chlorinated, brominated and iodinated compounds. The formation mechanism is still elusive, but there are indications that both macroalgae and planktonic organisms have the ability to produce such compounds. Earlier investigations have mainly dealt with brominated compounds [15,16,]. It has been shown that the flux of naturally produced brominated compounds from sea water was the main source of organobromine in the atmosphere [17]. Of the iodinated compounds, methyl iodide was regarded as the main compound governing the global iodine budget [18,19]. Recently, it has been shown that the diversity of iodinated halocarbons is larger than expected and that several iodinated compounds should be considered [20].

Chlorophenols have been used as flea repellents, fungicides, wood preservatives, mould inhibitors, etc. In 1980, about 200 000 tons of chlorophenols were manufactured annually worldwide [21]. For instance, Finnish saw mills, wood processing and textile industries used approximately 1300 tons of chlorophenols, mainly penta-, tetra- and trichlorophenols, against rot and blue stain [22]. Phenolics are also formed in the bleaching process of pulp. Pulp mills discharge a considerable volume of effluents (ca. 200 m^3 per metric ton of pulp) and the concentrations of chlorophenolics can vary between 0.1 and 300 µg/l of effluent water [2,23,24]. The atmospheric input, e.g., from waste incineration, has not been estimated. Studies of the distribution of chlorinated phenolics in sea water have been performed in coastal waters by Xie et al. [2], Paasivirta et al. [21], Folke and Birklund [25] and Abrahamsson and Klick [4].

The aim of this investigation was to determine the amounts of chlorinated phenolics and biogenic halocarbons released in the coastal waters of Sweden and in the Skagerrak. In accordance with this aim, water and sediment samples were collected from August 1989 to April 1991.

EXPERIMENTAL

Chemicals

The chlorinated phenolics used were 2,4-dichlo-

rophenol (DCP) (AB Reagents, Göteborg, Sweden), 2,6-dichlorophenol (2,6-DCP) (Nova Kemi, Göteborg, Sweden), 2,4,6-trichlorophenol (2,4,6-TCP) (Merck, Hohenbrunn, Germany), 3,4,5-trichlorophenol (3,4,5-TCP) (EGA-Chemie, Steinheim, Germany), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) (Aldrich, Gillingham, UK), 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP) (EGA-Chemie), pentachlorophenol (PCP) (Fluka, Buchs, Switzerland) and 2,6-dibromophenol (Kodak, Rochester, NY, USA). 3,4,5-Trichlorocatechol (TCC), tetrachlorocatechol (TeCC), 4,5,6-trichloroguaiacol (TCG) and tetrachloroguaiacol (TeCG) were kindly provided by Professor Wachtmeister, University of Stockholm, Sweden. Stock standard solutions were prepared in acetone (Merck, Darmstadt, Germany) and stored in a refrigerator.

The volatile halogenated hydrocarbons investigated were chloroform (Merck), 1,1,1-trichloroethane (Fluka), 1-iodopropane (Fluka), 2-iodopropane (Fluka), trichloroethene (Mallinckrodt, St. Louis, MO, USA), dibromomethane (Merck), bromodichloromethane (Fluka), chloroiodomethane (Fluka), 2-iodobutane (Fluka), dibromochloromethane (Fluka), tetrachloroethene (Merck), 1-iodobutane (Fluka), bromoform (Merck), diiodomethane (Fluka) and bromotrichloromethane (Fluka). Stock standard solutions were prepared in acetone (Merck) and stored at −18°C.

Sampling and description of sampling area

The Skagerrak is a fairly deep part of the North Sea with an average depth of 200 m. The water in the Skagerrak has its origin mainly in the north Atlantic, and enters through the northern North Sea. Along the Danish west coast the water entering the Skagerrak has its origin in the southern North Sea. The out-flowing surface water from the Kattegat influences only a minor part of the Skagerrak along the Swedish and Norwegian coast. The salinity in the Skagerrak is predominantly oceanic, except for the surface water along the Swedish west coast and the Norwegian south coast. The average current is a strong cyclonal circulation [26].

Water samples were collected along three transects on the Danish west coast (Table I) on three occasions: September 1990, November 1990 and April 1991. On each occasion each transect was sampled twice, except for September, where one of

TABLE I

DESCRIPTION OF TRANSECTS

Transect	Position
Hirtshals	N57°30′, E9°56′ to N58°01′, E9°36′
Hanstholm	N57°10′, E8°34′ to N57°41′, E8°12′
Tyborøn	N56°43′, E8°06′ to N56°43′, E6°38′

the transects was sampled just once. Along each transect seven stations were sampled and water was collected from different depths, giving a total of 30 water samples per transect. Salinity, temperature, oxygen, nutrients and chlorophyll were monitored throughout the investigation. Sediment samples were taken on two occasions along the Swedish west coast and in the deeper part of Skagerrak. The samples that were taken with a box corer were provided by Dr. B. Dennergård, Department of Marine Geology, University of Göteborg. A sediment core was also collected with a multiple corer [27] at depth 300 m, position N58°15′,E10°30′, and was provided by Dr. K. Nordberg, Department of Geology, University of Göteborg.

The sea water was collected from Niskin water sample bottles and stored in brown glass bottles (100 ml). The determination of the chlorophenols, chlorocatechols and chloroguaiacols were made shortly after the samples arrived at the department. Determination of the volatile hydrocarbons was made on board the ship less than 24 h after the samples were collected.

Analytical procedures

The chlorinated phenolics were determined as acetylated derivatives according to Abrahamsson and Xie [28] and Xie [29]. The determination of the volatile halocarbons were performed according to Abrahamsson and Klick [30].

The derivatization and liquid–liquid extraction procedures were performed directly in the sampling bottles. The phenolic compounds were extracted by adding 1 ml of hexane (Merck) containing 2,6-dibromophenol as internal standard (I.S.). The bottles were shaken for 3 min and the hexane phase (1 μl) was then used for gas chromatographic analysis. The volatile compounds were extracted by adding 1 ml of distilled pentane, containing bromotrichloro-

methane as internal standard, and shaking for 5 min. The extract was then injected on to the gas chromatographic column.

The chlorophenols, catechols and guaiacols were determined with a Carlo Erba HRGC 5300 gas chromatograph equipped with a nickel-63 electron-capture detector and on-column injector. The compounds were separated on a 30 m × 0.32 mm I.D. DB-1 fused-silica column (J & W Scientific). The GC conditions were as follows: hydrogen carrier gas flow-rate, 2 ml/min; nitrogen make-up gas flow-rate, 30 ml/min; injector and detector temperatures, 275°C, temperature programme, 100–230°C at 15°C/min, 230–260°C at 30°C/min.

The volatile halocarbons were determined with a Carlo Erba 4160 gas chromatograph equipped with a nickel-63 electron detector (275°C). The injector was an automatically driven Valco liquid chromatographic valve with a 15-μl loop. The compounds were separated on two fused-silica columns connected with a capillary glass connector. The precolumn was a 30 m × 0.32 mm I.D. DB-1701 (J & W Scientific) column with a film thickness of 0.1 μm. The separation column was a 30 m × 0.32 mm I.D. DB-5 (J & W Scientific) column with a film thickness of 1 μm. The hydrogen carrier gas flow-rate was 2 ml/min and the nitrogen make-up gas flow-rate was 30 ml/min. The oven temperature was held at 35°C for 2 min and then increased to 120°C at 10°C/min.

The chromatographic peaks were integrated using a Jones Model JCL 6000 chromatographic system.

RESULTS AND DISCUSSION

Volatile halocarbons

Even though biogenic halocarbons have been a focus of attention for several years, there are still a number of questions that have to be answered. The development of the liquid–liquid extraction method [30] enabled us to determine fifteen anthropogenic and biogenic volatile halocarbons. The main improvement was the combination of two separation columns of different polarity, whereby we could separate dibromomethane, bromodichloromethane and trichloroethene, which had previously been impossible. A chromatogram of a water sample is shown in Fig. 1. The low detection limits (below the
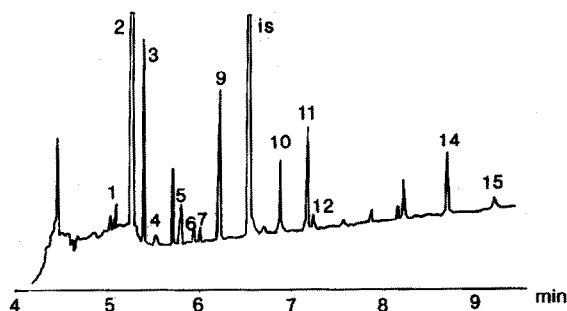
Fig. 1. Chromatogram for the volatile halocarbons. Transect Hirtshals, station 4 at 2 m depth, April 18th, 1991. 1 = 1.9; 2 = 41; 3 = 0.67; 4 = 1.2; 5 = 1.2; 6 = 0.46; 7 = 0.09; 9 = 1.9; 10 = 3.4; 11 = 0.14; 12 = 0.64; 14 = 3.6; 15 = 2.4 ng/l.

TABLE II

PRECISION AND DETECTION LIMITS FOR HALOCARBONS ACCORDING TO ABRAHAMSSON AND KLICK [29]

No.	Compound	Precision (%)	Detection limit (ng/l)
1	$CHCl_3$	9	2
2	CH_3CCl_3	8	0.2
3	CCl_4	10	0.05
4	CH_3CHICH_3	9	0.7
5	$CHClCCl_2$	8	0.4
6	CH_2Br_2	10	0.3
7	$CHBrCl_2$	10	0.2
8	$CH_3CH_2CH_2I$	7	0.2
9	CH_2ClI	3	0.03
10	$CH_3CHICH_2CH_3$	11	0.3
11	$CHBr_2Cl$	7	0.2
12	CCl_2CCl_2	9	0.07
13	$CH_3CH_2CH_2CH_2I$	12	0.4
14	$CHBr_3$	5	0.2
15	CH_2I_2	7	0.4

nanograms per litre level) and the precision of the method (Table II) make it suitable for distribution studies.

We have recently shown that biogenic volatile halocarbons are very diverse [20], and that both macroalgae and microorganisms are responsible for their formation. In order to establish the levels of anthropogenic and biogenic compounds in the Skagerrak, sampling was performed at several sampling sites over several years.

The biogenic compounds constitute the largest fraction of volatile halocarbons in the Skagerrak. Table III shows the mean values for both biogenic and anthropogenic halocarbons in surface waters (<6 m). The biogenic compounds are 1-iodopropane, 2-iodopropane, chloroiodomethane, 1-iodobutane, 2-iodobutane, diiodomethane, dibromo-

methane and bromoform. The anthropogenic compounds are tetrachloromethane, trichloroethene and tetrachloroethene. As can be seen from the chromatogram in Fig. 1, there were contamination problems from the ship, which interfered with the determination of chloroform and 1,1,1-trichloroethane. They are therefore excluded from Table III. Interestingly, the mean values for the biogenic halocarbons exceed the values for the anthropogenic compounds. The concentrations of chloroform and 1,1,1-trichloroethane are usually low (1–4 ng/l) in the Skagerrak.

TABLE III

MEAN SURFACE WATER CONCENTRATIONS OF BIOGENIC AND ANTHROPOGENIC HALOCARBONS ALONG THREE TRANSECTS IN THE SKAGERRAK

The values are given in ng/l. Biogenic compounds: 1-iodopropane, 2-iodopropane, chloroiodomethane, 1-iodobutane, 2-iodobutane, diiodomethane, dibromomethane and bromoform. Anthropogenic compounds: tetrachloromethane, trichloroethene and tetrachloroethene.

Transect[a]	September		November		April	
	Anthropogenic	Biogenic	Anthropogenic	Biogenic	Anthropogenic	Biogenic
1	2.6 ± 1.5	5.1 ± 2.1	4.8 ± 1.6	24 ± 14	3.8 ± 2.8	26 ± 14
2	1.7 ± 0.74	7.3 ± 6.6	3.4 ± 1.5	24 ± 42	1.8 ± 0.48	23 ± 5.8
3	2.1 ± 1.0	6.0 ± 2.8	2.9 ± 0.50	14 ± 15	5.8 ± 1.9	13 ± 3.4

[a] Transect 1: September, n = 10; November, n = 12; April, n = 10. Transect 2: September, n = 10; November, n = 10; April, n = 9. Transect 3: September, n = 8; November, n = 13; April, n = 14.

TABLE IV

COMPARISON OF MEAN CONCENTRATIONS (ng/l) OF INDIVIDUAL BIOGENIC COMPOUNDS FOR DIFFERENT SURFACE WATERS

Compound	Skagerrak, August 1989[a]	Skagerrak coastline, April 1990[b]	Skagerrak coastline, May 1990[b]	Skagerrak, September 1990	Skagerrak, November 1990	Skagerrak, April 1991	Antarctic Ocean[c], November 1989	Arctic Ocean[d], August 1991
Dibromomethane	0.43 ± 0.41	0.57 ± 0.23	0.87 ± 0.54	0.21 ± 0.25	0.31 ± 0.17	0.45 ± 0.22	0.30 ± 0.62	1.0 ± 0.6
Bromoform	5.1 ± 1.5	23 ± 16	22 ± 18	4.5 ± 4.2	4.9 ± 5.0	4.3 ± 6.8	2.7 ± 1.2	3.4 ± 1.6
Chloroiodomethane	1.3 ± 0.88	7.1 ± 2.6	7.6 ± 4.0	0.40 ± 0.26	0.90 ± 0.63	3.0 ± 3.0	0.07 ± 0.21	0.12 ± 0.07
2-Iodobutane	n.d.[e]	2.4 ± 0.48	1.6 ± 0.31	0.35 ± 0.21	1.3 ± 0.30	3.8 ± 0.22	0.32 ± 0.61	n.d.
Diiodomethane	5.2 ± 6.3	63 ± 26	45 ± 46	n.d.	15 ± 25	7.7 ± 8.3	n.d.	n.d.
No. of samples (n)	26	22	20	27	35	35	210	22

[a] Abrahamsson and Klick, unpublished data, centre of the Skagerrak.
[b] Abrahamsson and Klick, unpublished data, N58°,E11°5′.
[c] Klick and Abrahamsson [20].
[d] Abrahamsson, unpublished data, N86°4′,E55°3′.
[e] Not detected.

There are both seasonal and spatial variations in the amounts of biogenic halocarbons present in the water. Surprisingly, the levels of biogenic compounds did not differ between November and April. It would be easy to predict that the bloom of phytoplankton in April should lead to increased levels of brominated and iodinated substances. However, the chlorophyll content was measured throughout the investigation and no correlation could be found. This finding is not contradictory to the idea that phytoplankton could be involved in the formation of biogenic halocarbons, but it does imply that the amount of biogenic halocarbons is not related to the number of living cells present. One explanation might be differences in degradation rate.

Several individual compounds show seasonal variations. Table IV gives the mean values from different sampling occasions for surface waters in the Skagerrak. In addition, values from the Antarctic and the Arctic are given as references. In principle, the highest values were measured at stations close to the coastline (April and May 1990), which is due to the large macro algae belts. In the open ocean waters of the Skagerrak, the composition of biogenic substances varies with the seasons. This is pronounced for the iodinated compounds, but the same effect cannot be seen for the brominated compounds, for which the concentrations seem to be fairly constant during the year. The values for bromoform correspond well with other reported values in this area [5].

Waters of different origins contained different compositions of biogenic halocarbons. In the Skagerrak, where the mixing is complicated and the residence times are short, this could prove to be a valuable tool for the identification of different water masses. For example, bromoform and chloroiodomethane correlated well. For water with salinity (S) >35 there is a positive correlation (slope = 0.55; $r = 0.95$). However, a negative correlation was observed for waters with $33.8 < S < 34.0$ (slope = -0.01; $r = 0.90$). Interestingly, the correlation between bromoform and chloroiodomethane did not change with season. This allows us to infer that water, with its origin in the North Atlantic, transports these compounds conservatively and that their half-life in sea water is long. Additionally, bromoform and chloroiodomethane should have the same pelagic source.

We have shown that the load of biogenic volatile halocarbons exceeds that of the anthropogenic compounds. There are seasonal variations of biogenic iodinated halocarbons in the Skagerrak. The variation is less pronounced for brominated species. The amount of biogenic halocarbons cannot be correlated with the chlorophyll content in the water. In other words, biogenic halocarbons could be formed for a specific reason, or microorganisms other than phytoplankton could be responsible for their formation. Additionally, waters of different origins contain different proportions of biogenic halocarbons, and this relationship seems to prevail for an extended period of time.

Chlorinated phenolics

For trace determinations of chlorinated phenolic compounds in sea water and sediment, gas chromatography with electron-capture detection is the commonest chromatographic technique. A simple and rapid pretreatment procedure to increase the volatility and stability of the phenolics is derivatization with acetic anhydride to convert them to their non-polar derivatives. The sea water samples are buffered with $NaHCO_3$ prior to derivatization in order to ensure pH 9 and thus favour the dissociated form of the phenol. The acetylation step only takes a few min. Sample manipulation is minimized as both the derivatization step and the extraction of the derivatives into the organic phase can be performed directly in the sample bottles. With a 100-ml sea water sample we can detect chlorophenols at levels as low as a few ng/l or less. The sediment samples were extracted with sodium carbonate solution. The phenolate anions formed were acetylated with acetic anhydride and then extracted into the organic phase. With this pretreatment method and chromatographic technique we were able to determine chlorophenols in sediment at a level of 0.1 ng/g dry sediment. The method requires only 1 g of sediment. These factors make it possible to analyse large numbers of samples in a relatively short time.

Fig. 2 shows a typical chromatogram of chlorinated phenols in a sediment sample. Earlier investigations in our laboratory using GC–MS confirmed the identity of the derivatives [31].

The distribution of most chlorinated organics in the environment is determined by their lipophilicity. It has been shown that a convenient way to describe
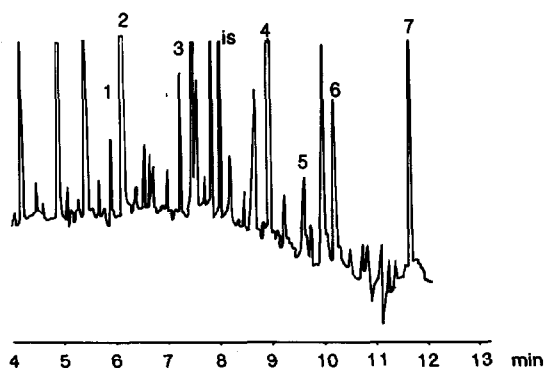
Fig. 2. Chromatogram of chlorinated phenols in the sediment core at level 22–24 cm. The sediment core was collected at position N58°15′, E10°30′. The concentrations of the individual chlorophenols are given in Table IV.

the lipophilicity of a compound is the partition coefficient between octanol and water (K_{ow}). It has been shown that this parameter is linearly correlated with partition coefficients between water and soil, sediment or biota [32]. The distribution of chlorophenolics is governed by both their hydrophilic and their lipophilic properties. It was shown by Xie et al. [2] that the ionizable phenolic compounds were distributed according to the distribution ratio (D) rather than K_{ow}. The distribution ratio depends on both the dissociation constant (K_a) and K_{ow}, and thus reflects their fate in the marine environment. The value of D will accordingly indicate the ability of the compounds to associate with organic matter and/or to bioaccumulate (Table V).

As can be seen from Table V, the effect is dramatic for the strongest acids. Consequently, at the pH encountered in sea water pentachlorophenol and possibly 2,3,4,6-tetrachlorophenol will be transported mainly in their dissociated form. In sea water additional features have to be considered such as the formation of ion pairs. It has been shown by Westall et al. [34] and Abrahamsson et al. [35] that the phenolate ions can form ion pairs with preferably sodium and potassium ions, and this will consequently influence the distribution ratio. This will effect D at pH > 8.

2,3,4,6-Tetrachlorophenol and PCP were the only phenolics that could be determined throughout the transects. The range was < 1–100 ng/l. The precision, given as the relative standard deviation, was 6% for PCP at concentrations close to the detection limit of 1 ng/l (ten times the standard deviation of the blank). The average concentration of PCP did not vary significantly between the transects or the sampling occasions: September 53 ± 33 ng/l, November 36 ± 62 ng/l, April 34 ± 37 ng/l. In an investigation in the North Eastern part of the Skagerrak, close to a paper and pulp mill, the average concentration of PCP was of the same magnitude [4].

The residence time in the Skagerrak is short and

TABLE V

pK_a, LOG K_{ow}, LOG D AND DETECTION LIMITS FOR PHENOLIC COMPOUNDS

Compound[a]	pK_a[b]	Log K_{ow}[b]	log D (pH 7)	Detection limit (ng/l)
2,4-DCP	8.09	3.21	3.18	2
2,6-DCP	6.79	2.84	2.42	2
2,4,6-TCP	6.21	3.75	2.89	1
3,4,5-TCP	7.81	4.36	4.3	1
2,3,4,5-TeCP	6.61	4.82	4.28	1
2,3,4,6-TeCP	5.62	4.42	3.02	1
PCP	4.9	5.04	2.94	1
4,5,6-TCG	7.2	3.74	3.52	1
TeCG	6.26	4.45	3.64	1
3,,4,5-TCC		3.71		

[a] DCP = Dichlorophenol; TCP = trichlorophenol; TeCP = tetrachlorophenol; PCP = pentachlorophenol; TCG = trichloroguaicol; TeCG = tetrachloroguaiacol; TCC = trichlorocatechol.
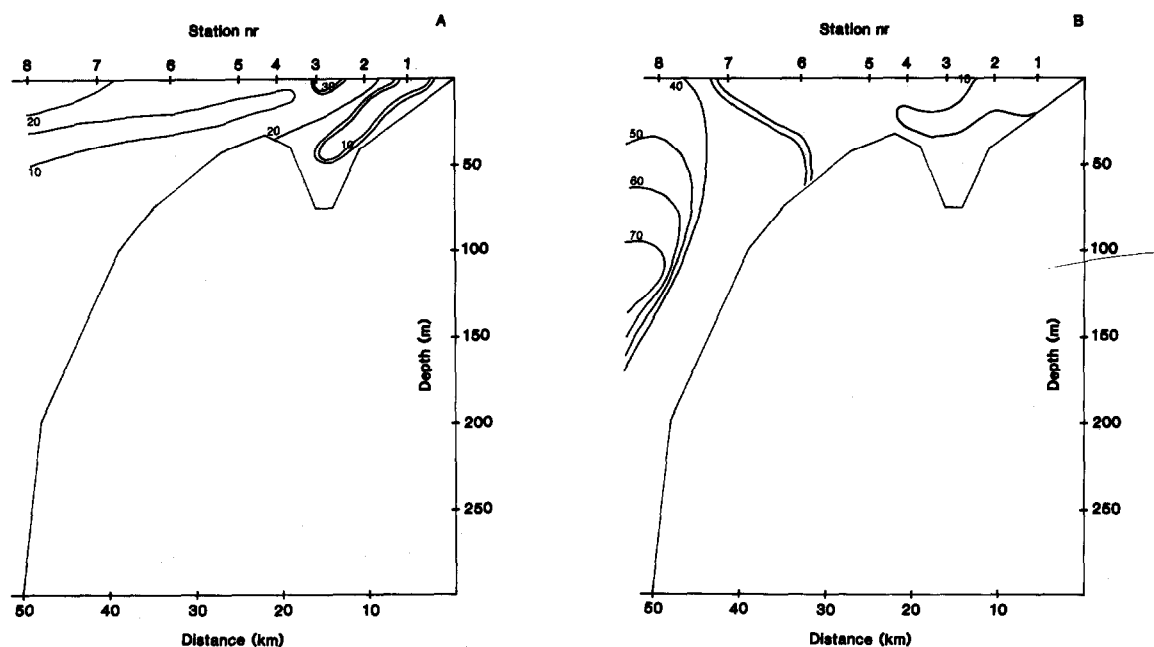[b] pK_a and log K_{ow} from Xie and Dyrssen [33].

Fig. 3. Distribution of pentatchlorophenol at transect 1 in November 1990. The concentrations are given in ng/l. (A) November 12th, 1990; (B) November 14th, 1990.

it exhibits complex mixing. This implies that the distribution of different constituents in the water changes rapidly. In Fig. 3 the isopleths for PCP at transect 1 are shown for two different sampling dates in November. Within this period of only 2 days, the distribution pattern changed drastically.

In order to study the fraction of PCP associated with the organic layer of particles, water samples

TABLE VI

CONCENTRATIONS OF CHLOROPHENOLS IN A SEDIMENT CORE COLLECTED AT POSITION N58°15', E10°30'

The concentrations are given in ng/g wet sediment.

Depth (cm)	2,6-CP	2,4-DCP	2,,4,6-TCP	3,4,5-TCP	2,3,4,6-TeCP	2,3,4,5-TeCP	PCP
0–2	57	440	210	240	16	32	230
2–4	180	250	18	–[a]	19	–	4.4
4–6	120	150	7.7	41	13	–	4.7
6–8	–	30	–	–	–	–	22
8–10	195	359	7.3	54	7.7	30	24
22–24	140	950	42	130	7.6	47	39
28–30	–	–	–	–	–	–	–
30–32	–	–	–	–	–	–	–
32–34	–	22	9.8	–	–	–	–
34–36	150	650	26	120	37	29	–
36–38	–	–	–	–	–	–	–
38–40	120	–	–	–	24	–	–
40–42	250	580	39	220	58	94	11

[a] Dashes indicate not detected.

were filtered with 0.45-μm filters and were compared with unfiltered water samples. No significant difference could be observed.

The deeper parts of the Skagerrak are known as accumulation areas for suspended matter from the North Sea [6]. Accordingly, sediment samples were analysed for their content of chlorinated phenolics at several positions in the Skagerrak. For comparison, sediment was collected from accumulation areas in the Kattegat.

The sediment from the deepest parts (water depths of 300 and 650 m) had a high load of chlorinated phenolics. Unfortunately, at the time of the analysis at the station at 650 m, we did not have sufficient standard compounds for quantification. However, it could be seen that the sediments contained chlorinated phenolics, guaiacols and cathecols. A sediment core was collected with a multiple corer at a depth of 300 m. The core was sliced into 2-cm depth intervals; the total length was 42 cm. The age of the core was determined to be at least 50 years and not older than 150 years [36]). Table VI shows the concentrations of the individual chlorophenols in the different 2-cm layers of the sediment core. In this sediment, no chlorinated guaiacols or catechols could be determined. This could be due to degradation and/or transformation reactions [37,38].

A number of paper and pulp mills are situated in the coastal areas of Sweden and Norway and have been operational since the beginning of this century. At a core depth of more than 22 cm, the sediment was deposited before 1950. We still found fairly high concentrations of chlorinated phenols. The levels could probably be related to these industrial activities. The higher relative content of dichlorophenols indicates degradation activity, probably microbiologically mediated.

To conclude, the load of chlorinated phenolics in the water phase is low, except for pentachlorophenol. However, they are accumulated in the deeper parts of the Skagerrak.

ACKNOWLEDGEMENT

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