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Release of halocarbons from an industrial estuary

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ABSTRACT

In order to study the release of low molecular weight halocarbons from a contaminated river into the adjacent sea and into the atmosphere, an investigation was carried out in the Elbe estuary, FRG, in October 1986. Results for the halocarbons chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene and tetrachloroethylene in relation to salinity, tidal phase and geographical position in the estuary are presented. The results show that release of halocarbons into the estuary acts as an atmospheric source for all compounds investigated, and that evaporation is a rapid and favoured process since the halocarbons are strongly supersaturated in the estuary. The halocarbons are known to be globally spread via the atmosphere, and later found in remote areas like Arctic waters.

1. Introduction

When tracing and dating water masses for oceanographic purposes, certain anthropogenic halocarbons, e.g. 1,1,1-trichloroethane (methyl chloroform), carbon tetrachloride and tetrachloroethylene, can be utilized as chemical tracers. In our investigations of the halocarbons in polar waters (Eklund et al., 1981; Dyrssen and Fogelqvist, 1981; Fogelqvist, 1985; Krysell and Wallace, 1988), it was assumed that the major source of substances was the industrial belt in the Northern Hemisphere (30–60° N). The transport of halocarbons from industrial areas could, however, be either atmospheric or oceanic, or both, as was concluded in one investigation of Arctic waters (Fogelqvist, 1985).

An investigation of the Elbe estuary offered an opportunity to study the transfer of halocarbons from a river in an industrialized area into the sea, as well as into the atmosphere. Seawater from the North Sea, into which the Elbe river discharges, is transported into Arctic waters by the Norwegian Atlantic current. Since transport of the halocarbons via the atmosphere is much faster, we sought to establish whether loss of halocarbons from the estuarine water to the atmosphere is significant, and if so, how fast this process is.

Higher molecular weight chlorinated organic compounds, the pesticides and polychlorinated biphenyls (PCBs), the behaviour of which differs from the low molecular halocarbons dealt with in this paper, have been studied in the Elbe estuary by Duinker et al. (1982) and Sturm and Gandrass (1988). Properties like higher lipophilities and lower volatilities make the pesticides and PCBs subject to other transport mechanisms.

2. The studied area

The Elbe estuary is characterized by strong tidal influence from the North Sea, the tidal zone being approximately 170 km long. Even though

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the annual mean flow in the river is 722 m^3/s (Duinker et al., 1982), it varies very much with tidal phase, and the flood is known to be strong enough to create a net flow into the river close to the mouth.

A significant contributor to the contamination of the Elbe estuary is the city of Hamburg and the industries in the surrounding areas. Effluent water from urban areas is known to contain tetrachloroethylene in considerable amounts (Fogelqvist and Krysell, 1986), as well as chloroform formed during water and sewage treatment (Bellar et al., 1974, Rook, 1974). Several other possible sources of different halocarbons are situated around the estuary, like the industrial areas of Stade and along the Kiel canal (Nord-Ostseekanal).

3. Physico-chemical properties of halocarbons

The use of low molecular weight halocarbons for tracer studies like the one described here implies certain conservative properties. Variations in the concentration of a compound in space as well as in time could be due either to chemical or physical processes, e.g., evaporation, adsorption to particles and sedimentation, or some biologically-mediated flux. Chemical decomposition can be ruled out, since these substances are very stable against hydrolysis in the aquatic environment, with half-lives of the order of hundreds of years (Mabey and Mill, 1978; Fogelqvist, 1984).

On the basis of the lipophilities of the halocarbons, defined by their octanol-water partition coefficients, the significance of both adsorption to particles and bioaccumulation are discussed in other publications (Fogelqvist, 1984; Krysell and Wallace, 1988). The conclusions in both cases are that such processes are of very little importance for the aquatic transport mechanisms of low molecular weight halocarbons, and in this study they are regarded as negligible.

Despite the fact that the particle load occasionally reached values as high as 400 mg seston/l, ignoring particle bound halocarbons is justified for the following reason: Partition coefficients ($\log K_{ow}$) in the range of 2.0 to 2.8 for the halocarbons studied (Hansch, 1979), and partition of chlorinated organics between particles and water as observed in the Elbe estuary by Duinker et al. (1982), lead to an estimated fraction of less than 0.4 per mille of the total amount that is adsorbed/accumulated (cf. Table I in Duinker et al., 1982). In comparison, PCBs with partition coefficients 3 to 4 orders of magnitude higher are to a large extent particle bound. As illustrated by Duinker et al. (1982), an increasing number of chlorine atoms in the molecules also increases the adsorption to particles, as well as the partition coefficients. Since the water samples in this investigation are analysed unfiltered, total concentrations of the halocarbons are obtained.

Dilution with seawater and subsequent transport into the adjacent sea and evaporation into the atmosphere are the two most plausible processes that remain as sinks for the halocarbons. The effect of dilution and mixing of the estuarine water with the seawater can be investigated by studying the concentration of the compound of interest in relation to the salinity, as will be demonstrated here. Evaporation as a pathway for halocarbons is regarded as a realistic possibility since the compounds included in this investigation all have very high volatilities. The combination of low or moderate solubilities in water and relatively high vapour pressures results in partition coefficients, i.e., Henry's Law constants, in the range of $H = 0.1$ to $H = 1.0$ at 14°C (Dilling, 1977; Mackay and Shiu, 1981; Fogelqvist, 1985; Yurteri et al., 1987), where $H = C_{air}/C_{water}$, the same unit used for concentrations in both air and water. Less contaminated air blowing in from the sea with the normally westerly winds keeps the air/sea interface out of equilibrium and enhances the evaporation.

As well as an understanding of the processes which remove halocarbons from the aquatic environment, it is also necessary to consider possible in situ production. It is known that haloforms like chloroform and, in seawater, bromoform are formed through the breakdown of organic substances in the presence of chlorine (Bellar et al., 1974; Rook, 1974). This is possibly an important source of chloroform in the Elbe estuary, as a result of processes taking place in water treatment plants in urban areas like the city of Hamburg, but can be neglected once the residual chlorine has disappeared from the water. The other halocarbons dealt with in this

investigation are not produced in the estuary to an extent that could influence the results.

4. Experimental section

Sampling. The sampling sites are shown in Fig. 1. All sampling was performed in plexiglass water samplers (Hydrobios, FRG) at a depth of 1 m, and took place between 8 and 30 October, 1986. The samples for halocarbon determination were stored in glass bottles before analysis. Generally, the determinations were carried out within 12 h from sampling, but in some cases samples were stored up to 96 h. At each site, sampling was performed 9 times during a complete tidal cycle of 12 h, starting at the occurrence of slackwater just after high tide and ending at the same point in the next cycle.

Salinity (conductivity). The determination of the conductivity was carried out using a "Konduktometer CG 851" (Schott, FRG), and the conductivity data are collected in a separate report (Fogelqvist et al., 1988). Approximate salinities were calculated from the measured conductivities using the standard formula for sea water (Grasshoff, 1983). For comparison, salinities were calculated from the densities of 3 of the samples, the small resulting differences emerging from the different ionic composition of the Elbe water as compared to sea water. The in situ temperature varied from 14–15°C at stations O and H to 10° at the outer stations A and S. During the sampling period, the temperature at station G dropped from 14 to 11°.

Turbidity. The turbidity was measured as mg seston/l by filtration of 100 ml of water using membrane filters (pore size 0.45 μm) and subsequent drying of the filters overnight at 60°. Upstream of Hamburg, the water contained 40–60 mg/l. Downstream the values varied between 23 and 418 mg/l.

Halocarbon determinations. The halocarbons were determined by extraction of the water

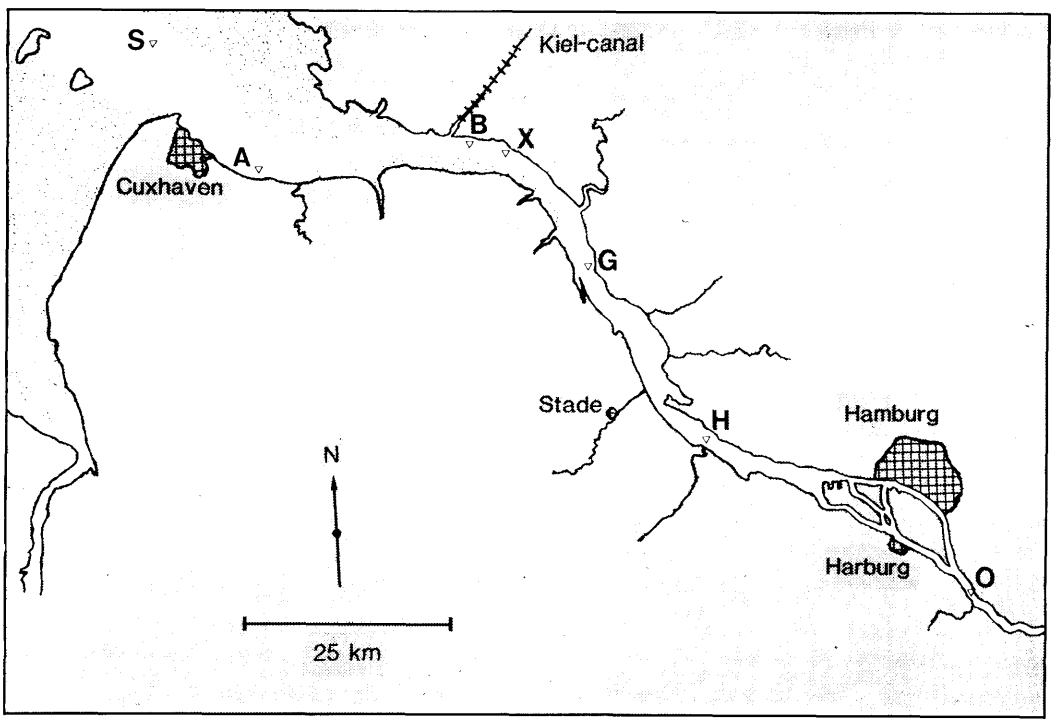

Fig. 1. Map of the studied area with the sampling sites indicated (triangles). Station G was sampled twice (G and G2, on 13 and 28 October), and station X was included as a high-turbidity site.

samples with pentane at a phase ratio p/w of 1/20, followed by gas chromatographic analysis of the extracts (Fogelqvist, 1985). Only unfiltered water was used, and hence particle bound halocarbons were also extracted into the pentane. The particles (20 to 400 mg/l) cannot compete with the pentane (50 ml per 1 sample) for the halocarbons. The pentane extract was injected directly onto the gas chromatographic column through an electrically triggered rotary valve (Valco Inc., USA) with an 11.5 μl sample loop (31.4 μl for station S) (Fogelqvist et al., 1986). The rotary valve was mounted above the gas chromatograph, and the column was directly attached to it through a hole in the oven wall. The separation column consisted of a 30 m of 0.32 mm id fused silica capillary with 1.0 μm SPB-5 as stationary phase (Supelco Inc., USA).

5. Discussion of the results

All data are given in a separate report (Fogelqvist et al., 1988) together with details on

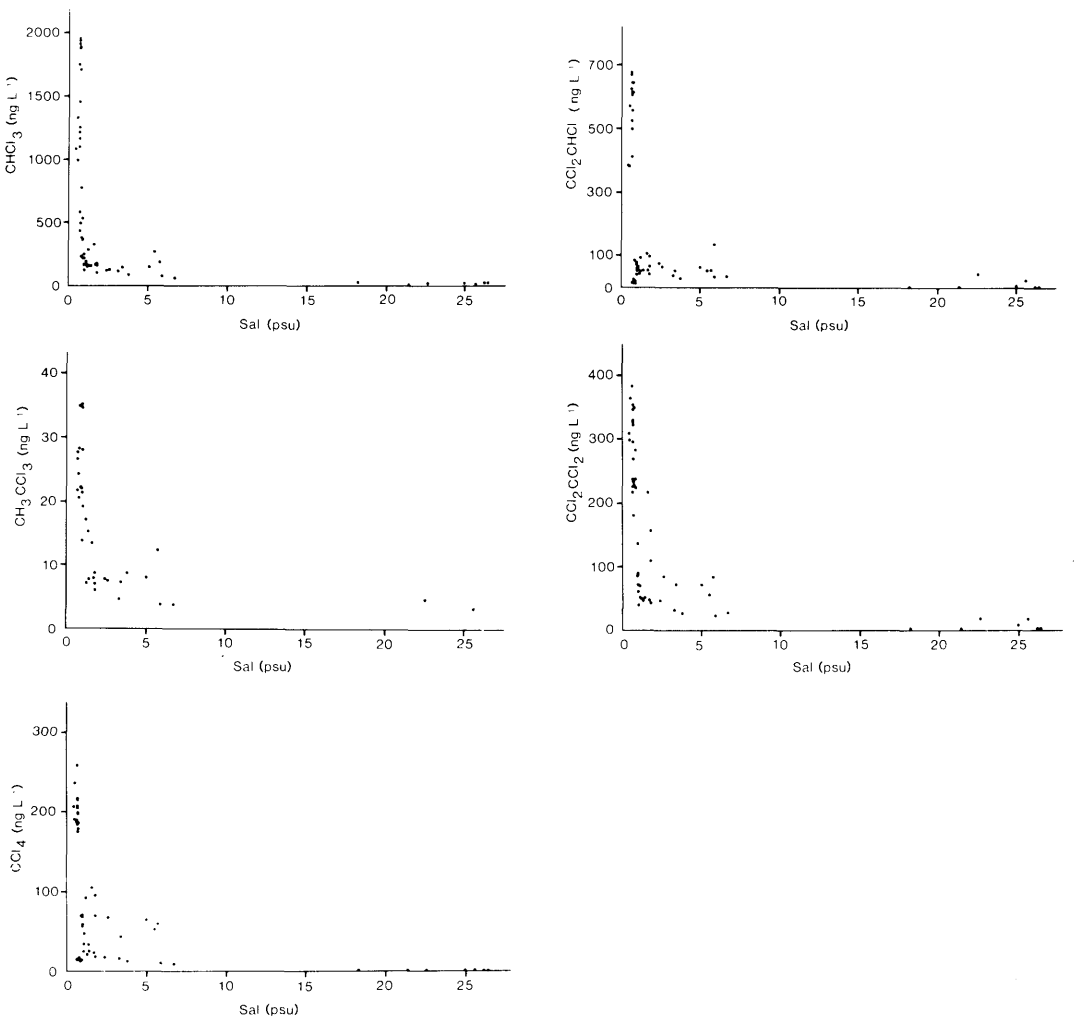

Fig. 2. Halocarbon concentration versus salinity for all samples

the sampling. It is thus possible to relate the concentration to the tidal phase and to the salinity. These data are used in Figs. 2–5, which constitute the basis for the following discussion and conclusions.

Concentration versus salinity. From plots of halocarbon concentration versus salinity for the different sampling sites (Fig. 2), it is evident that great losses of halocarbons occur during the transport downstream. In every case, there is a pronounced deviation from the straight line that would have been expected if only mixing with seawater was occurring. The steep declines in the inner, i.e., low salinity, parts of the estuary clearly indicate a rapid loss of all the halocarbons from the water mass. This is less pronounced for 1,1,1-trichloroethane, and the reason for that is shown in Fig. 3, from which an input of 1,1,1-trichloroethane into the middle of the estuary is obvious. The most plausible explanation for such great losses of halocarbons from the water is evaporation into the atmosphere.

Concentration versus distance. The concentrations of the different halocarbons at low tide and high tide, respectively, along the estuary are illustrated in Fig. 3. With plots of this kind, it is possible to observe inputs and losses along the estuary. The most striking features of the plots are the following: already at station O, upstream of Hamburg, the water contains high concentrations of all the halocarbons measured, except for 1,1,1-trichloroethane. At Hamburg, between stations O and H, there is an input of at least carbon tetrachloride, trichloroethylene and tetrachloroethylene to the estuary. Between stations H and G, the 1,1,1-trichloroethane concentration suddenly increases, strongly suggesting an input from the Stade area. The Kiel canal, which

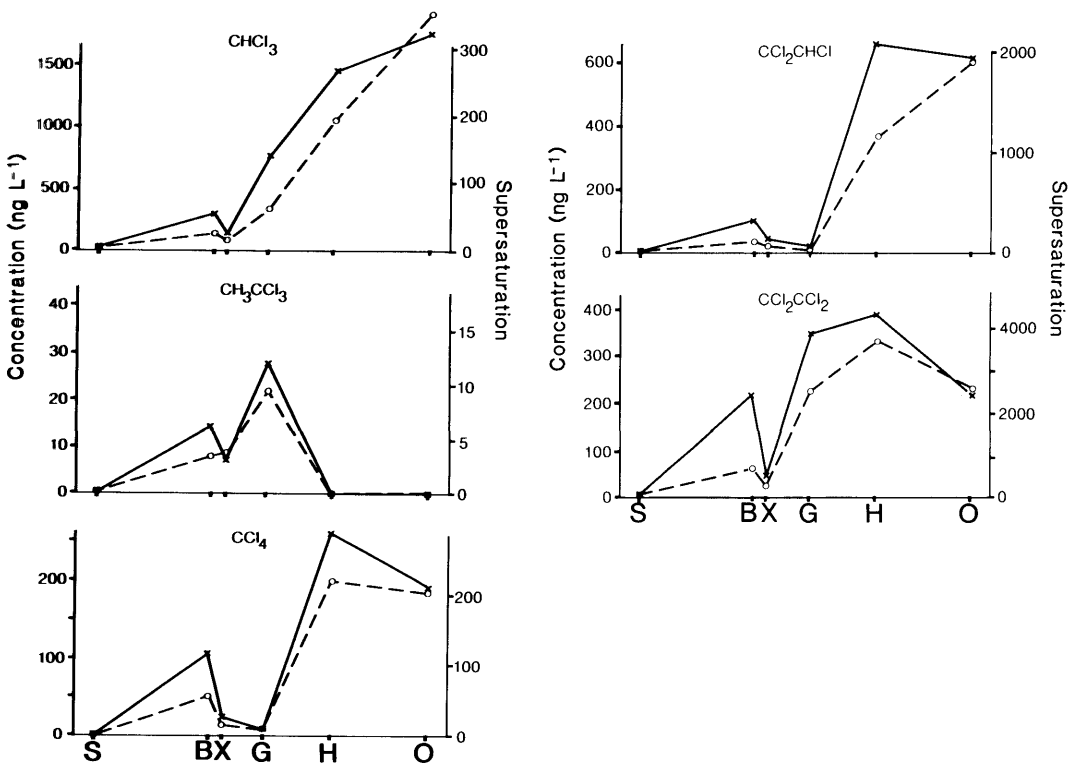

Fig. 3. The plots show concentration (C) and supersaturation (C/C_{eq}) of the different halocarbons versus distance, i.e. geographical position in the estuary. The positions of the different sampling stations are given in Fig. 1. The full lines represent low tide; the dashed lines high tide.

discharges into the river just downstream of station B, apparently acts as an additional source for all of the halocarbons measured.

It is also obvious that when no significant inputs exist, e.g., between stations H and G for chloroform, carbon tetrachloride and trichloroethylene, the concentrations drop very markedly, indicating rapid losses into the atmosphere. This is not very surprising, since calculations show supersaturations in the range of 200–1000 times the concentration at equilibrium (C_{eq}), with the atmosphere in the inner part of the estuary (Fig. 3), assuming Northern Hemisphere atmospheric mixing ratios of 130 pptv for chloroform (Class and Ballschmitter, 1987), 205 pptv for 1,1,1-trichloroethane (Prinn et al., 1983), 135 pptv for carbon tetrachloride (Simmonds et al., 1983), 16 pptv for trichloroethylene (Jesson, 1980), 30 pptv for tetrachloroethylene (Singh et al., 1983) and Henry's Law constants (H_c) at 14 °C according to Dilling (1977) and Mackay and Shiu (1981) (see also Table 1).

Plots of halocarbon concentration versus turbidity at the different sampling stations show no correlation. This indicates that adsorption onto particles is negligible, and that such a process cannot explain the fast removal of the halocarbons from the water.

An attempt was made to estimate the total yearly flux of halocarbons from the water into the air. The formula $F = K(C_{max} - C_{eq})$ was used (Liss and Slater, 1974), where F equals the flux (g km^{-2} h^{-1}), K is a rate coefficient taken as approximately equal to 15 cm h^{-1}, C_{max} is the maximum concentration in the water according to Fig. 3, and C_{eq} stands for the concentration corresponding to equilibrium with the air using the same Henry's Law constants and mixing ratios as above. Estimating the total riverine surface area at 375 km^2, the flux (Fx) in kg yr^{-1} of each halocarbon could be roughly calculated (Table 1). This type of calculation is of course subject to several uncertainties, e.g., in the atmospheric mixing ratios, which probably are higher than estimated in the area due to discharges directly into the air. Hence the results should only be regarded as a simple estimate of the magnitude of the maximum fluxes.

Table 1. *Estimated total yearly flux (Fx) of the halocarbons from the water into the air*

	$CHCl_3$	CH_3CCl_3	CCl_4	CCl_2CHCl	CCl_2CCl_2
H_c (14 °C)	0.13	0.57	1.02	0.29	0.25
C_{max} (ng l^{-1})	1880	28	259	674	384
C_{eq} (ng l^{-1})	5.3	2.1	0.9	0.3	0.9
F (g km^{-2} h^{-1})	280	3.9	39	100	57
Fx (10^3 kg yr^{-1})	350	3.0	49	120	39
M_{atm} (10^6 kg)	663	1045	689	82	153
Fx/M_{atm} (%)	0.05	0.0003	0.007	0.14	0.0025

M_{atm} equals the total mass of each compound in the atmosphere.

Table 2. *The ratio between concentrations at low tide and high tide for each halocarbon at each station*

Station: / Compound	S	B	X	G	H	O
chloroform	0.85	2.24	1.76	2.15	1.40	0.93
1,1,1-trichloroethane	n.m.*	1.67	1.99	1.27	n.m.	n.m.
carbon tetrachloride	0.99	1.99	1.92	1.05	1.30	1.05
trichloroethylene	1.06	2.66	1.89	1.98	1.79	1.02
tetrachloroethylene	0.82	3.91	1.87	1.56	1.15	0.96
Average	0.93	2.49	1.89	1.60	1.41	0.99

*n.m.: not measured.

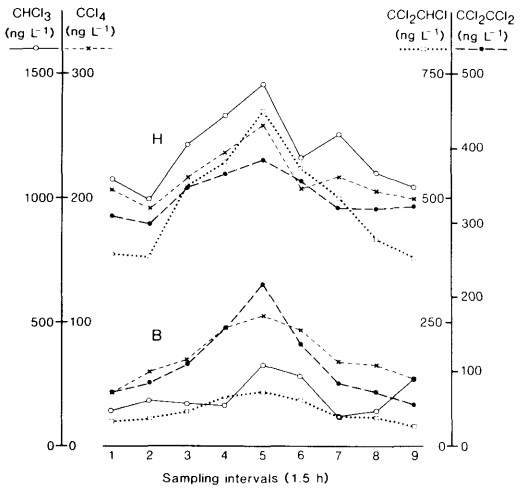

Fig. 4. Halocarbon concentration versus a 12-h tidal cycle, where 1 means the sample taken at high tide, 5 at low tide and 9 at high tide again. Data from an inner station (station H) are plotted together with data from an outer station (station B).

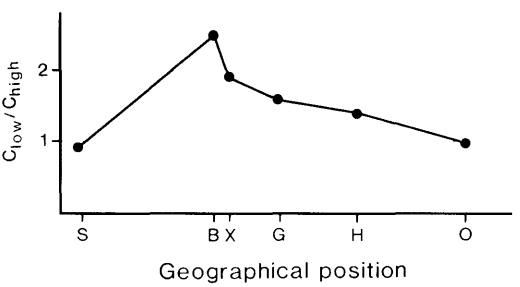

Fig. 5. The relative variations in concentration at low and high tide. The average ratio (C_{low}/C_{high}) for all halocarbons measured plotted against distance along the river. The station notations are marked on the horizontal axis (cf. Fig. 1).

Assuming a total mass of the atmosphere of 5.2 $\times$ 10^{18} kg and the mixing ratios stated above, the yearly contributions from the Elbe estuary amount to 0.0003–0.14% of the total global burden (Table 1). The higher values, 0.14% for trichloroethylene and 0.05% for chloroform, could partly be due to their relatively short lifetimes in the atmosphere, 0.02 and 1.5 years, respectively.

Concentration versus tidal cycle. The plots of halocarbon concentrations versus tidal cycle in Fig. 4 show that during flood, the river water is diluted with water from the German Bight, and hence the concentrations decrease. Even at station H, where the salinity is very low over the entire cycle, this phenomenon is evident.

Relative variation of concentrations within the tidal cycle. The concentrations of all halocarbons at a particular station vary with the tidal cycle in a similar way. The magnitude of the variation is, however, significantly higher near the mouth of the river, as can be seen from Table 2 and Fig. 5, where the ratio of halocarbon concentration at low tide to high tide against position in the estuary is given.

6. Conclusions

The investigation shows that discharges of low molecular weight halocarbons into the Elbe river act as an important atmospheric source, since evaporation is a favoured process in the strongly supersaturated water. As a consequence, the water leaving the estuary contains low molecular weight halocarbons at relatively moderate concentrations. Through the atmosphere, the halocarbons can be distributed world-wide on a relatively short time scale and detected in remote areas such as Arctic surface waters where, due to low temperatures and concentrations, transport from the air into the water is favoured.

7. Acknowledgements

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