Pergamon

The distribution of man-made and naturally produced halocarbons in a double layer flow strait system

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Abstract—The Bosphorus Strait, which connects the Black Sea and Mediterranean Sea via the Marmara Sea, is characterised by two distinct water masses. The upper layer consists of low density Black Sea water (sigma-t 10-11) flowing southward, and it is underlain by high density water (sigma-t >28) of Mediterranean origin flowing northward. The sharp density gradient between the two layers is due to the difference in salinities. Here we report measurements on a suite of low molecular weight halocarbons together with basic hydrographic parameters in the strait.

Concentrations of the transient tracers chlorofluorocarbons CFC-11 ($CFCl_3$), CFC-113 (CCl_2FCClF_2) and carbon tetrachloride (CCl_4) were highest in the Cold Intermediate Black Sea Water (CIBSW), which is formed in the Black Sea during winter. This layer disappeared within the contraction region of the Bosphorus where a hydraulic jump occurs. The Marmara Sea deep water at the entrance to the Bosphorus Strait carried low amounts of CFCs indicating an equilibrium with the atmosphere 6–11 years earlier. Varying amounts of other halocarbons such as chloroform ($CHCl_3$), dibromomethane (CH_2Br_2), methyl iodide (CH_3I) and chloro-iodomethane (CH_2ClI) could be used for the identification of water masses of different origin. Around the Bosphorus–Marmara Junction (BMJ) in the Istanbul area, the upper water layer contained elevated levels of most of the halocarbons. This is attributed not only to contamination but also to natural production in the productive eutrophic waters of the region. Methyl iodide and chloro-iodomethane showed elevated concentrations of 0.7–0.9 ng/l and 0.4–0.6 ng/l, respectively, in the upper water layer of the BMJ region, and also in near-bottom water at the northern exit of Bosphorus (0.2 and 0.1 ng/l, respectively). Chloroform (23 ng/l) and dibromomethane (10 ng/l) were also found within the pycnocline in the BMJ region and could be traced in a plume stretching northward along the pycnocline. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Low molecular weight halogenated hydrocarbons, in the following called halocarbons, appear in the marine environment as anthropogenic contaminants or as natural substances, produced either by marine algae or through various physical and chemical processes. The anthropogenic halocarbons are either discharged to the atmosphere and

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then enter the seawater via the sea surface, or are part of domestic and/or industrial effluents discharged directly to the water. Their different sources and transport pathways to a specific marine area make them useful as tracers for the study of water mixing and advective transport processes in the area.

The chemical similarities (hydrophobic organic compounds of high volatility containing halogens, for which an electron capture detector has high and selective response) allow simultaneous gas chromatographic measurements. Thereby, each seawater sample is given a multidimensional signature of tracer compounds.

The halocarbons used for this work represent a variety of sources. They are (1) chlorofluorocarbons (CFCs, Freons) including carbon tetrachloride (CCl_4, which can also be written CFC-10), (2) chlorinated chemicals for industrial use such as chloroform and carbon tetrachloride, and (3) naturally produced substances such as dibromomethane, methyl iodide and chloro-iodomethane.

The first group, the man-made chlorofluorocarbons, is distributed worldwide via the atmosphere. The CFCs traditionally used as marine transient tracers are CFC-11 ($CFCl_3$), CFC-12 (CF_2Cl_2) and CFC-113 (CCl_2FCClF_2); those used in this work are CFC-11 and CFC-113, which will be treated together with carbon tetrachloride (CCl_4). Since they were first manufactured, their atmospheric concentrations have increased, and are still increasing. What is important for the use of CFCs as tracers is that we know, from production and release data, their atmospheric history, i.e. their source functions (Cunnold *et al.*, 1986; Simmonds *et al.*, 1988; Fisher and Midgley, 1993). They are chemically stable compounds and have atmospheric residence times between 40 (CCl_4) to more than 100 years (74, 111 and 90 years for CFCs 11, 12 and 113, respectively). As a consequence, efficient global mixing, which is accomplished in a couple of years, leads to well-known atmospheric, time-dependent, concentrations. Furthermore, since their biological and chemical degradation in seawater is generally slow, they can be regarded as conservative tracers in comparison with the time-scales of water mixing in the ocean. Recent observations, however, indicate that carbon tetrachloride is not stable in warm seawater (J. M. Lobert, personal communication) or in oxygen depleted waters (Krysell *et al.*, 1994; Wallace *et al.*, 1994) so its use as a transient tracer might be restricted to polar regions.

The equilibrium concentrations at the air–sea interface as a function of temperature and salinity are well documented for CFC-11, CFC-12 (Warner and Weiss, 1985) and CFC-113 (Bu and Warner, 1995). A water parcel, after it loses its contact with the atmosphere, carries a signal which assigns an "age" to it, meaning the time elapsed since it was last in contact with the atmosphere. The concentration of a single CFC tracer is of limited use if one does not know the magnitude of mixing with other water masses; also one has to assume that the contents of the water parcel do not change during the transport, by the formation or decomposition of the tracers. This assumption is used for the so-called "freight train" model (Wallace and Moore, 1985). A better approach is to use the ratio of two CFCs which stays constant and can be treated as a conservative tracer independent of dilution by entrainment of water containing no CFCs. The assumption that the entrained water carries no signal of CFCs is an important restriction in the use of the tracers; otherwise the source waters have to be investigated and taken into account when interpreting the data. Furthermore, the saturation of the surface water has to be taken into account. Haine and Richards (1995) have evaluated the error in the "ratio age" depending on the depth of the surface mixed layer.

Two CFCs, CFC-11 and CFC-12, have been used for a long time as transient tracers in

studies on ocean mixing and transport processes (e.g. Bullister and Weiss, 1983; Weiss *et al.*, 1985; Smethie *et al.*, 1988; Rhein, 1994). However, although the concentrations of both CFCs are increasing in the atmosphere, their ratio has stayed virtually constant since the mid 1970s. For that reason, CFC-113 was added to the set of CFC-tracers (Wisegarver and Gammon, 1988), as it appeared in the atmosphere in the beginning of the 1970s; the ratio CFC-113/CFC-11 has increased so quickly that it might be possible to assign ages to younger water masses with a resolution of about a year. On the other hand, carbon tetrachloride has been included in the measurements (in polar regions) as being the oldest transient tracer with a history that stretches back to the first decade of the 20th century (Krysell and Wallace, 1988; Krysell, 1992).

The second group, the industrially produced chlorinated chemicals, is used as intermediates in the chemical industry or as solvents. This work considers carbon tetrachloride and chloroform (the former, however, will be treated together with the chlorofluorocarbons). Chloroform might be directly discharged via industrial effluents, or formed as an end product of the chlorination of water for disinfection purposes, e.g. in sewage treatment or as an anti-fouling agent for cooling water in power plants. Both treatments involve the chlorination of organic material, and chloroform is formed as the main end product. There are also strong indications that chloroform is produced naturally in near-shore algae belts (Nightingale *et al.*, 1995).

The third group consists of the halocarbons of biogenic origin. They have been found at high levels in coastal areas close to macroalgal belts, but also in the open ocean, indicating production by pelagic algae. The dominating brominated compound is bromoform (Dyrssen and Fogelqvist, 1981; Fogelqvist, 1985), followed by dibromomethane (Gschwend *et al.*, 1985; Reifenhäuser and Heumann, 1992b; Moore and Tokarczyk, 1993). Chlorination of seawater with its content of bromide ions also leads to the formation of brominated halocarbons (Fogelqvist *et al.*, 1982; Fogelqvist and Krysell, 1991).

Methyl iodide is generally regarded as a biogenic halocarbon with no anthropogenic sources, possibly produced by marine algae in the surface layer of the ocean. Recently, a natural but abiotic photochemical reaction mechanism for production of methyl iodide was demonstrated (Moore and Zafiriou, 1994). It has been measured in the Pacific Ocean at mean concentration levels of 0.5–1.1 ng l^{-1} (Rasmussen *et al.*, 1982) and 1.5 ng l^{-1} (Singh *et al.*, 1983). Similar levels have been observed in the Atlantic Ocean, 0.7 ng l^{-1} (Lovelock, 1975) and 0.6 ng l^{-1} (Tanzer and Heumann, 1992). Somewhat higher concentrations were obtained in the South Polar Sea during the bioactive period of the Antarctic summer (Fogelqvist and Tanhua, 1995). Methyl iodide seems to be present in the surface water of all oceans, but it has been shown that the highest concentrations are associated with macro algae in the coastal zone (Lovelock, 1975; Manley and Dastoor, 1987).

Methyl iodide constitutes one of the important carriers of iodine from the ocean to the atmosphere and thereby from sea to land, as pointed out by Lovelock *et al.* (1973) and Singh *et al.* (1983). Since then it has been shown that other iodinated halocarbons, e.g. chloro-iodomethane and di-iodomethane, probably play a similar role (Reifenhäuser and Heumann 1992a; Klick and Abrahamsson, 1992).

Like methyl iodide, chloro-iodomethane is thought to have natural sources, either through algal production or from photochemical transformation of di-iodomethane (Moore and Tokarczyk, 1992; Moore and Zafiriou, 1994). Other observations (Fogelqvist and Tanhua, 1995) indicate that while methyl iodide was found only in the upper 50 m of

the ocean, chloro-iodomethane was found, though at low concentrations, in the water column at all depths.

THE STUDY AREA

The study area, the Bosphorus Strait (Fig. 1), is a strait which connects the Black Sea and the Mediterranean through the Sea of Marmara and the Dardanelles Strait. It is
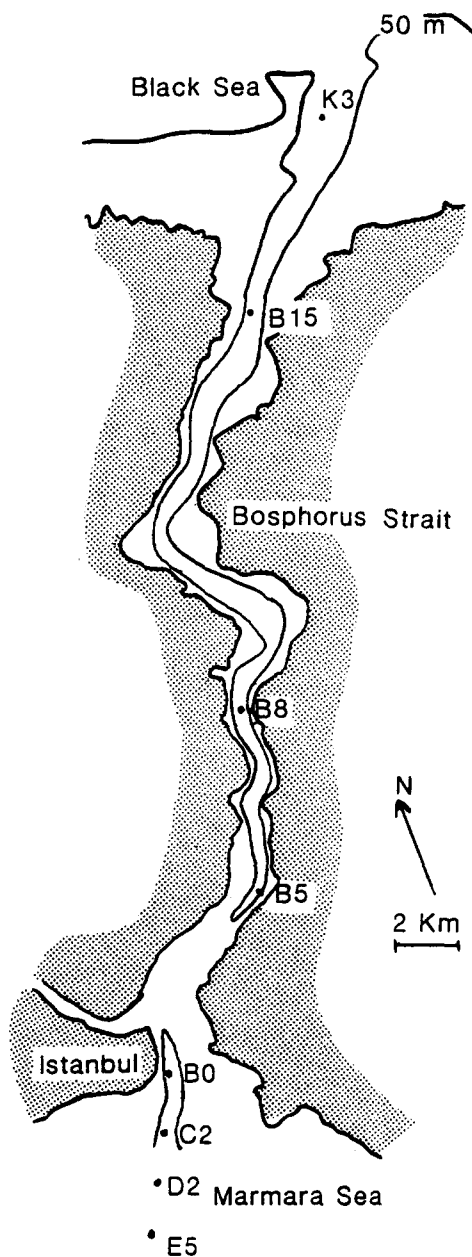
Fig. 1.   The study area, the 50 m depth contour line and the stations sampled for halocarbons, 1 September 1992.

characterised by a well defined two layer stratification and an associated two layer system of exchange of properties.

The inflowing water of the Dardanelles Strait undercurrent is of Mediterranean origin and is characterised by its high salinity (38.5–38.7) and temperature (13.1–16.5°C). It propagates eastward along the Marmara Sea Basin and reaches the Bosphorus Strait after a mean residence time of between 5 years (Ünlüata et al. (1990), calculated from volume fluxes in the Dardanelles and the Bosphorus) and 6–7 years (Özsoy et al., 1986, calculated from salinity and dissolved oxygen data). During this time it is enriched in nutrients and depleted in oxygen: there is a strong, permanent pycnocline (Ünlüata and Özsoy, 1986). This water, which forms the north flowing undercurrent in the Bosphorus Strait, enters the Bosphorus with temperatures and salinities between 12.5–14.5°C and 35–38.5, respectively. Within the Bosphorus, the Mediterranean water becomes less saline, and enters the Black Sea with a salinity of nearly 35. The northward flow of the lower layer through the Bosphorus Strait is driven by the difference in density, predominantly governed by the salinity differences, between the Marmara and Black Seas (Oguz et al., 1990).

The southward flow in the upper layer of the strait is driven by the difference in the sea level between the two ends, which is usually 20–40 cm (Gunnerson and Öztergut, 1974; Bükükay, 1989). As a result, relatively fresh water from the Black Sea (salinity 17–18) flows toward the Sea of Marmara above a countercurrent of more saline water of Mediterranean origin.

The flow rates through the Bosphorus, based on long term average salinity and steady state mass balance (Ünlüata et al., 1990), are 600 km³/yr (20,000 m³/s) for the upper layer and 300 km³/yr (10,000 m³/s) for the lower layer. The same computations yield a turbulent entrainment exchange from lower to upper layer of 85 km³/yr, whereas the reverse flow is less than 60 km³/yr. The magnitude of this flow is subject to significant temporal variability, depending mainly on variability of fresh water inflow into the Black Sea and on wind-driven circulation.

The flow within the Bosphorus is highly variable with time and space. Both the upper and lower layer currents are higher in the southern section of the Bosphorus than in the northern, with surface currents typically in excess of 100 cm/s and up to 350 cm/s, whereas the lower layer current is about 50–100 cm/s. At the northern exit both surface currents and lower layer current speeds are lower (40–50 cm/s and 20 cm/s, respectively).

The flow within the Bosphorus Strait is controlled by hydraulic jumps, a topographic contraction in the central part of the strait (between stations B5 and B8; see Fig. 1) and two sills, one of which is located at the southern end at a depth of 36 m and the other at the northern end of the Bosphorus at a depth of 56 m (Ünlüata et al., 1990).

METHODS

Water samples were taken with Niskin samplers (General Oceanics, U.S.A.), mounted on a rosette with a CTD-sonde (Seabird SBE-9, U.S.A.) supplying salinity and temperature data. The water was drawn into 100 ml glass syringes immediately after the samplers were on deck. In order to avoid contamination from ambient air, the syringes were kept submerged in seawater in a stainless steel bucket at all times. Of the subsample, an accurately known volume of approximately 40 ml was injected into the analytical system.

Samples were analysed promptly for halocarbons by a purge and trap system coupled to

Compound	Limit of detection (ng/l)
CFC-11	0.02
CFC-113	0.01
CH_3I	0.02
$CHCl_3$	0.21
CCl_4	0.003
CH_2Br_2	0.09
CH_2ClI	0.02

a gas chromatograph with an electron capture detector. The purge and trap system was built at the laboratory in Göteborg, and is described in more detail elsewhere (Krysell and Nightingale, 1994). The gas chromatograph used was a Hewlett Packard 5890A, equipped with a 75 m long, 0.53 mm ID column (DB 624, J & W Scientific). Extraction of the halocarbons from the water samples was accomplished by purging with an inert ultrapure gas (nitrogen) for 20 min at a flow rate of 50 ml/min and at ambient temperature. The volatile compounds were trapped in an open, coiled stainless steel tube lowered into a Dewar flask and placed over boiling liquid nitrogen. Desorption of the trap was subsequently accomplished by heating the trap with boiling water. The volatiles were then passed directly to the gas chromatographic (GC) column by the carrier gas (helium) at a flow rate of 8 ml/min. Make-up gas for the detector was nitrogen at a flow rate of 20 ml/min. The chromatographic runs were isothermal at 50°C. Integration of the peaks was performed on a Hewlett Packard 3369A integrator but peak heights were found to give more reproducible results than areas, and were therefore used for quantification.

A gaseous standard calibrated against international scales (for CFC-11; Scripps Institute of Oceanography, U.S.A. and for CFC-113; Plymouth Marine Laboratory, U.K.) was used for the calibration of the CFCs. For the other halocarbons measured, liquid standards were gravimetrically prepared in pentane solutions. For injection of the gaseous standard, a gas sampling loop was used, whereas the liquid standard was injected directly into the purge chamber. Since the electron capture detector is not linear over the concentration range of interest, standard curves were calculated from standard injections of different volumes by fitting a polynomial function of second degree. The detection limits, calculated as twice the standard deviation of a low concentration standard for the various compounds are listed in Table 1.

RESULTS AND DISCUSSION

Water samples were collected from the research vessel R/V BILIM of METU-IMS, Turkey, during a cruise from 27 August to 3 September 1992. The stations were located in a transect along the strait from the Sea of Marmara to the Black Sea (Fig. 1).

The transect was repeated four times, and here we present results from the most complete set of data collected during the investigation on September 1.

Figure 2 shows the longitudinal sections of temperature and salinity based on CTD profiles obtained simultaneously with the water-sampling. The south flowing upper layer
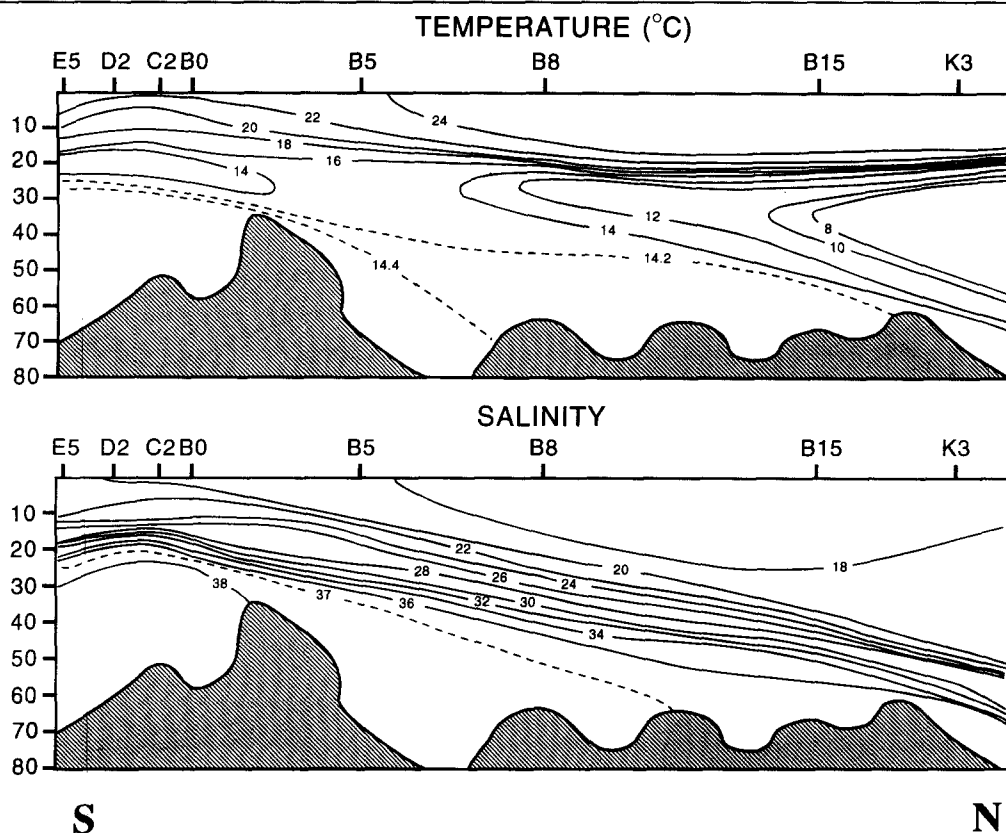
Fig. 2. Temperature and salinity transects for the Bosphorus Strait based on CTD profiles taken 1 September 1992.

of Black Sea water enters the strait at a salinity of 17–18 and a temperature of 25–26°C, and leaves at a salinity of 20–22 and lower temperatures (21–22°C) due to partial mixing along the strait. It is also evident that the warm surface layer at the northern exit of Bosphorus is underlain by a relatively cold water layer (<8°C), the Cold Intermediate Black Sea Water (CIBSW), at stations K3 and B15. The CIBSW, formed during winter in the Black Sea, vanishes between stations B8 and B5 due to the partial mixing induced by the hydraulic controls. Current measurements made on 1 September 1992, the same day as the halocarbon data were collected, indicated an upper flow of about 5,000 m³/s and a flow of about 10,000 m³/s in the lower layer (Özsoy et al., 1992).

The distribution patterns of the various halocarbons in the Bosphorus Strait vary due to the different sources, and they can be separated into three groups which are treated separately in the following.

Chlorofluorocarbons

The longitudinal transects of the chlorofluorocarbons CFC-11, CFC-113 and carbon tetrachloride are shown in Fig. 3. The three figures have certain similarities; low concentrations in the inflowing Mediterranean water, the highest values in the intermedi-
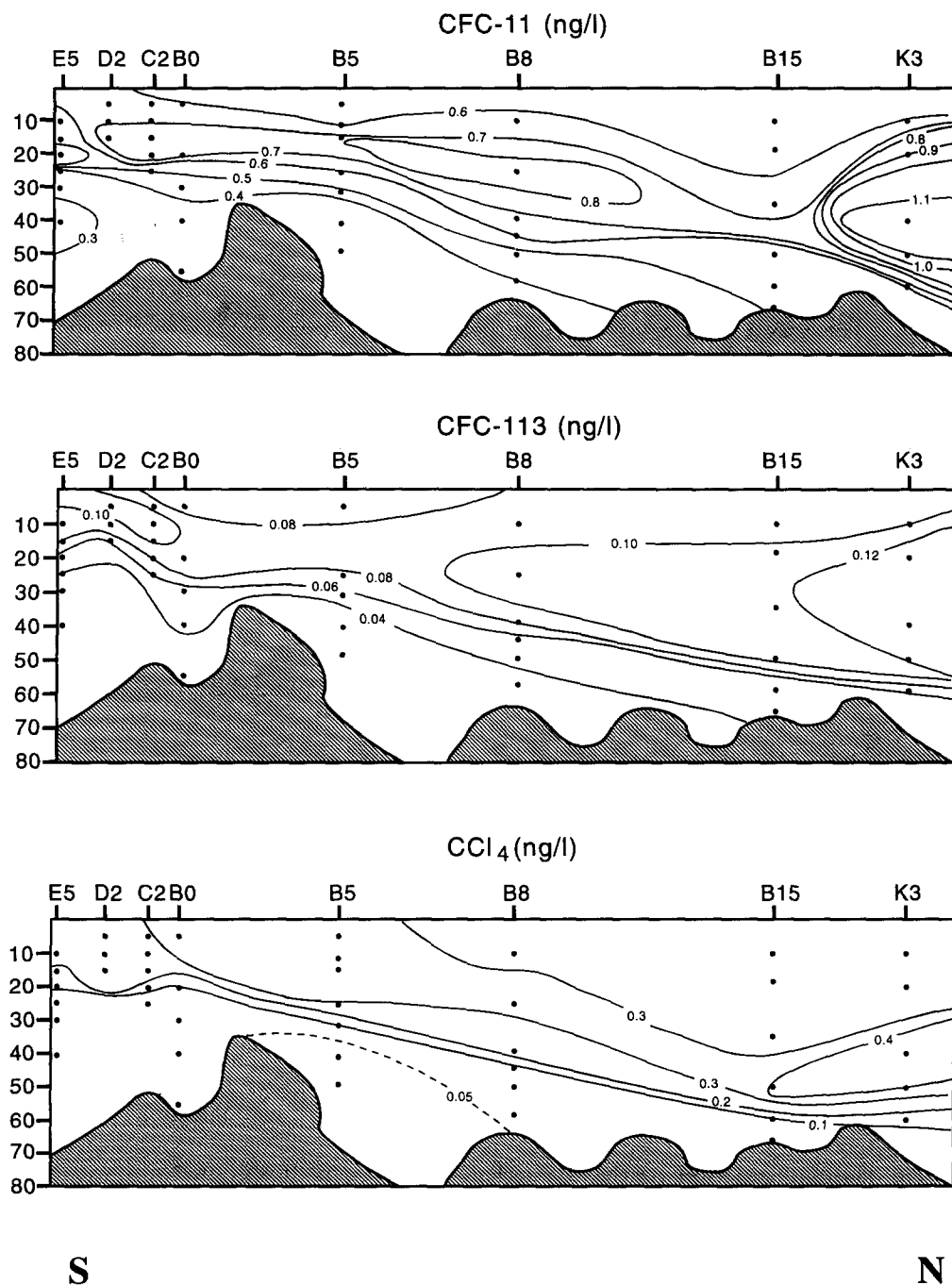
CFC-11 (ng/l)

CFC-113 (ng/l)

CCl$_4$ (ng/l)

S   **N**

Fig. 3.   CFC-11, CFC-113 and carbon tetrachloride (CCl$_4$) distributions in the Bosphorus Strait. The isolines are based on data obtained in the sampling points marked with dots. Generally, the isolines are equidistant; when exceptions are included for clarity, they are marked as dotted lines.
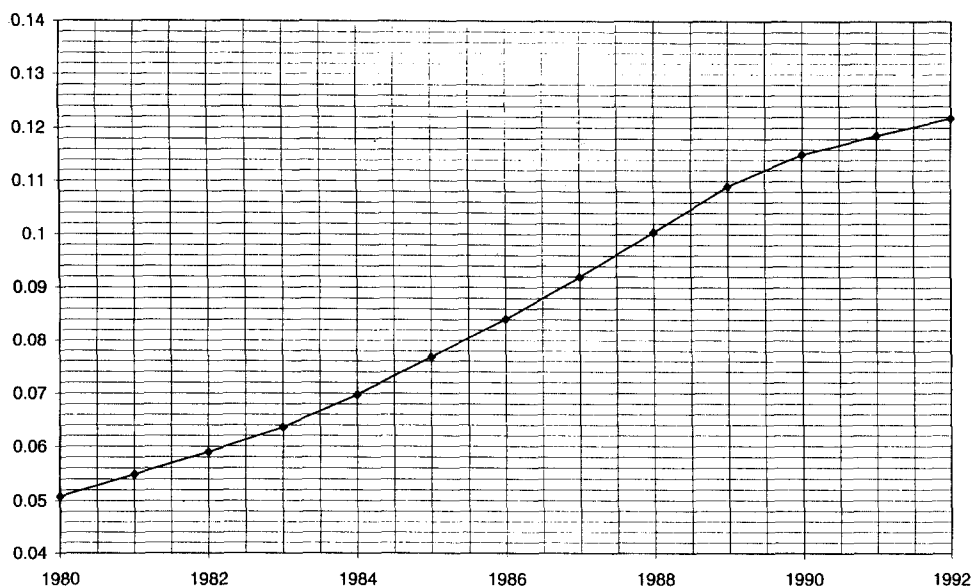
Fig. 4.   The ratio of CFC-113/CFC-11 concentrations in seawater of 14°C and a salinity of 38 (winter conditions in the Mediterranean Sea) in equilibrium with the atmosphere as a function of time.

ate layer at the entrance to the Black Sea and only a minor influence from the Istanbul area.

The lowest concentrations of the chlorofluorocarbons, i.e. the "oldest" water mass, were found in the deep water (salinity >38) at station E5 located at the southern exit of the Bosphorus. The average concentrations of CFCs there are 0.31 ± 0.02 and 0.020 ± 0.003 ng l^{-1} for CFC-11 and CFC-113, respectively, and the ratio CFC-113/CFC-11 is 0.065 ± 0.010. If this water had been equilibrated to 100% saturation with the atmosphere in the Mediterranean Sea during wintertime with surface water of 14°C and a salinity of 38, the CFC concentrations at E5 below 30 m were those of a water-mass sinking from the surface in about 1981 (±1.5 years) or 1982 (±1.5 years) based on CFC-11 or CFC-113, respectively, applying the "freight train" model (Wallace and Moore, 1985). Usually the saturation is not 100%, but if we assume the relative saturation in the surface water to be the same for both CFCs, the ratio would not be affected. Figure 4 shows the ratio CFC-113/ CFC-11 in the surface water over the years 1980–1989, again assuming salinity and temperature conditions of the Mediterranean Sea during winter. A ratio of 0.065 ± 0.010 indicates that the deep water, when entering the Bosphorus from the Marmara Sea, was at the surface in the Mediterranean Sea in 1983 (±2 years). It should be mentioned, however, that the CFC-113 values used in this calculation are close to the detection limit. As pointed out by Haine and Richards (1995), there is an uncertainty in the "ratio age" depending on the depth and seasonal variation of the surface mixed layer at the time for equilibration. At a maximum mixed layer depth of 200 m the apparent age is up to 1 year more than the real age. Taking this error into account, a time interval of between 6 and 11 years has passed since equilibration, which is more than the estimated mean residence time of about 5–7 years (Özsoy et al., 1986; Ünlüata et al., 1990) for the lower layer in the Marmara Sea. The difference can be explained by the fact that equilibration with air takes place an unknown

time before the water enters the Marmara Sea. Furthermore, the calculation is based not on an average over the entire water mass but on a discrete value obtained in a distinct water parcel that does not necessarily reflect the average residence time.

As can be seen in Fig. 3, the highest concentrations were measured in the intermediate water at the northern exit, which is identified as the Cold Intermediate Black Sea Water (CIBSW; see Fig. 2). The origin of the CIBSW (or the Cold Intermediate Layer, CIL, as it is also named) has been discussed in the literature. Tolmazin (1985), from a thorough review of present knowledge of the development of Northwestern Shelf Water in the Black Sea, draws the conclusion that the CIBSW originates in that area. The measured concentrations of CFC-11 and CFC-113 in the CIBSW layer at station K3 are 0.95–1.14 ng/l and 0.12–0.14 ng/l, respectively. These concentration ranges would correspond to 100% saturation of the relatively shallow (25 m) winter surface layer of the Northwestern Shelf with a salinity of 18, if the temperature was within the range of 2–5°C. As this is a normal temperature range for the surface water of the Northwestern Shelf in February–March, the coldest period before the onset of spring warming and isolation of the CIBSW under a thermocline (Tolmazin, 1985), this observation supports the hypothesis that the Northwestern Shelf is the origin of the CIBSW, since the temperature in other parts of the Black Sea does not reach such low levels.

An influence from the densely populated and industrialised region on both sides of the strait might also explain the elevation of the concentration levels above calculated equilibrium concentrations, of CFC-11 and CFC-113 in the surface water. However, carbon tetrachloride concentrations are unexpectedly low, especially in the surface layer. The data available in the literature on the solubility of carbon tetrachloride do not explain the observed partition between water and air elsewhere in the oceans. This is another reason to treat carbon tetrachloride data with great care. Furthermore, as mentioned above, carbon tetrachloride seems to decay in warm as well as in anoxic waters, possibly by hydrolysis or reduction (Tanhua *et al.*, 1996).

Chloroform and dibromomethane

Distributions of chloroform and dibromomethane are shown in Fig. 5. These two compounds differ from the chlorofluorocarbons and carbon tetrachloride (Fig. 3) in the sense that there is a pronounced source in the surface water in the vicinity of Istanbul.

The most striking feature in the distribution of chloroform (Fig. 5a) is that the highest concentrations were found in the upper layer at the Bosphorus–Marmara Junction (BMJ) extending to the region between stations B5 and B8 where the topographic contraction of the Bosphorus causes a hydraulic jump. Keeping in mind that the surface currents in the area are southbound, it seems reasonable to draw the conclusion that the source for these high levels lies in the domestic and industrial effluents from the Istanbul area. There is also a diffuse source of chloroform in the surface layer along the strait, possibly due to dispersed discharges of effluents from the communities along the strait. However, recent reports on the biogenic production of chloroform by algae (Nightingale *et al.*, 1995), and the exceptionally high primary production in the BMJ area (see below) do not exclude natural production.

The Istanbul sewage water is periodically chlorinated, and is then a significant source of chloroform. However, no chlorination of the sewage was taking place at the time of the investigation and only a weak signal of chloroform was observed in the vicinity of the
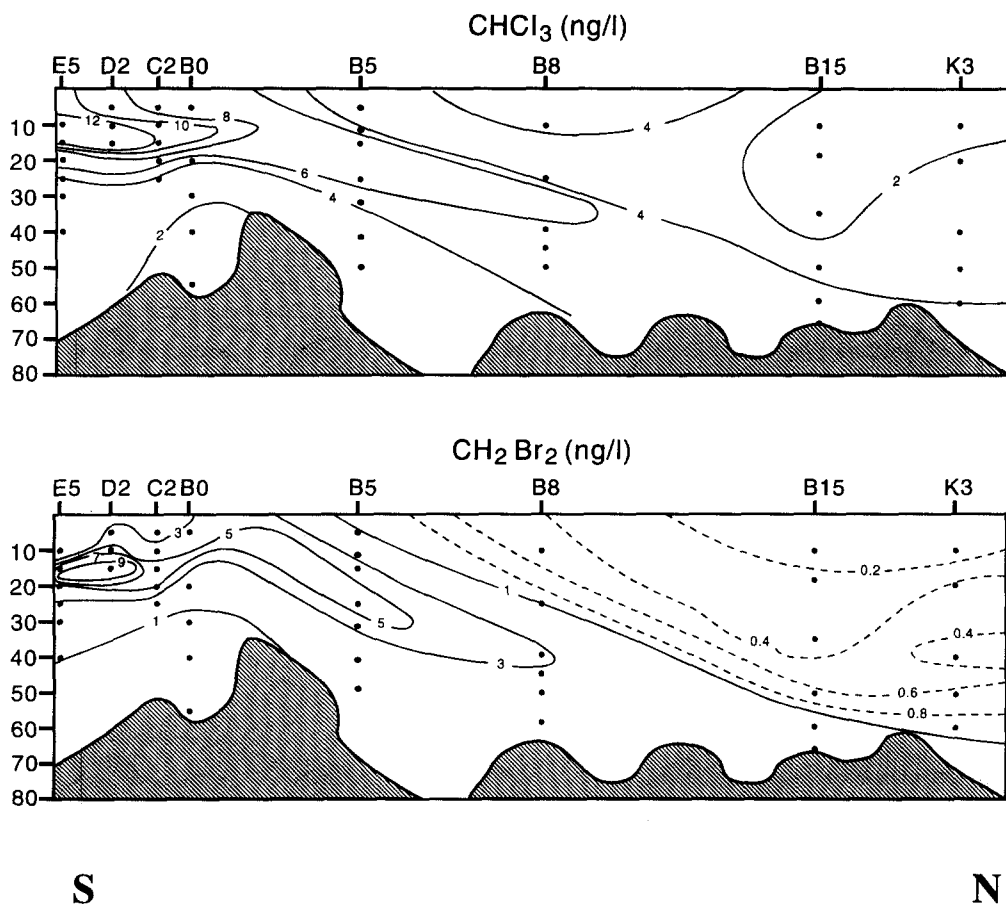
CHCl₃ (ng/l)

CH₂Br₂ (ng/l)

S   **N**

Fig. 5. The distributions of chloroform (CHCl₃) and dibromomethane (CH₂Br₂) in the Bosphorus Strait. For explanation of details, see Fig. 3.

sewage outlet. The discharge diffusers are located at the southern end of the Bosphorus at 56 m depth.

The distribution of dibromomethane is similar to that of chloroform (Fig. 5b). However, it is likely that the sources are not the same. There seems to be a source of dibromomethane at about 15–20 m depth at stations D2 and C2. This could be related to an algal bloom in the water, and need not be an anthropogenic input. It has been shown that the BMJ region is highly enriched in dissolved nutrients due to domestic wastes and to entrainment of nutrient-rich water from the lower to the upper layer of the Bosphorus (Bastürk *et al.*, 1986). This entrainment is due to the hydraulic jump in the strait. In the BMJ area, the total primary production is estimated to 103 g C/m²/yr. The maximum production occurs in the spring, and an autumn peak appears around November. During the summer, when the nutrient supply from the bottom layer of the Sea of Marmara is consumed, it has been shown that land based sources play an important role, causing a local increase in primary production in the late summer. Thus, the region has higher algal production and chl-*a* concentrations than other regions of the Marmara Sea and the southwestern Black Sea
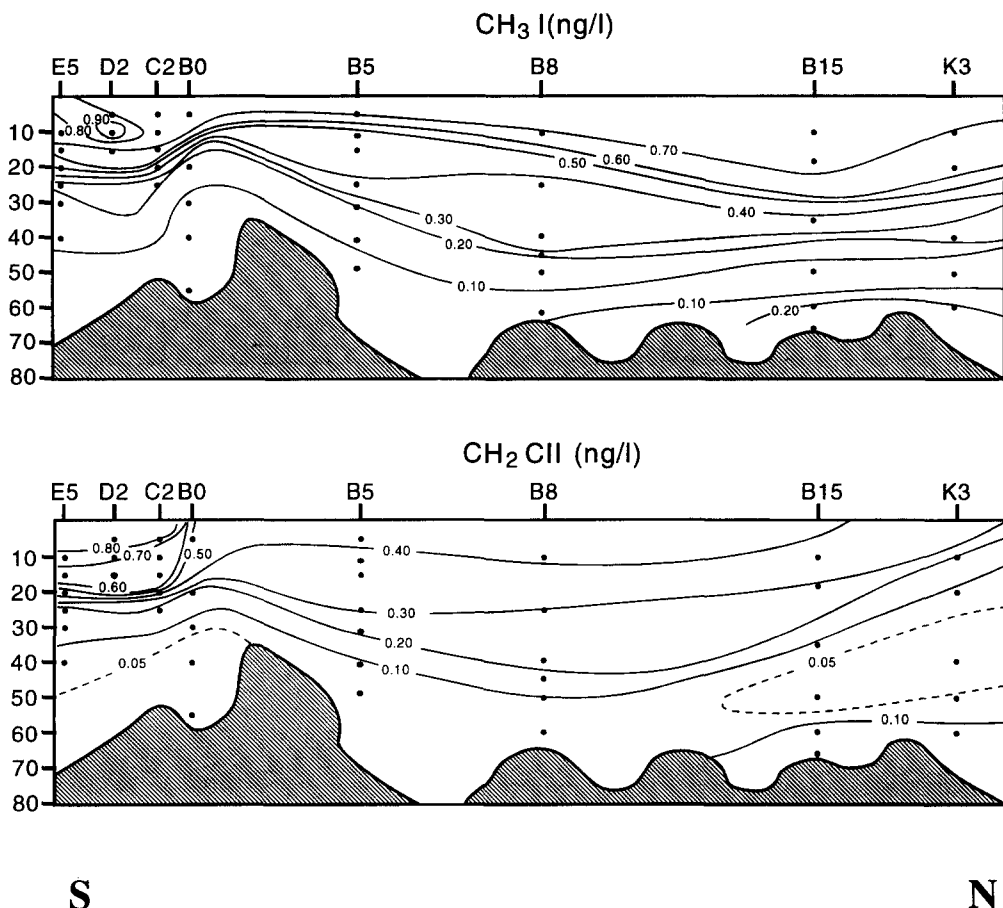
CH₃ I(ng/l)

CH₂ CII (ng/l)

S   **N**

Fig. 6.   The distributions of methyl iodide (CH₃I) and chloro-iodomethane (CHCII) in the
Bosphorus Strait. For explanation of details, see Fig. 3.

(Göçmen, 1988). However, further investigations should be made to elucidate the relative contributions of waste discharges and *in situ* production to the chloroform and dibromo-methane concentrations in the region.

Wherever the sources of chloroform and dibromomethane may be, the two compounds have a similar distribution along the strait. The point sources are in the pycnocline, and there is a distribution along the interface, i.e. along an isopycnal surface, between the surface Black Sea water and underlying Mediterranean water. It is possible that a similar plume stretches along the pycnocline further south into the Marmara Sea.

Methyl iodide and chloro-iodomethane

Two iodinated compounds, methyl iodide and chloro-iodomethane were measured during the study. Their distributions in the Bosphorus are shown in Fig. 6, where it can be

seen that they have similar distribution patterns. High concentrations of both compounds were found in the upper 10–15 m all along the Bosphorus (0.65–0.70 ng l^{-1} CH$_3$I and 0.30–0.49 ng l^{-1} CH$_2$ClI). The highest concentrations, up to 0.90 ng l^{-1} CH$_3$I and 0.93 ng l^{-1} CH$_2$ClI were detected in the upper layer of the BMJ region, where there was also a considerable source of chloroform and dibromomethane (see above). However, the iodinated halocarbons do not form an isopycnal plume, as do chloroform and dibromomethane. A close look at the salinity distribution in Fig. 2(b) reveals that the point sources for chloroform and dibromomethane are both at about 15 m depth (in the pycnocline) whereas the iodinated compounds appear to have sources closer to the surface. The nearly homogeneous distribution of the iodinated compounds in the upper layer all along the strait north of the BO station indicates that they emanate from diffuse, probably natural, sources within the upper layer of the strait and/or the Black Sea, either by algal production or through photochemical transformation of other halocarbons. Additional inputs by pelagic algal production in the BMJ, lead to the higher levels of iodinated halocarbons in this region.

Methyl iodide and chloro-iodomethane were also measured at relatively high concentrations in the deep water at stations B15 and K3, as compared with the overlying water masses and the inflowing Marmara Sea deep water. This relative increase in deep water implies another, probably benthic, production on the slopes of the Bosphorus close to the exit to the Black Sea.

CONCLUSIONS

In addition to the traditional halogenated transient tracers CFC-11, CFC-113 and carbon tetrachloride, a few other halocarbons, chloroform, dibromomethane methyl iodide and chloro-iodomethane, were used for the characterisation of water masses in the Bosphorus Strait. These other halocarbons have source functions that are less well known, but can nevertheless provide complementary information concerning movement and mixing of water masses.

Chlorofluorocarbon measurements in the inflow to the Bosphorus from the deep layer of the Marmara Sea indicate that a time period of 6–11 years has elapsed since that water was in contact with the atmosphere in the Mediterranean Sea.

The concentration ranges of CFC-11 and CFC-113 in the Cold Intermediate Black Sea Water (CIBSW) are consistent with their being dissolved the previous winter in the surface water of the Northwestern Shelf in the Black Sea at a salinity of 18, if the temperatures were between 2 and 5°C. As this is a normal temperature range during the coldest period before the build-up of a new thermocline and the isolation of the CIBSW from the surface, this supports the hypothesis of Northwestern Shelf being the origin of CIBSW.

Carbon tetrachloride concentrations are lower than expected, and point to a need for further investigations on the Henry's Law constants at various temperatures and salinities as well as possible decay in warm and/or anoxic seawater.

Elevated concentrations of chloroform, dibromomethane, methyl iodide and chloro-iodomethane in the Bosphorus Marmara Junction (BMJ) may be attributed to natural production, either biotic or abiotic processes, but anthropogenic inputs, especially of chloroform, must also be considered.

REFERENCES

Bastürk Ö., I. Salihoglu, C. Saydam and A. Yilmaz. (1986) Oceanography of Turkish Straits. First annual report, Vol II. Health of the Turkish Straits II. Chemical and environmental aspects of the Sea of Marmara. Institute of Marine Sciences, METU, Erdemli, Içel, Turkey, 86 pp.

Bu X. and M. J. Warner (1995) Solubility of Chlorofluorocarbon 113 in Water and Seawater. *Deep-Sea Research*, **42**, 1151–1161.

Bullister J. L. and R. F. Weiss (1983) Anthropogenic chlorofluoromethanes in the Greenland and Norwegian Seas. *Science*, **221**, 265–268.

Büyükay M. (1989) The surface and internal oscillations in the Bosphorus, related to meteorological forces. M.S. Thesis, Institute of Marine Sciences, METU, Erdemli, Icel, Turkey, 169 pp.

Cunnold D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, C. A. Cardelino, A. J. Crawford, P. J. Fraser and R. D. Rosen (1986) Atmospheric lifetime and annual release estimates for $CFCl_3$ and CF_2Cl_2 from 5 years of ALE data. *Journal of Geophysical Research*, **91**(D10), 10,797–10,817.

Dyrssen D. and E. Fogelqvist (1981) Bromoform concentrations in the Arctic Ocean in the Svalbard area. *Oceanologica Acta*, **4**, 313–317.

Fisher D. A. and P. M. Midgley (1993) The production and release to the atmosphere of CFCs 113, 114 and 115. *Atmospheric Environment*, **27A**, 271–276.

Fogelqvist E. (1985) Carbon tetrachloride, tetrachloroethylene, 1,1,1-trichloroethane and bromoform in Arctic seawater. *Journal of Geophysical Research*, **90**, 9181–9193.

Fogelqvist E. and M. Krysell (1991) Naturally and anthropogenically produced bromoform in the Kattegatt, a semi-enclosed oceanic basin. *Journal of Atmospheric Chemistry*, **13**, 315–324.

Fogelqvist E. and T. Tanhua (1995) Iodinated C1-C4 hydrocarbons released from ice algae in Antarctica. In: *Proceedings of the International Conference on Naturally-Produced Organohalogens*, 14–17 September 1993, Delft, The Netherlands.

Fogelqvist E., B. Josefsson and C. Roos (1982) Halocarbons as tracer substances in studies of the distribution pattern of chlorinated waters in coastal areas. *Environmental Science and Technology*, **16**, 479–482.

Göçmen D. (1988) Fluctuations of chlorophyll-a and primary productivity as related to physical chemical and biological parameters in Turkish coastal waters. M.S. Thesis, Institute of Marine Sciences, METU, Erdemli, Içel, Turkey, 137 pp.

Gschwend P. M., J. K. MacFarlane and K. A. Newman (1985) Volatile halogenated organic compounds released to seawater from temperate marine macroalgae. *Science*, **277**, 1033–1035.

Gunnerson C. G. and E. Öztergut (1974) The Bosphorus. The Black Sea geology, chemistry and biology, memoir 20. *American Association of Petroleum Geologists*, 249–278.

Haine T. W. N. and K. J. Richards (1995) The influence of the seasonal mixed layer on oceanic uptake of CFCs. *Journal of Geophysical Research*, **100**(C6), 10,727–10,744.

Klick S. and K. Abrahamsson (1992) Biogenic volatile iodated hydrocarbons in the ocean. *Journal of Geophysical Research*, **97**, 12,683–12,687.

Krysell M. (1992) Carbon tetrachloride and methyl chloroform as tracers of deep water formation in the Weddell Sea, Antarctica. *Marine Chemistry*, **39**, 297–310.

Krysell M. and P. D. Nightingale (1994) Low molecular weight halocarbons in the Humber and Rhine estuaries determined using a new purge-and-trap gas chromatographic method. *Continental Shelf Research*, **14**, 1311–1329.

Krysell M., E. Fogelqvist and T. Tanhua (1994) Removal of the transient tracer carbon tetrachloride from anoxic seawater. *Geophysical Research Letters*, **21**, 2,511–2,514.

Krysell M. and D. W. R. Wallace (1988) Arctic ocean ventilation studied with a suite of anthropogenic halocarbon tracers. *Science*, **242**, 746–749.

Lovelock J. E. (1975) Natural halocarbons in the air and in the sea. *Nature*, **256**, 193–194.

Lovelock J. E., R. J. Maggs and R. H. Wade (1973) Halogenated hydrocarbons in and over the Atlantic. *Nature*, **241**, 194–196.

Manley S. L. and M. S. Dastoor (1987) Methyl halide (CH_3X) production from the giant kelp, Macrocystis, and estimates of global production by kelp. *Limnology and Oceanography*, **32**, 709–715.

Moore R. M. and R. Tokarczyk (1992) Chloro-iodomethane in N. Atlantic waters: a potentially significant source of atmospheric iodine. *Geophysical Research Letters*, **19**, 1779–1782.

Moore R. M. and R. Tokarczyk (1993) Volatile Biogenic Halocarbons in the Northwest Atlantic. *Global Biogeochemical Cycles*, **7**, 195–210.

Moore R. M. and O. C. Zafiriou (1994) Photochemical production of methyl iodide in seawater. *Journal of Geophysical Research*, **99**, 16,415–16,420.

Nightingale P. D., G. Malin and P. S. Liss (1995) Production of chloroform and other low molecular weight halocarbons by some species of macroalgae. *Limnology and Oceanography*, **40**(4), 680–689.

Oguz T., E. Özsoy, M. A. Latif and U. Ünlüata (1990) Modelling of hydraulically controlled exchange flow in the Bosphorus Strait. *Journal of Physical Oceanography*, **20**, 945–965.

Özsoy E., T. Oguz, M. A. Latif and U. Ünlüata (1986) Oceanography of the Turkish Straits-First Annual Report, Volume I: Physical Oceanography of the Turkish Straits. Institute of Marine Sciences, METU, Erdemli, Içel, Turkey, 233 pp.

Özsoy E., I. Salihoglu, M. A. Latif, A. F. Gaines, S. Besiktepe, S. Tugrul, T. Oguz, Ö. Bastürk, C. Saydam, S. Yemenicioglu and A. Yilmaz (1992) Monitoring via direct measurements of the modes of mixing and transport of wastewater discharges into the Bosphorus underflow. Second progress report. Institute of Marine Sciences, METU, Erdemli, Içel, Turkey.

Rasmussen R. A., M. A. K. Khalil, R. Gunawardena and S. D. Hoyt (1982) Atmospheric methyl iodide (CH3I). *Journal of Geophysical Research*, **87**, 3086–3090.

Reifenhäuser W. and K. G. Heumann (1992a) Determinations of methyl iodide in the Antarctic atmosphere and the South Polar Sea. *Atmospheric Environment*, **26A**, 2905–2912.

Reifenhäuser W. and K. G. Heumann (1992b) Bromo- and bromochloromethanes in the Antarctic atmosphere and the South Polar Sea. *Chemosphere*, **24**, 1293–1300.

Rhein M. (1994) The deep western boundary current: tracers and velocities. *Deep-Sea Research*, **41**, 263–281.

Simmonds P. G., D. M. Cunnold, F. N. Alyea, C. A. Cardelino, A. J. Crawford, R. G. Prinn, P. J. Fraser, R. A. Rasmussen and R. D. Rosen (1988) Carbon tetrachloride liftetimes and emissions determined from daily global measurements during 1978–1985. *Journal of Atmospheric Chemistry*, **7**, 35–58.

Singh H. B., L. J. Salas and R. E. Stiles (1983) Methylhalides in and over the eastern Pacific (40°N–32°S). *Journal of Geophysical Research*, **88**, 3684–3690.

Smethie W. M., D. W. Chipman, J. H. Swift and K. P. Koltermann (1988) CFMs in the Arctic Mediterranean Seas: evidence for formation of bottom water in the Eurasian Basin and deep water exchange through Fram Strait. *Deep-Sea Research*, **35**, 347–369.

Tanhua T., E. Fogelqvist and Ö. Bastürk (1996) Reduction of volatile halocarbons in anoxic seawater, results from a study in the Black Sea. *Marine Chemistry*, submitted.

Tanzer D. and K. G. Heumann (1992) Gas chromatographic trace-level determination of volatile organic sulfides and selenides and of methyl iodide in the Atlantic surface water. *International Journal of Environmental and Analytical Chemistry*, **48**, 17–31.

Tolmazin D. (1985) Changing coastal oceanography of the Black Sea. I: Northwestern Shelf. *Progress in Oceanography*, **15**, 217–276.

Ünlüata Ü. and E. Özsoy (1986) Oceanography of the Turkish straits—first annual report—Vol. II. Health of the Turkish straits. I: Oxygen deficiency of the Sea of Marmara. Institute of Marine Sciences, METU, Erdemli, Içel, Turkey, 55 pp.

Ünlüata Ü., T. Oguz, M. A. Latif and E. Özsoy (1990) On the physical oceanography of the Turkish Straits. In: *The physical oceanography of sea straits*, L. J. Pratt, editor, NATO/ASI Series, Kluwer, Dordrecht, pp. 25–60.

Wallace D. W. R. and R. M. Moore (1985) Vertical Profiles of CCl_3F (F-11) and CCl_2F_2 (F-12) in the Central Arctic Ocean Basin. *Journal of Geophysical Research*, **90**, 1155–1166.

Wallace D. W. R., P. Beining and A. Putzka (1994) Carbon tetrachloride and chlorofluorocarbons in the South Atlantic Ocean, 19°S, *Journal of Geophysical Research*, **99**, 7803–7819.

Warner M. J. and R. F. Weiss (1985) Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Research*, **32**, 1485–1497.

Weiss R. F., J. L. Bullister, R. H. Gammon and M. J. Warner (1985) Atmospheric chlorofluoromethanes in the deep equatorial Atlantic. *Nature*, **314**, 608–610.

Wisegarver D. P. and R. H. Gammon (1988) A new transient tracer: measured vertical distribution of CCl_2FCClF_2 (F-113) in the North Pacific Subarctic gyre. *Geophysical Research Letters*, **15**, 188–191.