

Reduction of volatile halocarbons in anoxic seawater, results from a study in the Black Sea

Toste Tanhua^{a,*}, Elisabet Fogelqvist^a, Özden Bastürk^b

^a Department of Analytical and Marine Chemistry, University of Göteborg and Chalmers University of Technology, S-412 96 Göteborg, Sweden

^b Institute of Marine Sciences, Middle East Technical University, P.O. Box 28, 33731 Erdemli, İçel, Turkey

Received 24 October 1994; accepted 15 December 1995

Abstract

The Black Sea is characterised by an oxic surface water layer and anoxic deep water rich in both hydrogen sulphide and methane, and in between a suboxic zone with very low concentrations of both oxygen and hydrogen sulphide. This makes the Black Sea a useful site for the study of oxidation–reduction reactions in seawater.

In this study, the distributions of tetrachloromethane, trichloromethane, 1,1,1-trichloroethane, dibromomethane, dibromochloromethane and bromodichloromethane across the oxic–anoxic interface were related to the oxygen/hydrogen sulphide concentrations and thereby the redox potential gradient.

All of the investigated halocarbons decrease rapidly in concentration as the oxygen decreases, most likely due to reduction. The results show that the higher the redox potential of a halocarbon, the higher up in the water column, i.e. at a higher oxygen level, reduction occurs. Most of the tetrachloromethane is transformed to trichloromethane as an intermediate product.

1. Introduction

1.1. The pathways of halocarbons in the marine environment

Halogenated methanes, ethanes and ethenes (halocarbons) are widely found in the marine environment. Chlorinated and, to a lesser extent, brominated halocarbons are widely used as solvents, cleaning agents, in fire extinguishers and as intermediates in the chemical industry. To some extent, these

chemicals will eventually end up in the seawater. Halocarbons do not only have anthropogenic sources; there are also natural sources in production by marine organisms. It has been shown, in monospecific cultures, that various bromo-, chloro- and bromochloro-methanes are being produced by benthic macroalgae and released to the water (Gschwend et al., 1985; Manley et al., 1992; Klick, 1993; Collén et al., 1994; Nightingale et al., 1995). Recently, Tokarczyk and Moore (1994) showed that some species of pelagic phytoplankton also produce halocarbons. Furthermore, algae living in sea-ice produce brominated methanes (Sturges et al., 1992) as well as iodinated hydrocarbons (Fogelqvist and Tanhua, 1995). Halocarbons, such as tetrachloromethane

* Corresponding author.

(CCl₄) and 1,1,1-trichloroethane (CH₃CCl₃), are used together with chlorofluorocarbons (CFCs) as presumably conservative tracers for oceanic studies of large-scale mixing processes.

Here we present results from an investigation in the Black Sea with special emphasis on the distribution of the halocarbons between the oxic and the anoxic water masses. The compounds dealt with in this paper are: tetrachloromethane (CCl₄, carbon tetrachloride); trichloromethane (CHCl₃, chloroform); 1,1,1-trichloroethane (CH₃CCl₃, methyl chloroform); dibromochloromethane (CHBr₂Cl); bromodichloromethane (CHBrCl₂); and dibromomethane (CH₂Br₂).

There is a need for better understanding of the processes that are responsible for the removal of halocarbons in the environment. Several studies have been carried out under various conditions, both field experiments in natural environments and laboratory experiments, in order to elucidate the fate of halocarbons in the environment both under the influence of microorganisms (e.g., the following articles and references therein: Little et al., 1988; Vannelli et al., 1990; Lovley and Woodward, 1992; Semprini et al., 1992) and abiotic processes such as a study on the transformation of CCl₄ by pyrite (Kriegman-King and Reinhard, 1994).

A few observations of degradation of halocarbons in oceanic seawater have been reported. Butler et al. (1991) observed an oceanic consumption of CH₃CCl₃ in the tropical Pacific and a breakdown of CCl₄ was observed by Krysell et al. (1994) in suboxic and anoxic water layers of the Gotland Basin in the

Baltic Sea. Wallace et al. (1994) made similar observations in the Atlantic Ocean, in water layers with low oxygen concentrations. Observations of unexpectedly low concentrations of CCl₄ in the Black Sea Water flowing out through the Bosphorus Strait raised the question whether breakdown under the influence of the anoxic waters within the Black Sea might be the cause for the low concentrations (Fogelqvist et al., 1996).

An overview of various chemical mechanisms for the transformation of halocarbon molecules is provided by Vogel et al. (1987). Removal of halocarbons may be of abiotic, mammalian or microbial nature. Abiotic processes are generally considered to be slow in comparison with biotic pathways, but may be of significant importance in the time-scales of ocean circulation. The mammalian pathway is of minor importance in the oceans, and is not considered at all in this study. Microbial transformation, such as transformations catalysed by cytochrome P450, may be of great importance in the marine environment. Regardless of the nature of transformation, halocarbons may be transformed by processes requiring electron transfers, i.e. reduction and oxidation, or by processes where no electron transfer takes place, i.e. substitution reactions, of which hydrolysis is considered important in seawater. In this paper, we will mainly deal with oxidation–reduction reactions, since the Black Sea water column is characterised by a gradient in redox potential.

The carbon atoms in halogenated organics are at a higher oxidation level compared with hydrocarbons due to the presence of halogen substituents. The

Table 1
Reduction of halocarbons, from Vogel et al. (1987)

<i>First step of reduction:</i>				
$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} - \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \\ \text{X} \end{array}$	+	Reduced compound	$\xrightarrow{\text{Slow}}$	$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} - \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} + \text{Oxidized compound} + \text{X}^-$
<i>Overall reaction, with three possible pathways of reduction:</i>				
$\text{RX} + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{RH} + \text{X}^-$				hydrogenolysis
$\text{RX}-\text{RX} + 2\text{e}^- \rightleftharpoons \text{R}=\text{R} + 2\text{X}^-$				dihalo-elimination
$2\text{RX} + 2\text{e}^- \rightleftharpoons \text{R}-\text{R} + 2\text{X}^-$				coupling

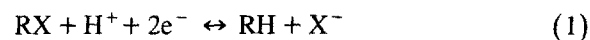
The first step is the rate-limiting step. In the second step, the reaction follows one of three possible pathways.

greater the substitution with halogen atoms, the higher the oxidation level. Also, an increased number of halogen substituents generally increases the redox potential of the compound, as does replacing chlorine with bromine. The increase in redox potential is supported by theoretical computational calculations on the redox potential of halomethanes made by Waller and McKinney (1993). Some transition metals and several biologically active electron donors found in the marine environment have lower redox potential than the halocarbons, and can be oxidised by them. These reactions may occur in both biotic and abiotic systems.

Reduction reactions are described in detailed by Vogel et al. (1987). Reduction of halocarbons is a two-step reaction, in which the first step involves formation of an alkyl radical. This step is in most cases the rate-limiting step (Vogel et al., 1987). The second step follows one of three different reactions (Table 1). In the simplest reaction, a hydrogen atom substitutes for the halogen atom, a reaction called hydrogenolysis. Another possibility involves the loss of a second halogen atom and the formation of an alkene via dihalo-elimination. Finally, two radicals may join in a dimerisation, which is called coupling.

For the halocarbons investigated in this study, dihalo-elimination cannot happen because of the constitution of the molecules. Of the remaining two possibilities hydrogenolysis is believed to be the most important, since the halocarbon concentration is in the order of 10^{-12} M, and the radical formed is thus far more likely to react with a hydrogen ion (10^{-8} M) than with a radical of its own kind.

Some possible half-reactions are listed in Table 2, along with their redox potentials based on data from Vogel et al. (1987). The pH, temperature and halide ion concentrations are adjusted to the conditions in the suboxic layer in the Black Sea. All halocarbon concentrations are set to be equal. The redox potential is calculated according to the Nernst equation for the following reaction:



$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{X}^-][\text{RH}]}{[\text{H}^+][\text{RX}]} \right) \quad (2)$$

where E is the redox potential at actual conditions; E° is the redox potential at the standard state; R is

Table 2

Reduction-oxidation half-reactions of halocarbons, oxygen and nitrate

Reaction	E (V)
$\frac{1}{4}\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2\text{O}$ 100% O_2 saturation	0.75
$\frac{1}{4}\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2\text{O}$ 10% O_2 saturation	0.74
$\frac{1}{4}\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2\text{O}$ 1% O_2 saturation	0.72
$\frac{1}{2}\text{CCl}_4 + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CHCl}_3 + \frac{1}{2}\text{Cl}^-$	0.58
$\frac{1}{2}\text{CHBrCl}_2 + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_2\text{Cl}_2 + \frac{1}{2}\text{Br}^-$	0.56
$\frac{1}{2}\text{CHBr}_2\text{Cl} + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_2\text{BrCl} + \frac{1}{2}\text{Br}^-$	0.55
$\frac{1}{2}\text{CHBr}_2\text{Cl} + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_2\text{Br}_2 + \frac{1}{2}\text{Cl}^-$	0.51
$\frac{1}{2}\text{CHBrCl}_2 + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_2\text{BrCl} + \frac{1}{2}\text{Cl}^-$	0.48
$\frac{1}{2}\text{CH}_3\text{CCl}_3 + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_3\text{CHCl}_2 + \frac{1}{2}\text{Cl}^-$	0.48
$\frac{1}{2}\text{CHCl}_3 + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_2\text{Cl}_2 + \frac{1}{2}\text{Cl}^-$	0.47
$\frac{1}{2}\text{CH}_2\text{Br}_2 + \frac{1}{2}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{CH}_3\text{Br} + \frac{1}{2}\text{Br}^-$	0.43
$\frac{1}{5}\text{NO}_3^- + \frac{6}{5}\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{10}\text{N}_{2(\text{g})} + \frac{1}{2}\text{H}_2\text{O}$	0.65
$\frac{1}{2}\text{NO}_3^- + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{NO}_2^- + \frac{1}{2}\text{H}_2\text{O}$	0.38

The redox potentials for halocarbons are taken from Vogel et al. (1987) recalculated to the conditions in the suboxic zone in the Black Sea ($\text{pH} = 7.75$, $T = 8.25^\circ\text{C}$, chloride activity = 0.32 M and bromide activity = 0.0005 M), while the concentrations of a halocarbon and its product are equal. Redox potentials for oxygen and nitrate are calculated, for the same conditions, from listed E° -values (Handbook of Chemistry and Physics, 1986).

the universal gas constant; T is the absolute temperature; n is electron equivalents transferred; and F is Faraday's constant.

It is worth noticing that all the halocarbon reductions have higher reduction potentials than that of nitrate to nitrite. This implies that halocarbons are potential electron acceptors, and might serve as such when the oxygen concentration decreases. Reduction is thus favoured thermodynamically by the high redox potential for halocarbons, but no information about the kinetics for the reaction is obtained. A slow rate of reaction will, of course, restrict the reduction of halocarbons in nature. However, a semi-empirical relation, based on the Marcus relation (Ebersson, 1987), between the one-electron redox potential of an organic compound and the rate of reduction has been developed. This relation has been used to estimate rates of reduction for halocarbons (Curtis and Reinhard, 1994) with good agreement to experimental results. Tratnyek et al. (1991) conclude that one-electron redox potentials are good molecular descriptors with which to correlate the specific rates of reduction. In this relation, the rate constant, k'_{RX} ,

for the rate-limiting first step in reduction of halocarbons is dependent on the redox potential of the electron acceptor, E_{RX} , and the redox potential of the electron donor, E_D , by:

$$\log k'_{RX} = \alpha \frac{nF}{2.3RT} (E_{RX} - E_D) + \beta \quad (3)$$

where R is the universal gas constant; T is the absolute temperature; n is electron equivalents transferred; F is Faraday's constant; and α and β are empirical constants. In a natural system like the Black Sea it is difficult to address one single electron donor and hence to determine its redox potential. However, assuming that the same electron donor is active in the reduction of all the halocarbons investigated here and that the constants α and β are the same, then the reduction rate is higher for those halocarbons with higher redox potentials.

In this paper we present the distribution of some halocarbons and their concentration changes with depth of the water column. We will relate these changes to the oxygen and hydrogen sulphide concentrations and discuss possible pathways for their transformation in the oxic–anoxic interface.

1.2. The study area

The Black Sea is the world's largest permanently anoxic basin. It receives fresh water input from precipitation and river run off that exceeds the rate of evaporation and thus there is a surface water layer with relatively low salinity. Below the surface layer there is a deep water mass with an inflow of high-salinity water of Mediterranean origin through the Bosphorus Strait (Özsoy et al., 1993). Between these two water masses there is a shallow, salinity-dependent density gradient that prevents ventilation of the deep layer. Due to the oxidation of sinking organic matter from the euphotic zone, the deep water becomes anoxic and rich in both hydrogen sulphide and methane. The Black Sea water turns anoxic at ~100-m depth and remains so down to the bottom at >2000 m. Although the depth of the pycnocline, with the shift from oxic to anoxic conditions, varies slightly from one location to another, the density surface where the shift occurs is well defined and consistent throughout the Black Sea. Therefore, plots of properties versus density (measured as sigma-theta,

σ_θ) are more useful than property–depth profiles, when investigating chemical reactions within the redoxcline.

A typical, and for our discussion very important feature of the Black Sea is the existence of a suboxic zone between the oxic and the anoxic waters (Codi-poti et al., 1991; Bastürk et al., 1994; Murray et al., 1995). The suboxic zone is roughly at σ_θ values between 15.65 and 16.15, the water above it being oxic and the water below anoxic, and is characterised by low concentrations of both hydrogen sulphide (<5 μM) and oxygen (<10 μM) and is generally 20–50 m thick. The water column of the Black Sea with its well-defined oxygen gradient, and thereby a gradient in redox conditions, is the scene for many reduction–oxidation reactions and is a suitable location to study such reactions in the marine environment.

In this paper we present results from five deep stations in the southern part of the western basin of the Black Sea.

2. Methods

2.1. Sampling

Data presented in this study were collected 19–20 December 1993 on R/V “Bilim” of the Institute of Marine Sciences (METU). Five offshore stations in the deeper parts of the Black Sea were selected for this study in order to eliminate possible effects from the coast and from shelf sediments. Twelve samples were taken at each station, with emphasis on the depths in and around the suboxic layer, but with less resolution in the surface and the deep water masses. Water samples were collected 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.

2.2. Nutrients, oxygen, hydrogen sulphide

Measurements of nitrate, nitrite, phosphate, silicate, oxygen and hydrogen sulphide were made by technical staff from IMS-METU on board the ship immediately after sampling. Nutrient determinations were performed with a Technicon II Autoanalyzer.

Oxygen was measured by a modified Winkler method according to Carritt and Carpenter (1966). Hydrogen sulphide measurements were made by iodometric titration (Fonselius, 1983). Before the water samples were transferred into titration flasks, all flasks and reagents were flushed with oxygen-free argon gas for 1–2 min.

2.3. Halocarbons

Subsamples for halocarbon determinations were drawn into 100-ml ground glass syringes and stored under seawater prior to analysis, which was performed within 5 hr of sampling. The halocarbons were measured with purge-and-trap sample work-up followed by gas chromatographic separation and detection by electron capture detector. A similar analytical setup is described by Krysell and Nightingale (1994). A sample volume of 40 ml was injected to the purge-and-trap system. The halocarbons were stripped off by bubbling with an inert gas (N_2) at a flow rate of 80 ml min^{-1} for 20 min. The halocarbons were passed on to a cold trap consisting of an open stainless-steel tube (0.5 m long and ID 0.75 mm), immersed in the vapours of liquid nitrogen in a Dewar flask at a temperature of about -150°C . The trap was then heated with boiling water. The halocarbons were desorbed and transferred to the gas chromatographic column. Two lines of the entire analytical procedure worked in parallel employing two separate fused silica columns (J & W, DB 624, 75 m long and ID 0.53 mm) in the gas chromatograph (Varian 3400 GC) with two electron capture detectors. The GC oven was temperature programmed from 70°C , with a hold time of 4 min in the beginning of the chromatographic run, to 140°C with a temperature increase of 5°C min^{-1} , after which the oven was kept at the higher temperature for 4 min. The two parallel lines allowed analysis of ~ 5 samples per hour. The standardisation of CCl_4 and CH_3CCl_3 was accomplished by comparison with a gaseous standard, introduced into the purge flow through a loop valve. The gaseous standard was calibrated against the known concentration of CCl_4 and CH_3CCl_3 in marine air. We assigned a mixing ratio of 109 ± 5 ppt for CCl_4 and 145 ± 7 ppt for CH_3CCl_3 in the marine air over the Black sea in December 1993 (CCl_4 data from J.H. Butler,

NOAA/CMDL, pers. commun.; CH_3CCl_3 data from Prinn et al., 1995). For standardisation of other halocarbons, a liquid standard, gravimetrically prepared in Turkey shortly before the cruise and diluted into methanol during the cruise, was injected into the stripping chamber through a valve with an internal loop of $2\text{-}\mu\text{l}$ volume. Stripping efficiencies were measured and compensated for. The detection limits range from 0.01 pM for CCl_4 , 0.1 pM for all brominated halocarbons, 0.5 pM for CH_3CCl_3 and 1 pM for CHCl_3 with an uncertainty of the measurements which is estimated to be within $\pm 10\%$.

3. Results and discussion

3.1. Oxygen

Displayed in Fig. 1 are the oxygen and hydrogen sulphide concentrations for the five stations examined. The hydrogen sulphide data were inversely correlated with oxygen concentration, calculated on a molar basis, where 1 mol of H_2S is equivalent to 2 mol of O_2 since 2 mol O_2 of is required for oxidation H_2S of to sulphate (Fonselius, 1969). Thus, a negative oxygen concentration in Figs. 1 and 5 denotes the presence of hydrogen sulphide. In the oxic zone there is a continuous oxygen gradient from the subsurface maximum down to $\sigma_\theta \approx 15.6$. Between σ_θ 15.6 and 16.3 both oxygen and hydrogen sulphide are very close to zero (O_2 concentrations within

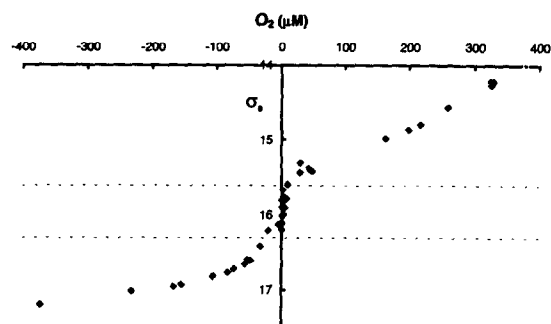


Fig. 1. Oxygen concentration versus density at five offshore stations in the Black Sea. A negative oxygen concentration denotes the presence of hydrogen sulphide (calculated on a molar basis, see text). The suboxic zone between σ_θ 15.6 and 16.3 is marked with broken lines.

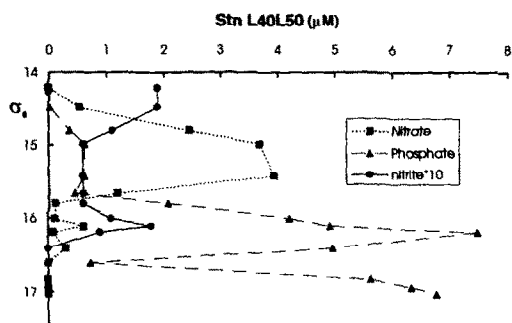


Fig. 2. Nitrate, nitrite and phosphate concentrations versus density at one of the stations (L40L50).

$\pm 10 \mu M$), which we define as the suboxic zone during our survey. At zero oxygen level, the water is truly anoxic. The redox potential of seawater depends on the redox reaction referred to, and does not have a unique value. This is due to the fact that free

electrons do not actually exist in the water, and that redox equilibrium is seldom reached in low-temperature environments in the sea. Furthermore, the use of electrodes is restricted in natural systems, since there are many significant redox couples encountered, to which they do not respond. Different redox couples can be used for describing a system's redox potential, such as nitrate reduction, Fe(III) reduction, sulphate reduction and production of methane. The use of H_2 concentration for analysing the redox chemistry of groundwaters has been suggested by Lovley et al. (1994). We have chosen the O_2 and H_2S concentrations as indicator of the gradient in redox potential.

A redoxcline is defined as the water layer where major shifts in the chemical composition of the water due to redox reactions take place. In the Black Sea, the redoxcline coincides with the suboxic zone.

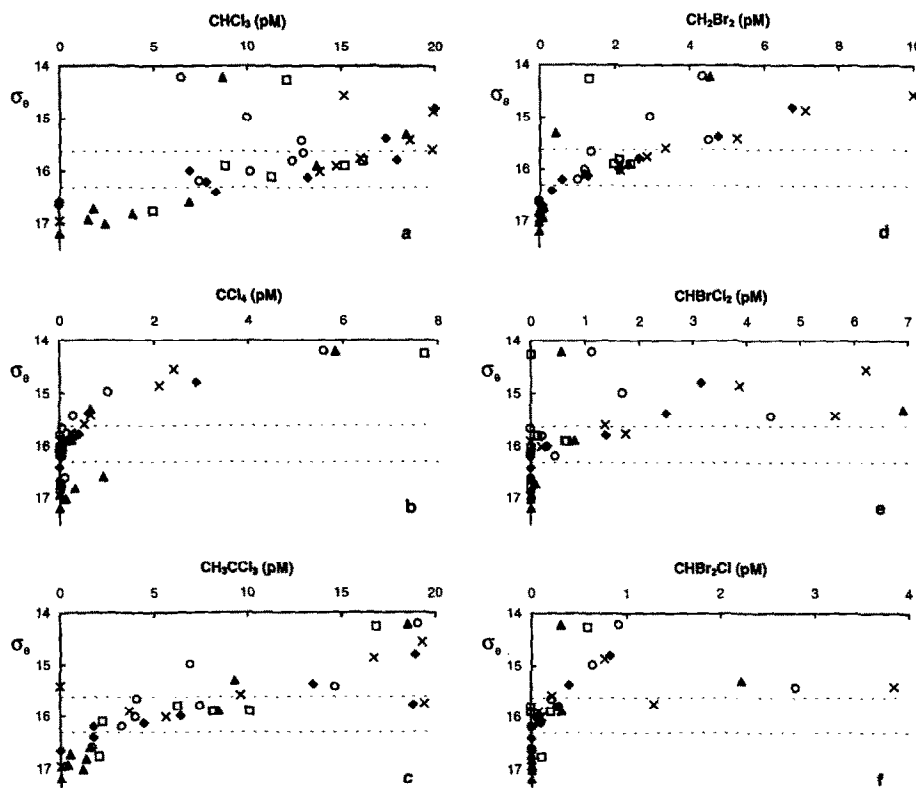


Fig. 3. Halocarbon concentrations versus density at five stations superimposed upon each other. The stations are marked with different symbols (\diamond = L40L20; \blacktriangle = M00L20; \times = M00L50; \circ = L40L50; \square = L30L50). The halocarbons are: (a) tetrachloromethane (CCl_4); (b) trichloromethane ($CHCl_3$); (c) 1,1,1-trichloroethane (CH_3CCl_3); (d) dibromomethane (CH_2Br_2); (e) bromodichloromethane ($CHBrCl_2$); and (f) dibromochloromethane ($CHBr_2Cl$). The suboxic zone between σ_θ 15.6 and 16.3 is marked with broken lines.

3.2. Nutrients

The nutrient profiles from one of the stations (L40L50, at position 41°40'N; 29°50'E) are shown in Fig. 2. Nitrate values are very low in the upper layer, increase towards depth due to nitrification of organic matter, and reach a maximum value at σ_θ 15.5, which is the level where oxygen drops below 10 μM . Under this maximum, nitrate values decrease due to reduction (denitrification), i.e. nitrate is used as an electron acceptor instead of oxygen. The nitrate reaches zero concentration at $\sigma_\theta \approx 16.0$. The nitrite profile shows a rather weak maximum just below the zone of denitrification, as would be expected, since nitrite is an intermediate product in the process of denitrification. The phosphate profile is affected by scavenging by $\text{MnO}_{2(s)}$ and $\text{FeOOH}_{(s)}$. For a more detailed discussion on the distribution of nutrients in the suboxic zone in the Black Sea, see Murray et al. (1995).

3.3. Halocarbons

The results of the halocarbon compounds are plotted versus density in Fig. 3. They are presented with all five offshore stations superimposed upon each other. The plots in Fig. 3 have one thing in common; the halocarbons show relatively high surface concentrations which decrease with depth to below the detection limit in the anoxic zone.

Tetrachloromethane is depleted from the water column at a shallower level than any of the other halocarbons. This can be explained by the differences in redox potentials (see Table 2) between the compounds, CCl_4 having the higher redox potential and therefore being reduced more readily. When CCl_4 is reduced, the first reduction product is CHCl_3 . Fig. 3a and b shows that the CHCl_3 concentration has a maximum at σ_θ 15.5, which is where CCl_4 has decreased to levels below 1 pM, i.e. $\sim 10\%$ of its highest level close to the surface. This apparent relation between CCl_4 and CHCl_3 is illustrated in Fig. 4, which shows the two halocarbons plotted versus density at one of the stations (L40L50). The increase in concentration of CHCl_3 between σ_θ 14.2 and 15.7 is of the same order of magnitude as the decrease of CCl_4 . A simple explanation would be that a large portion of CCl_4 is reduced to CHCl_3 ,

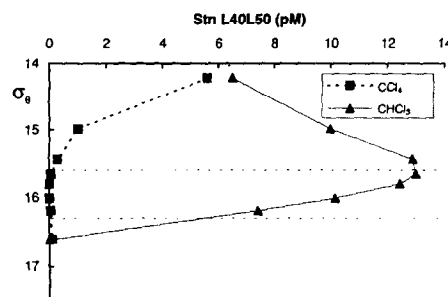


Fig. 4. Tetrachloromethane (CCl_4) and trichloromethane (CHCl_3) at one of the stations, L40L50, versus density.

and that CHCl_3 is an intermediate product in the reduction of CCl_4 in the marine system. Similar observations have been made in the Baltic Sea (S. Klick, E. Fogelqvist and T. Tanhua, unpublished results). At depth, where the oxygen concentration drops below 10 μM , CHCl_3 is further reduced and subsequently removed from the system.

Similar correlations for other reduction reactants and products than CCl_4 and CHCl_3 could, however, not be established. This is in part due to analytical difficulties, e.g. for the redox couples CH_3CCl_3 to CH_3CHCl_2 (sensitivity problems) and CHCl_3 to CH_2Cl_2 (contamination problems), and partly due to large differences in concentrations, e.g. CH_2Br_2 is a factor ten higher in concentration than the possible precursor CHBr_2Cl .

One cannot neglect other processes that may cause the observed increase in CHCl_3 : e.g., in situ production by planktonic algae, the possible effect from production by macroalgae living along the coasts (Nightingale et al., 1995), or hydrolysis of larger halogenated molecules through the so-called haloform reaction. It is also important to keep in mind that the main source of CCl_4 is in the atmosphere, and that a decrease in concentration towards depth can be expected even without any removal mechanism involved. However, as we are investigating the transformations in an environment with a dramatic gradient of increasingly reducing conditions with depth, it is reasonable to assume that the effects that are so obviously correlated with this gradient could be explained by redox reactions. Degradation by ammonia-oxidizing bacteria as described by Vannelli et al. (1990) would have reduced the halocarbon concentrations in the oxic water layers, where nitrifi-

cation occurs, but this was not observed. In fact, none of the investigated halocarbons were removed to any extent in the zone of nitrification, except CCl_4 , which was not degraded in the study described by Vannelli et al. (1990).

The decrease in halocarbons over the redoxcline might also be a result of other chemical processes, the most plausible of which would be hydrolysis. A decrease in the concentration of a halocarbon to less than 1% of its initial value would take ~ 7 times the half-life of the reaction. Jeffers et al. (1989) measured the rates of hydrolysis at various pH and temperature conditions, and claim that the hydrolysis rate is not a pH-dependent but a strictly temperature-dependent first-order reaction. CCl_4 would have a half-life of ~ 1000 yr under the conditions that are considered typical for the suboxic zone. The half-life of CHCl_3 would be considerably longer (Mabey and Mill, 1978). The residence time

of the deep water in the Black Sea is estimated to 2000 yr (Östlund and Dyrssen, 1986), so hydrolysis alone is not fast enough to explain the steep gradient over the redoxcline. However, some of the brominated halocarbons might have half-lives which are shorter than 100 yr under the same conditions, and hydrolysis may therefore have an impact on the decrease of those compounds.

The rates of the reduction are difficult to estimate, as they are dependent on the electron donors available and eventual catalysis by enzymes like cytochrome P450. However, they are positively correlated with the redox potentials by the Marcus relation. In other words, the reduction rates for CCl_4 , CH_3CCl_3 and CHCl_3 decrease in the same order as the redox potentials. Results from an investigation of reduction of halocarbons catalysed by iron porphyrins at neutral pH conditions (Klecka and Gonsoir, 1984) gives pseudo-first-order reduction half-

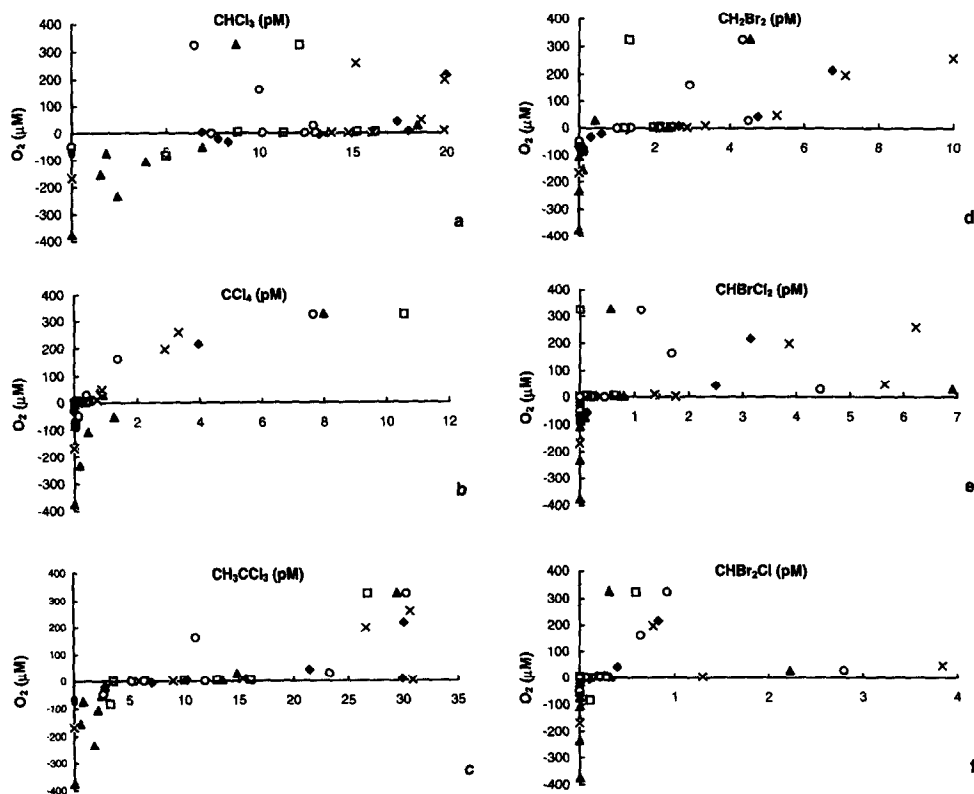


Fig. 5. Halocarbon concentrations versus oxygen concentration at five stations superimposed upon each other. The stations are marked with different symbols (\diamond = L40L20; \blacktriangle = M00L20; \times = M00L50; \circ = L40L50; \square = L30L50). A negative oxygen concentration denotes the presence of hydrogen sulphide (calculated on a molar basis, see text).

lives for the same compounds of 9 min, 12 days and 420 days, respectively. This is orders of magnitude shorter than the half-lives of hydrolysis.

The concentrations of all six halocarbons in Fig. 3 decrease as the water becomes more reducing. We have already discussed the fact that CCl_4 is depleted higher up in the water column than any of the other halocarbons. This is even more apparent in Fig. 5, where the halocarbon concentrations are plotted versus oxygen/hydrogen sulphide concentrations. CCl_4 shows a significant decrease already at fairly high oxygen concentrations (20–30% left at 200 μM O_2). For the other halocarbons there is a dramatic decrease in concentration at zero oxygen concentration. This is important, since it will restrict the use of CCl_4 as a conservative tracer of ocean circulation, not only in anoxic waters, but also in oxygen-depleted waters such as oxygen minima that occur around 1000-m depth in the ocean.

Fig. 6 gives an indication of where in the water column the halocarbons are depleted. The redox potentials for the one electron reduction reaction of the halocarbons are plotted versus the density where the halocarbon concentration has decreased to $\frac{1}{10}$ of its maximum concentration, as a measure of the depth where depletion of halocarbons occur. A correlation in this plot would indicate that, in fact, reduction is the main mechanism for removal of halocar-

bons in the Black Sea. Two of the halocarbons (CHBrCl_2 and CHBr_2Cl) appear twice in Table 2 since two reduction products are possible. Consequently, the reactions have different redox potentials, of which only the higher is plotted. The reduction of NO_3^- is complicated by the fact that so many different oxidation states are possible for N. The fact that NO_3^- is depleted at shallower depths than the halocarbons is in accordance with reduction of NO_3^- to N_2 , which has a high redox potential ($E = 0.65$ V; Murray et al., 1995). There seems to be a correlation between the “depletion depth” and redox potential, which supports the conclusion drawn, that reduction is the dominating breakdown mechanism in suboxic/anoxic waters.

The concentrations of the brominated halocarbons CH_2Br_2 , CHBrCl_2 and CHBr_2Cl displayed in Fig. 3 are comparatively low close to the surface ($\sigma_\theta < 14.5$) followed by a layer of high concentration. It is possible that there is a source at a subsurface layer due to algal production, or a loss by evaporation through the surface. Deeper down the concentrations decrease through the suboxic and into the anoxic zone, where the concentrations are below the limit of detection. It seems reasonable to draw the same conclusion as for CCl_4 , CHCl_3 and CH_3CCl_3 , i.e. that these compounds are removed by means of reduction. However, as mentioned above, the rates of

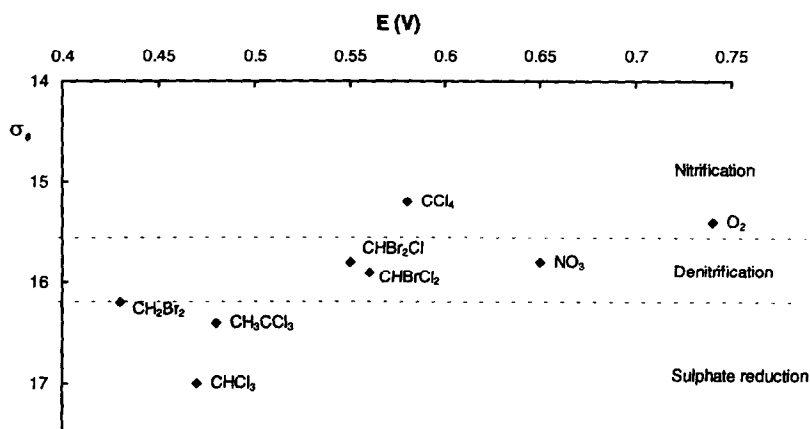


Fig. 6. Redox potentials of the halocarbons versus the “depletion depth”, which is the density surface where the halocarbon concentration drops to less than 10% of its maximum value. The redox potentials are adjusted to the conditions considered typical for the suboxic zone (see text). The values for reduction of NO_3^- to N_2 and O_2 to H_2O are also shown for comparison. The broken lines divide the water column into three significant different redox regimes; the zones of nitrification, denitrification and sulphate reduction.

hydrolysis might be high enough to constitute an alternative breakdown mechanism for brominated halocarbons.

From the distribution of halocarbons presented in this study, it is not possible to draw any conclusions whether the observed reduction of halocarbons are bacteria-mediated processes or pure chemical transformations, nor is it possible to ascribe any particular reducing agent as the active one. It is likely that a variety of reducing agents are active and probably emanate from organic matter sinking through the water column. In the Black Sea, there is a substantial flux of particulate organic matter (POM) from the photic zone and a remineralisation in the upper 100 m of the water column (Karl and Knauer, 1991). Decaying organic matter is furthermore likely to contain free iron porphyrins (as well as a number of other electron carriers available in living systems) available for catalysing the reduction of halocarbons. A number of other transition metal complexes including cobalt, chromium and nickel complexes, may also be involved in the reduction of halocarbons in a similar way.

Not only are the transition metal complexes active in reduction, but the free transition metal ions are also. Results reported by Klecka and Gonsoir (1984) indicate that free Fe(II) ions enhance the reductive dehalogenation of carbon tetrachloride to chloroform in aqueous solution, although at a slower rate than the transformation with iron porphyrins present. In the Black Sea, there is a concentration maximum of Mn, Fe and Co at the oxic–anoxic interface (Haraldsson and Westerlund, 1988), where these compounds are cycled between their reduced, soluble state and their oxidised, insoluble state and concentrated. It is possible that free Mn(II), Fe(II) and Co(II) could play an important role in the reduction of halocarbons in the marine environment.

4. Final remarks

Halocarbons, such as CCl_4 and CH_3CCl_3 , are used as presumably conservative tracers for oceanic studies of large-scale mixing processes. The fact that halogenated halocarbons are so easily reduced in oxygen-depleted environments, not necessarily completely oxygen free, is a cause for concern when

CCl_4 and CH_3CCl_3 are used as tracers. In fact, this study indicates that CCl_4 might be reduced in seawater already at an oxygen concentration of 200 μM . These results are in accordance with previous findings of unexpectedly low CCl_4 concentrations in oxygen-depleted waters (Krysell et al., 1994). Reduction might be the unexpected sink for CCl_4 in the South Atlantic Ocean observed by Wallace et al. (1994).

Whatever mechanism is responsible for the breakdown of halocarbons in the marine environment, the extremely low concentrations (pM ranges) imply that the reactions have very little impact on the system as a whole (metal speciation, nutrient distribution, etc.), but is significant only for the halocarbon chemistry itself. Our conclusion that halocarbons are readily reduced in a natural system with low oxygen concentration points to a possibly important sink for organohalogens.

Acknowledgements

This work was sponsored by the Swedish Natural Science Research Council (NFR), the Turkish Scientific and Technical Research Council (TUBITAK), the Swedish Institute (SI) and the Adlerbert Research Foundation. We would like to give special thanks to Kubilay Yilmaz for assistance with halocarbon measurements. We wish to thank anonymous reviewers for helpful comments on the manuscript. The authors further wish to thank the captain and crew of R/V “Bilim” and technical staff of METU-IMS for generous support during the cruise.

References

- Bastürk, Ö., Saydam, C., Salihoglu, I., Eremeeva, L.V., Konovalov, S.K., Stoyanov, A., Dimitrov, A., Cociasu, A., Dorogan, L. and Altabet, M., 1994. Vertical variations in the principle chemical properties of the Black Sea in the autumn of 1991. *Mar. Chem.*, 45: 149–165.
- Butler, J.H., Elkins, J.W., Thompson, T.M., Hall, B.D., Swanson, T.H. and Koropalov, V., 1991. Oceanic consumption of CH_3CCl_3 : Implications for tropospheric OH. *J. Geophys. Res.*, 96(D12): 22347–22355.
- Carritt, D.E. and Carpenter, J.H., 1966. Comparison and evaluation of currently employed modifications of the Winkler

- method for determining dissolved oxygen in sea water; a NASCO report. *J. Mar. Res.*, 24: 286–318.
- Codispoti, L.A., Friederich, G.E., Murray, J.W. and Sakamoto, C.M., 1991. Chemical variability in the Black Sea: implications of continuous vertical profiles that penetrated the oxic/anoxic interface. *Deep-Sea Res.*, 38(Suppl. 2): S691–S710.
- Collén, J., Ekdahl, A., Abrahamsson, K. and Pedersén, M., 1994. The involvement of hydrogen peroxide in the production of volatile halogenated compounds by *Meristella gelidium*. *Phytochemistry*, 36(5): 1197–1202.
- Curtis, G.P. and Reinhard, M., 1994. Reductive dehalogenation of hexachloroethane, carbon tetrachloride, and bromoform by atrahydroquinone disulfonate and humic acid. *Environ. Sci. Technol.*, 28: 2393–2401.
- Eberson, L., 1987. *Electron Transfer in Organic Chemistry*. Springer, Berlin, 233 pp.
- Fogelqvist, E. and Tanhua, T., 1995. Iodinated C₁–C₄ hydrocarbons released from ice algae in Antarctica. In: A. Grimvall and E.W.B. de Leer (Editors), *Naturally Produced Organohalogenes*. Kluwer, Dordrecht, pp. 295–305.
- Fogelqvist, E., Tanhua, T., Salihoglu, I. and Bastürk, Ö., 1996. The distribution of some man-made and naturally produced halocarbons in a double layer flow strait system. *Cont. Shelf Res.*, 16: 1185–1199.
- Fonselius, S., 1969. Hydrography of the Baltic deep basins, III. *Fish. Board Sweden, Ser. Hydrogr., Rep. No. 23*.
- Fonselius, S., 1983. Determination of hydrogen sulphide. In: K. Grasshof, M. Ehrhardt and K. Kremling (Editors), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, pp. 73–80.
- Gschwend, P.M., MacFarlane, J.K. and Newman, K.A., 1985. Volatile halogenated organic compounds released to seawater from temperate marine macroalgae. *Science*, 277: 1033–1035.
- Handbook of Chemistry and Physics, 67th Edition, 1986–1987. CRC Press, Boca Raton, FL, pp. D151–D158.
- Haraldsson, C. and Westerlund, S., 1988. Trace metals in the water columns of the Black Sea and Framvaren Fjord. *Mar. Chem.*, 23: 417–424.
- Jeffers, P.M., Wared, L.M., Woytowich L.M. and Wolfe, N.L., 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes, and propenes. *Environ. Sci. Technol.*, 23: 965–969.
- Karl, D.M. and Knauer, G.A., 1991. Microbial production and particle flux in the upper 350 m of the Black Sea. *Deep-Sea Res.*, 38(2): S921–S942.
- Klecka, G.M. and Gonsoir, S.J., 1984. Reductive dechlorination of chlorinated methanes and ethanes by reduced iron(II) porphyrins. *Chemosphere*, 13(3): 391–402.
- Klick, S., 1993. The release of volatile halocarbons to seawater by untreated and heavy metal exposed samples of the brown seaweed *Fucus vesiculosus*. *Mar. Chem.*, 42: 211–221.
- Kriegman-King, M.R. and Reinhard, M., 1994. Transformation of carbon tetrachloride by pyrite in aqueous solution. *Environ. Sci. Technol.*, 28: 692–700.
- Krystell, M. and Nightingale, P.D., 1994. Low molecular weight halocarbons in the Humber and Rhine estuaries determined using a new purge-and-trap gas chromatographic method. *Cont. Shelf Res.*, 14(12): 1311–1329.
- Krystell, M., Fogelqvist, E. and Tanhua, T., 1994. Apparent removal of the transient tracer carbon tetrachloride from anoxic seawater. *Geophys. Res. Lett.*, 21(23): 2511–2514.
- Little, C.D., Palumbo, A.V., Herbes, S.E., Lidstrom, M.E., Tyn-dall, R.L., Gilmer, P.J., 1988. Trichloroethylene biodegradation by a methane-oxidizing bacterium. *Appl. Environ. Microbiol.*, 54(4): 951–956.
- Lovley, D.R. and Woodward, J.C., 1992. Consumption of Freons CFC-11 and CFC-12 by anaerobic sediment and soils. *Environ. Sci. Technol.*, 26: 925–929.
- Lovley, D.R., Chapelle, F.H. and Wodward, J.C., 1994. Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Environ. Sci. Technol.*, 28: 1205–1210.
- Mabey, W. and Mill, T., 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. *J. Phys. Chem. Ref. Data*, 7(2): 383–415.
- Manley, S.L., Goodwin, K. and North, W.J., 1992. Laboratory production of bromoform, methylene bromide, and methyl iodide by macroalgae and distribution in nearshore southern California waters. *Limnol. Oceanogr.*, 37(8): 1652–1659.
- Murray, J.W., Codispoti, L.A. and Friedrich, G.E., 1995. Oxidation–reduction environments: The suboxic zone in the Black Sea. In: C.P. Huang, C.R. O'Melia and J.J. Morgan (Editors), *Aquatic Chemistry*. Adv. Chem. Ser., Am. Chem. Soc., 244: 157.
- Nightingale, P.D., Malin, G. and Liss, P.S., 1995. Production of chloroform and other low molecular weight halocarbons by some species of macroalgae. *Limnol. Oceanogr.*, 40(4): 680–689.
- Östlund, G.H. and Dyrssen, D., 1986. Renewal rates of the Black Sea Deep Water — Report on the chemistry of seawater, XXXIII. *Dep. Anal. Mar. Chem., Göteborg Univ., Göteborg*.
- Özsoy, E., Ünlüata, Ü. and Top, Z., 1993. The evolution of Mediterranean water in the Black Sea: interior mixing and material transport by double diffusive intrusions. *Prog. Oceanogr.*, 31: 275–320.
- Prinn, R.G., Weiss, R.F., Miller, B.R., Huang, J., Alyea, F.N., Cunnold, D.M., Fraser, P.J., Hartley, D.M. and Simmonds, P.G., 1995. Atmospheric trends and lifetime of CH₃CCl₃ and global OH concentrations. *Science*, 269: 187–192.
- Semprini, L., Hopkins, P.L., McCarty, P.L. and Roberts, P.V., 1992. In-situ transformation of carbon tetrachloride and other halogenated compounds resulting from biostimulation under anoxic conditions. *Environ. Sci. Technol.*, 26: 2454–2461.
- Sturges, W.T., Cota, G.F. and Buckely, P.T., 1992. Bromoform emission from Arctic ice algae. *Nature (London)*, 358: 660–662.
- Tokarczyk, R. and Moore, R.M., 1994. Production of volatile organohalogenes by marine phytoplankton. *Geophys. Res. Lett.*, 21(4): 285–288.
- Tratnyek, P.G., Hoigné, J., Zeyer, J. and Schwarzenbach, R.,

1991. QSAR analysis of oxidation and reduction rates of environmental organic pollutants in model systems. *Sci. Total Environ.*, 109/110: 327–341.
- Vannelli, T., Logan, M., Arciero, D.M. and Hooper, A.B., 1990. Degradation of halogenated aliphatic compounds by the ammonia-oxidizing bacterium *Nitrosomonas europaea*. *Appl. Environ. Microbiol.*, 56(4): 1169–1171.
- Vogel, T.M., Criddle, C.S. and McCarty P.L., 1987. Transformation of halogenated aliphatic compounds. *Environ. Sci. Technol.*, 21: 722–736.
- Wallace, D.W.R., Beining, P. and Putzka, A., 1994. Carbon tetrachloride and chlorofluorocarbons in the South Atlantic Ocean, 19°S. *J. Geophys. Res.*, 99(C4): 7803–7819.
- Waller, C.L. and McKinney, J.D., 1993. Theoretical investigation into the potential of halogenated methanes to undergo reductive metabolism. *J. Comput. Chem.*, 14(12): 1575–1579.