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Volatile halogenated organic compounds in European estuaries

OLIVER CHRISTOF, RICHARD SEIFERT & WALTER MICHAELIS*
*Institut für Biogeochemie und Meereschemie, Zentrum für Meeres – und Klimaforschung, Universität Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany (*Author for correspondence, e-mail: michaelis@geowiss.uni-hamburg.de)*

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Abstract. Sources, sinks, and distribution patterns of volatile halogenated organic compounds (VHOC) in estuaries were investigated during 5 cruises within the BIOGEST programme. Due to their chemical and physical properties (e.g. toxicity, persistence, mobility) these compounds are of considerable environmental concern. A wide range of compounds has been identified and quantified generally ranging from 0.1 ng l^{-1} to 350 ng l^{-1}. In some samples extraordinarily high values up to 4700 ng l^{-1} were observed indicating contribution from anthropogenic sources. Generally, concentrations of halogenated compounds of anthropogenic origin dominated those of prevalent natural origin. Data of selected VHOC are presented in relation to salinity, particular organic carbon, and total suspended matter. Furthermore the observed concentrations are compared with established water quality regulations. Distribution patterns of VHOC along the estuary indicated common sources for specific halogenated compounds. Decreasing concentrations of most VHOC along the estuary confirm that degassing to the atmosphere and dilution with sea water are the dominating processes controlling the fate of these compounds in estuaries.

Introduction

Volatile halogenated organic compounds (VHOC) are ubiquitous pollutants in the environment. They receive significant attention within the fields of biogeochemistry, analytical chemistry, biochemistry, remediation engineering, and atmospheric chemistry. Since many of these halogenated compounds show acute and chronic toxicity, genotoxity or carcinogenicity (Wellhörner 1990) their emissions have caused wide concern and frequently triggered a ban of their use. Moreover, almost all of these compounds are of relevance in processes related to climate changes and are suspected to contribute to the destruction of the ozone layer. Particularly bromine, on a per atom basis, is believed to be 50 times more effective as chlorine in ozone destruction (WMO 1999). Under the Montreal Protocol (Montreal

Protocol, 1987 and further increments) several of the VHOC are listed as ozone depletion substances and their phase-out is already achieved (chlorofluoromethanes) or will be executed during the next years (bromomethane in 2005). The European Union has set even stricter regulations for several compounds e.g. the use of bromomethane which is banned since 2001.

Furthermore, nearly all of these compounds are regulated under European directives for surface- and groundwater (EEC/76/464). In addition, numerous national and international authorities provided their own guidelines. For large rivers like the Rhine or the Elbe monitoring agencies have been established. These activities led to a strong decrease of VHOC concentrations in these rivers during the last decade (ICPR 1993; ARGE 1999).

Because of their chemical and physical properties, VHOC are widely distributed and can be found in many different compartments in the environment (groundwater, surface water, soil etc.). Their origin can be divided into natural and anthropogenic sources. Anthropogenic VHOC arise from their use in various chemical processes (solvents, intermediates etc.), in chlorination of water for different purposes (Mills et al. 1998), and as fumigants (Yates et al. 1998). For an update of quantities of VHOC produced and released by the industry see Fetzner (1998) and UNEP, Ozone Secretariat (1999). Naturally produced VHOC have a wide range of sources and so far 3570 halogenated organic compounds have been detected (Gribble 2001). Observed source include: fungi, different marine algae (Geschwend et al. 1985; Ekdahl et al. 1998), higher plants (Harper 2000), volcanic emissions (Jordan et al. 2000), soils (Keppler et al. 2000) as well as biomass burning (Lobert et al. 1999) and halogen exchange reactions (Class & Ballschmiter 1988). Organisms are thought to use these compounds in chemical defence and as feeding deterrents (Hay 1992; Gribble 1994). However, some VHOC have natural as well as anthropogenic sources e.g. tribromomethane, trichloromethane and trichloroethene (Abrahamsson et al. 1995; Nightingale et al. 1995). Even compounds like trichlorofluoromethane which were thought to be of exclusively anthropogenic origin were observed in volcanic emissions (Jordan et al. 2000).

In addition to their use in industry, agriculture and households, VHOC have been used as tracers of water movement (Fogelqvist et al. 1982; Krysell 1991) and for characterisation of water masses. Main targets in VHOC research are (I) investigation of the emissions from biological and anthropogenic sources and their contribution to global budgets (Lobert et al. 1999), (II) degradation and transformation in different environmental media via bacteria, oxidation and reduction (Fetzner 1998), (III) possibilities for the reduction of pesticide emissions from agriculture areas (Yates et al. 1998) and (IV) their relevance in atmospheric chemistry (WMO 1999).

Different methods for determinations of halocarbons in water have been applied since the first report on these compounds in marine air and water by Lovelock et al. (1973) including extraction by organic solvents (Fogelqvist 1985), direct head-space analysis (Mehran et al. 1986) and purge-and-trap techniques (Krysell & Nightingale 1994) whereby the latter is now commonly applied. Electron Capture Detector (ECD) and mass spectrometry (MS) are used for detection and identification. For a detailed comparison of applied methods see Dewulf and Van Langenhove (1997).

Estuaries are among the most complex and dynamic systems in the environment. They are objects to intense shipping and mostly accommodate huge cities and industrial sites. Additionally, they represent a unique environmental region, with a high biological activity which can act as source and/or sink for different compounds. They are subject to diverse processes – tidal effects, mixing, particle interaction, various inputs of natural and anthropogenic sources – and thus of particular scientific and environmental interest regarding the concentration, distribution and dynamics of VHOC. Although there have been investigations in estuaries regarding VHOC (Dewulf & Van Langenhove 1997 and references therein, Dewulf et al. 1998; Miermanns et al. 2001) generally these studies are focussing on the outer estuary (salinity ranges from 30 to 35). Only a few investigations (e.g. Dyrssen et al. 1990; Van Zoest & Van Eck 1991) cover the whole salinity gradient.

Here we present VHOC data from 5 cruises within the BIOGEST project. We report on an analytical system developed by our laboratory, the concentration range and composition, anthropogenic and natural sources and transformation processes of VHOC in these European estuaries.

Method

An analytical set up for the determination of VHOC based on a purge-and trap method, followed by thermodesorption, cryofocussing, and GC/MS was constructed and adopted to the analytical requirements.

Prior to analysis all glassware, including the sample flask, was washed with distilled water, rinsed with acetone, and heated at 220 °C for 3 hrs. Water samples were obtained with a Niskin sampler and transferred into Duran glass bottles, which were completely filled and sealed with Teflon caps to avoid any headspace. Samples were stored in cool and dark until purging which was performed generally within 12 hours after their recovery. Tests showed that the concentrations of the target compounds were not significantly affected during this time of storage. Trichloromethane-d was added as an internal standard before sealing. The water samples were not filtered in order to obtain total concentrations of the target compounds including any VHOC adsorbed onto particular matter. Generally, duplicate samples were analysed.

After inserting the bottle into the purge-and-trap, the volume was adjusted to 550 ml and then the samples were purged with Helium at a flow rate of 75 ml min^{-1} for 30 min at 55 °C in an ultrasonic water bath. The stripped compounds were trapped on glass tubes (159 mm × 6 mm, Chrompack) filled with 120 mg Tenax TA (mesh 20/35, Chrompack) and cooled to –40 °C via CO_2. After purging the tubes were sealed with 1/8" brass end caps with Teflon ferrules and stored at –40 °C until further analysis. Test runs with standards of different concentrations showed no loss, changes in structure or contamination during 10 months of storage. Tenax tubes were conditioned at 250 °C with a constant flow of Helium (100 ml min^{-1} 3 hrs) and the Teflon ferrules were heated at 250 °C for 3 hrs to avoid contamination of the sorption tubes (Dewulf et al. 1998). Water was removed from the stripping gas stream by a system of water traps – a condenser (kept at 1 °C) followed by a Nafion dryer (length 1 m, i.d. 2 mm, Permapure Inc.) and a glass tube filled with magnesium perchlorate ($Mg(ClO_4)_2$) – between the sample and the Tenax tubes. It is mentioned in several publications, that water traps like $Mg(ClO_4)_2$ can cause chromatographic problems, discriminate compounds or produce artefacts (Dewulf et al. 1996; Dewulf & Van Langenhove 1997; Urhan & Ballschmiter 1998). Diverse tests gave evidence that our water traps worked properly and did not effect the quantifications or disturbed the performance on the GC/MS.

Trapped VHOC are released by a thermodesorption system fitted on a GC. The direction of the gas flow is controlled by a 8-port electronic Valco valve which is placed between the thermodesorption unit (TD) and cryo trap (CT). The Valco valve is held isothermally at 180 °C to prevent any condensation. The Tenax tube is fixed in the TD which is connected to the Valco valve by a stainless 1/16" capillary and is heated to 190 °C for desorption of the sample compounds. The CT consists of a 50 μl tube filled with 4 mg Tenax TA (mesh 60/80, Chrompack). It is fitted to a thermoelement measuring desorption and trap temperatures (220 °C and –40 °C). Temperatures are established by a heating wire and a CO_2 cooling device, respectively. A coating brass liner links the CT unit to the Valco valve and the capillary column. An electronic control unit manages the time of desorption and injection as well as the temperature for trapping and desorption of the CT.

Separation and detection was performed by gas chromatography (GC 8060, Fisons Instruments) coupled with mass spectrometry (MD 800, Fisons Instruments). Instrumental parameters of the mass spectrometer were: mass range 33–300 amu, scan mode: EI, scan speed: 0.7 s/scan, ionisation energy 70 eV, interface temperature 250 °C, source temperature 200 °C. A GasPro^{TM}

Table 1. Composition of the standard solution with one internal standard (IS): retention time (RT), quantification masses (m/z), purge efficiency (PE), limit of detection (LOD), CAS-number, boiling point (Bp). The numbers in front of the compounds refer to the peak number given in Figure 2

No	VHOC	RT [min]	quantification mass [m/z]	PE [%]	LOD [ng l^{-1}]	Bp [°C]	CAS number
2	chloromethane	11.9	50	91.2	0.083	–24	74-87-3
8	dichloromethane	18.9	49	80.6	0.081	40	75-09-2
12	trichloromethane	21.5	83	93.1	0.093	61	67-66-3
14	tetrachloromethane	21.9	117	96.0	0.091	77	56-23-5
7	chloroethane	18.1	64	94.2	0.110	12	75-00-3
15	1.1-dichloroethane	23.1	63	88.6	0.097	57.3	75-34-4
21	1.2-dichloroethane	27.1	62	79.8	0.115	84	107-06-2
18	1.1.1-trichloroethane	25.0	97	95.3	0.112	74	71-56-6
23	1.1.2-trichloroethane	30.1	97	78.1	0.260	114	79-00-5
3	chloroethane	12.5	62	95.2	0.100	–13.9	75-01-4
6	1.1-dichloroethene	16.9	61	95.6	0.120	37	75-35-4
9	*trans*-1.2-dichloroethene	19.0	61	92.4	0.095	47.5	156-60-5
11	*cis*-1.2-dichloroethene	21.3	61	81.6	0.093	60	156-9-2
16	trichloroethene	23.6	130	90.6	0.100	87	79-01-6
20	tetrachloroethene	26.6	166	93.5	0.099	121	127-18-4
4	bromomethane	14.7	94	87.9	0.150	3.6	74-83-9
17	dibromomethane	24.7	174	80.2	0.260	97	74-95-3
24	tribromomethane	31.4	173	77.3	0.210	149.5	75-25-2
10	bromochloromethane	19.8	49	76.3	0.230	68	74-97-5
19	bromodichloromethane	25.3	83	76.8	0.180	90.1	75-27-4
22	dibromochloromethane	28.3	127	79.3	0.163	119	124-48-1
1	dichlorodifluoromethane	9.5	85	97.8	0.075	–29.8	75-71-8
5	trichlorofluoromethane	15.6	101	97.8	0.076	23.7	75-69-4
13	trichloromethane-d	21.6	84	82.7	0.096	60.9	865-49-6

GSC capillary column (length 30 m, i.d. 0.32 mm, J&W Scientific) was used with a Helium carrier gas pressure of 67 kPa. The GC oven was held for 10 min at 40 °C, heated at a rate of 6 °C min^{-1} to 220 °C, held isothermally for 10 min, heated at a rate of 25 °C min^{-1} to 240 °C, and held isothermally for 10 min.

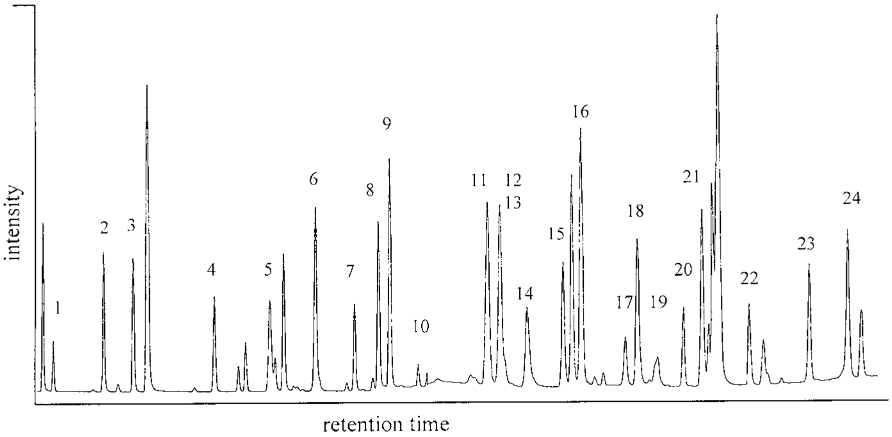

Figure 1. Total ion chromatogram of the standard solution. The numbers above the peaks refer to the compound names given Table 1.

A standard mixture for the determination of retention time (RT), purge efficiency (PE), response factors, limit of detection (LOD), and reproducibility was prepared at different concentration levels in analytical grade methanol (Merck). In addition 20 single compounds were used to guarantee the correct identification of the VHOC. The standards were injected into degassed water, which had been purged free from VHOC, and analysed analogous to real samples. The PE was found to vary between 76.3% and 97.8% ($n = 8$). The reproducibility test for all VHOC investigated gave standard deviations below 8% and detection limits varied between 0.08 ng l^{-1} and 0.26 ng l^{-1}. Quantification was attained against internal standard (trichloromethane-d) and compound identification was achieved by comparison of retention times and mass spectra. For each parameter the different standard concentrations were tested at least 8 times. Blank tests on the system did not show any detectable contamination. Analytical parameters are summarised in Table 1; a total ion chromatogram (TIC) of a standard solution is presented in Figure 1.

For direct measurements at sampling sites the GC is equipped with a ECD/FID-Tandem, allowing identification and quantification of the VHOC without the MS. The analytical system also provides the possibility for the injection of air samples by a sample loop.

Results

Samples were taken during 5 cruises within the BIOGEST project: Rhine (November 1997), Scheldt (May & October 1998), Loire (September 1998) and Thames (February 1999). During the 5 cruises more than 50 distinct VHOC have been identified. The 23 most abundant compounds are listed in Table 1. For discussion they were classified in groups due to their chemical structure (Table 2).

Concentration versus salinity

The observed VHOC concentrations along the investigated estuaries are highly variable but can nevertheless be classified into three general distribution pattern types (Figure 2). For types 1 and 2, the mixing of riverine water with seawater is the main factor determining the concentration of VHOC along the salinity gradient. Type 1 represents a dilution of VHOC enriched river water with sea water, while type 2 represents the reverse, i.e. an increase of the concentration along the estuary with increasing salinity. Type 1 can further be divided into sources originating: (a) in the upper part (salinity 0 to 5) and (b) in the middle part (salinity 5 to 25) of the estuaries. For both type classes we found deviations from the linear relation expected if only dilution was the main process. This can be attributed to (I) degassing to the atmosphere and (II) additional sources/point entries (Dyrssen et al. 1990; Krysell & Nightingale 1994). Type 3 distribution patterns show no dependence on salinity, but can also reveal point entries.

The marked compounds given in Table 2 will be discussed in detail due to their abundance and relevance in the environment as well as for human health. Additionally, these VHOC are representatives originating from various sources in the estuaries (e.g. power plants, harbour, ships, city, algae and other natural sources). The observed concentrations were compared with the water quality regulations given by the EU and other authorities (Table 3).

Chlorinated methanes

Chloromethane concentrations in the Scheldt showed no general distribution pattern. While in October a source in the upper and in the middle part of the estuary occurred no dependence on salinity was observed in May (type 3). Chloromethane in the Loire and Thames represents an increase along the salinity gradient (type 2), suggesting a marine source. In all cases chloromethane and bromomethane show corresponding distribution pattern along the estuaries, whereby chloromethane is the dominating compound. Although no correlation with nutrients and chlorophyll a was found a natural

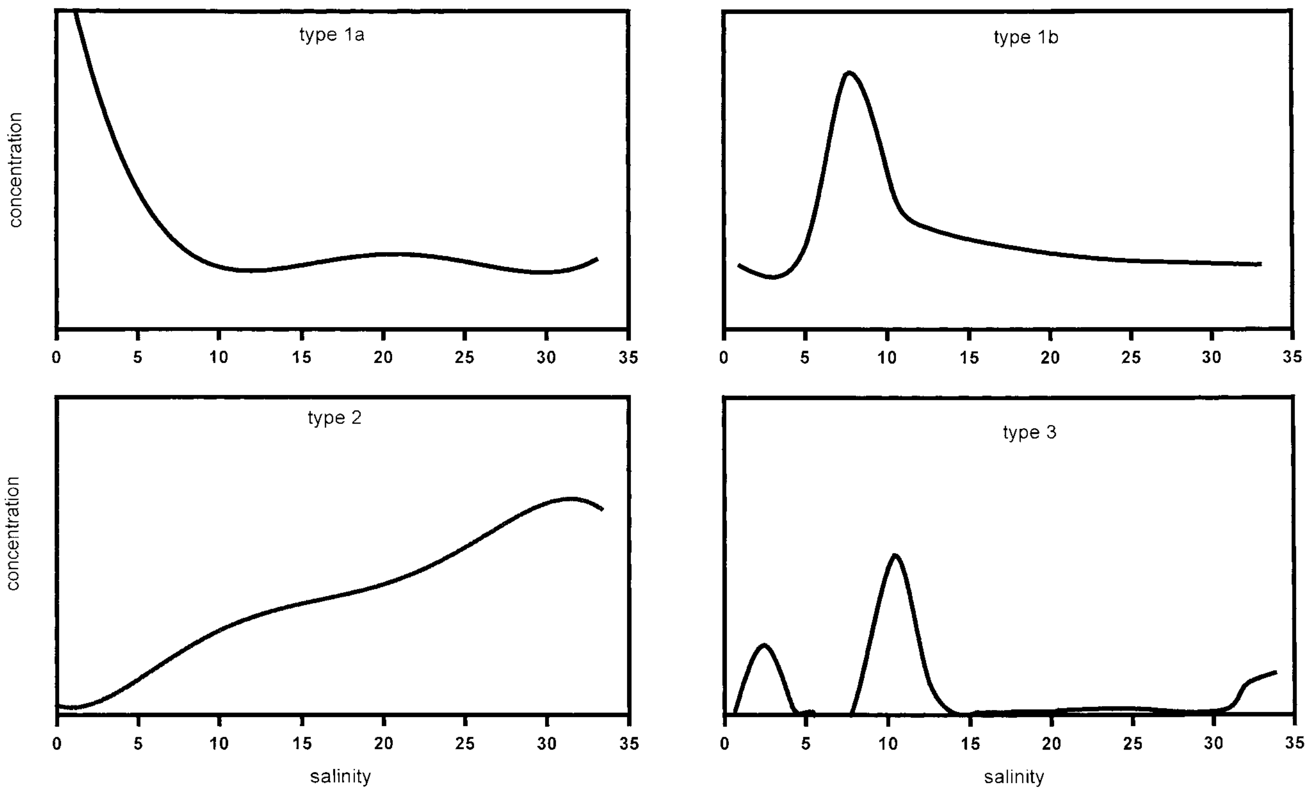

Figure 2. VHOC concentration versus salinity along the estuary.

Table 2. Concentrations ranges (ng l^{-1}) of selected VHOC in the estuaries of the Scheldt (May and October), Thames, Loire and Rhine

	Scheldt (May 1998) (*n* = 15)	Scheldt (Oct. 1998) (*n* = 14)	Thames (Feb. 1999) (*n* = 15)	Loire (Sep. 1998) (*n* = 14)	Rhine (Nov. 1997) (*n* = 15)
chloromethane	**2.2–5.5**	**3.4–111.7**	**7.6–63.9**	**2.2–83.2**	**0.6–9.4**
dichloromethane	0.3–2924	1.4–156.3	7.3–161.3	1.7–46.7	6.6–4976.8
trichloromethane	**6.2–356**	**5.4–2921**	**2.0–120.2**	**2.0–35.8**	**14–104.1**
tetrachloromethane	bdl–1.8	1.6–71.6	0.9–30.2	bdl–2.2	bdl–8.5
chloroethane	0.1–2.1	0.3–8.3	bdl–4.3	0.1–10.1	bdl–1.3
1,1-dichloroethane	0.1–7.2	0.1–13.7	bdl–13.1	bdl–5.7	bdl–1.9
1,2-dichloroethane	**0.1–145.1**	**0.5–91.3**	**1.1–7.0**	**1.5–28**	**0.9–101.2**
1,1,1-trichloroethane	**0.1–11.6**	**0.5–16.8**	**2.3–47.8**	**bdl–34.4**	**bdl–11.8**
1,1,2-trichloroethane	bdl–16.6	bdl–16.2	bdl	bdl	bdl–2.2
chloroethene	0.3–7.9	0.2–36.3	0.4–7.4	1.2–4.9	0.1–5.8
1,1-dichloroethene	bdl–1.7	0.1–4.0	0.2–6.4	bdl–4.4	bdl–0.6
trans-1,2-dichloroethene	bdl–1.4	bdl–2.6	bdl–3.8	bdl	bdl–0.2
cis-1,2-dichloroethene	0.1–24.8	0.2–67.2	0.1–79.0	bdl–14.6	bdl–22.6
trichloroethene	**0.1–78.5**	**1.0–169.3**	**2.2–101.2**	**0.3–42.6**	**bdl–39.8**
tetrachloroethene	**0.1–93.2**	**0.4–90.5**	**0.7–208.2**	**0.1–1199.7**	**bdl–19.3**
bromomethane	**0.5–1.9**	**0.3–10.4**	**0.6–5.7**	**1.1–15.8**	**bdl–2.3**
dibromomethane	**8.0–137.7**	**7.0–126.5**	**bdl–4.8**	**bdl–47.7**	**bdl–8.1**
tribromomethane	**18.7–156.1**	**7.9–235.4**	**bdl–13.6**	**bdl–49.6**	**bdl–91.5**
bromochloromethane	0.2–5.7	bdl–0.2	0.2–5.2	bdl–1.2	bdl–0.6
bromodichloromethane	**0.2–54.8**	**0.2–6.2**	**1.5–34.5**	**0.2–7.1**	**bdl–10.1**
dibromochloromethane	**1.1–36.3**	**0.2–22.7**	**bdl–39.0**	**bdl–7.7**	**bdl–9.8**
dichlorodifluoromethane	**bdl–23.5**	**bdl–3.8**	**1.4–9.8**	**bdl–6.1**	**bdl–7.2**
trichlorofluoromethane	**bdl–1.2**	**bdl–5.5**	**0.9–8.7**	**0.1–5.9**	**0.1–910**

bdl = below detection limit, *n* = number of samples.

origin is most likely, because no anthropogenic source was identified and chloromethane is known to be emitted from natural sources (Harper et al. 2000). Rhew et al. (2000) also report strong correlation between emissions of bromomethane and chloromethane in salt-marshes and suggest that these gases emanate from similar, most probably natural, processes. Furthermore, recent investigations, summarised by Butler (2000), suggest that only 1%

Figure 3. Investigated European estuaries within the EU project 'Biogas transfer in estuaries'.

of the chloromethane in the troposphere can be assigned to anthropogenic activities.

Trichloromethane is one of the main by-products of water chlorination and an ubiquitously used solvent but is also produced by certain marine algae. Our results indicate for trichloromethane sources in the low salinity range (<10) of all investigated estuaries. Two deviations from the general trend were observed: (I) a pronounced point source (2921.2 ng l^{-1}) at salinity 32 in the Scheldt in May. As no correlation with nutrients and chlorophyll a was observed, this increase is most probably attributed to an anthropogenic input, as intense shipping was observed during sampling. (II) trichloromethane and all other trihalomethane concentrations are increased at salinity 12 in the Loire (up to 36 ng l^{-1}) clearly indicating water chlorination to be the source of this point entry. The sample was taken nearby an industrial site.

Apart from the point entry in the Scheldt (May) concentrations exceeding the water quality regulations were observed for dichloromethane during the Scheldt cruise in May (2924 ng l^{-1}) and Rhine (4796.8 ng l^{-1}).

Table 3. Comparison of international water quality requirements for selected VHOC in μg l^{-1} (after Rippen 1996; Irmer et al. 1997 and references therein)

VHOC	LAWA[a]		ICPR[b]	EU[a+b]	USA[a+b]		WHO[a+b]
	(A)	(T)	(T)	(T)	(A)	(T+F)	(T)
dichloromethane	10	1		10			20
trichloromethane	0.8	1	0.6	40	1240	0.19	30
tetrachloromethane	7	3	1	10		0.4	2
1,2-dichloroethane	2	1	1	3	20000	0.94	30
1,1,1-trichloroethane	100	1	1				2000
trichloroethene	20	1	1	70	21900	2.7	30–70
tetrachloroethene	40	1	1	80	840	0.8	10–40
tribromomethane						8.5–80	100
bromodichloromethane				15		0.16–16	
dibromochloromethane				25		0.8–80	
Σ trihalomethanes		100		100		80	200

(T): drinking water supply, (A): aquaticecology, (F): professional finish,
LAWA: Länder Arbeits Gemeinschaft Wasser, ICPR: International Commission for the Protection of the Rhine,
[a]Rippen 1996, [b]Irmer et al. 1997.

Chlorinated ethanes

1,2-Dichloroethane is a widely used solvent and synthesis intermediate in the industry. It is set under strict water quality regulations. During both Scheldt cruises a decrease of concentrations with increasing salinity was observed (type 1a), while in the other estuaries low concentrations and no dependence on salinity was noticed.

Till the phase-out of the chlorofluoromethanes 1,1,1-trichloroethane was used as educt in the production for theses compounds. During our investigations 1,1,1-trichloroethane was detected strictly below the given limits (Table 3). The highest concentrations were observed in the Thames (47.8 ng l^{-1}). Our results indicate a riverine source with decreasing concentrations at increasing salinity for all investigated estuaries (type 1a). Recent investigations by Montzka et al. (1999) claimed that the influence of this compound on the total atmospheric chlorine load has now peaked and will decline in the next five to ten years. For both Scheldt cruises the correlation coefficient between these chlorinated ethanes suggest a common source.

Chlorinated ethenes

Trichloroethene and tetrachloroethene are among the most common pollutants in ground- and surface-waters (Abelson 1990; Butler & Hayes 1999).

Even though natural sources (e.g. algae) have been reported for these compounds in the marine environment (Abrahamsson et al. 1995; Quack & Suess 1999; Dimmer et al. 2001) no natural production is to be expected in the lower salinity range. Trichloroethene and tetrachloroethene were among the quantitative dominating compounds in all investigated estuaries and exhibit a type 1a distribution pattern. In some cases additional point entries were found, whereby tetrachloroethene concentrations (1199.7 ng l^{-1}) exceeded the given limits in the Loire.

Brominated methanes

Tribromomethane can originate from chlorination of water and from natural production. The abundance of trihalomethanes by the chlorination of water depends on sunlight, temperature, the residual chlorine input, type of organic matter and salinity (Galapate et al. 1999; Kuivinen & Johnsson 1999). Seasonal variations in biological emissions from marine biomass for VHOC, including tribromomethane, have been reported by Klick (1992). Constantly high concentrations for tribromomethane (up to 357 ng l^{-1}) were found during both Scheldt sampling campaigns at intermediate salinities (type 1b), nearby an industrial site. Due to these results and similar distribution patterns with dibromochloromethane the most likely source is chlorination of water. The distribution pattern for tribromomethane in the Loire shows a source at high salinity (25–27). Although no correlation with chlorophyll a and nutrients was observed its biological emission can not be excluded.

Dibromomethane showed a similar distribution pattern as tribromomethane. Remarkable are the high concentrations (up to 137 ng l^{-1}) at low salinity (10–12) during both Scheldt cruises. Krysell & Nightingale (1994) also found higher concentration in the low salinity range and assumed a biogenic source because no anthropogenic input for dibromomethane could be identified. Due to the similar distribution with tribromomethane an anthropogenic source is most likely.

Bromochloromethanes

Dibromochloromethane and bromodichloromethane originate as by-products in water chlorination (Kuivinen & Johnsson 1999) and from emissions of different algae (Nightingale et al. 1995). Because of their potential health risk their concentration in surface water is regulated. They showed low concentrations and similar distribution patterns as tribromomethane and trichloromethane during our sampling campaign.

Chlorofluoromethanes

Trichlorofluoromethane has widely been used as coolant till its phase – out in 1997 (Montreal Protocol 1987). It is the basis for the calculation of the ozone depletion potential (WMO 1999). Despite the regulations it is still in use in different processes. Any concentration in the surface water would be a definite hint for an anthropogenic input. The observed concentrations are generally lower than 2 ng l^{-1} even though an extremely high concentration was found in the Rhine (910 ng l^{-1}). Obviously, this compound is still released into the environment and might be present in the atmosphere even longer than predicted (WMO 1999). The detected concentrations during all cruises did not show any dependence on salinity and are typical examples for type 3.

Dichlorodifluoromethane, today used as replacement for trichlorofluoromethane, showed similar behaviour and concentration ranges as trichlorofluoromethane. Only during the Scheldt cruise in May one local entry (23.5 ng l^{-1}) emerged. Comparison with other parameters did not show any correlation.

Discussion

A correlation of VHOC with total suspended matter (TSM) and particulate organic matter (POC) provides information about adsorption processes. Our results indicate no correlation with TSM and POC and therefore adsorption on particulate material can be regarded as being an unimportant process in the investigated estuaries. Other investigations in estuaries (Dyrssen et al. 1990; Dewulf et al. 1996; Roose et al. 2001) showed similar results. The low sorption can be expected because of the low K_{ow} (octanol-water coefficient) values of most of the VHOC (Dewulf et al. 1996). Nevertheless, as illustrated by Duinker et al. (1982) an increasing number of halogen atoms in the water also increases the adsorption to particles, as well as the partition coefficient. For this reason it is important to analyse unfiltered water to obtain the total concentration of the VHOC. Furthermore, high correlation coefficients of VHOC with chlorophyll a hint to natural sources but this was not observed for the investigated estuaries. High anthropogenic inputs may conceal the natural production. Moreover, natural production of VHOC depends also on sunlight, salinity and algae species and shows diurnal variations (Manley et al. 1992; Ekdahl et al. 1998). Therefore, a lack in correlation with chlorophyll a does not exclude existing natural sources for the VHOC investigated.

Common sources of different compounds can be identified by determining the respective correlation coefficients (Krysell & Nightingale 1994).

Table 4. Correlation coefficients between selected VHOC

VHOC	Scheldt May 1998	Scheldt Oct. 1998	Thames Feb. 1999	Loire Sep. 1999	Rhine Nov. 1997
tribromomethane vs. dibromomethane	0.49	**0.92**	**0.78**	0.55	**0.84**
tribromomethane vs. bromodichloromethane	0.08	0.34	0.50	0.01	0.03
tribromomethane vs. dibromochloromethane	**0.66**	**0.91**	**0.62**	0.02	0.21
tribromomethane vs. bromochloromethane	0.01	0.05	0.53	0.07	0.11
tribromomethane vs. bromomethane	0.25	0.29	0.23	0.35	0.02
tribromomethane vs. trichloromethane	0.10	0.38	0.59	0.22	0.01
dibromomethane vs. bromomethane	0.10	0.12	0.16	0.08	0.01
dibromomethane vs. bromodichloromethane	**0.68**	0.41	0.61	0.37	0.01
dibromomethane vs. dibromochloromethane	0.30	**0.89**	**0.72**	0.43	0.20
chloromethane vs. bromomethane	0.15	**0.79**	**0.87**	**0.91**	0.33
bromodichloromethane vs. dibromochloromethane	0.03	0.56	**0.85**	**0.84**	0.02
trichloromethane vs. chloromethane	0.25	0.18	0.59	**0.70**	0.05
trichloromethane vs. bromodichlloromethane	0.15	**0.88**	**0.80**	0.47	**0.86**
trichloromethane vs. dibromochloromethane	0.46	0.55	**0.95**	0.29	0.02
tetrachloroethane vs. trichloroethene	**0.94**	**0.89**	**0.87**	**0.94**	0.02
trichloroethene vs. 1,2-dichloroethane	**0.92**	**0.87**	0.22	0.34	0.10
tetrachloroethene vs. 1,2-dichloroethane	**0.97**	**0.85**	0.44	0.50	0.46
trichloroethene vs. 1,1,1-trichloroethane	**0.74**	**0.98**	**0.98**	0.01	0.04
tetrachloroethene vs. 1,1,1-trichloroethane	**0.89**	**0.89**	**0.79**	0.01	0.05

The results in Table 4 indicate common sources for trichloroethene and tetrachloroethene in all investigated estuaries, except for the Rhine. For both Scheldt cruises common sources for 1,2-dichloroethane and 1,1,1-trichloroethane were identified. Correlation coefficients for chloromethane and bromomethane in the Thames (0.87) and Loire (0.91) underline the already proposed common, most possibly natural, source. The correlation coefficient for tribromomethane and dibromochloromethane for the Scheldt cruises supports the suggestion of chlorination of water as an anthropogenic source. Of course a combination of man-made and natural sources will reduce the correlation between the compounds (Krysell & Nightingale 1994).

Conclusion

During 5 cruises within the BIOGEST project 50 VHOC have been identified and quantified. The applied analytical set-up showed low detection limits and a high reproducibility for a wide range of the analysed compounds. Trichloroethene, tetrachloroethene, dichloromethane, trichloromethane, and, for the Scheldt, dibromomethane and tribromomethane were the quantitative dominating compounds. Generally, anthropogenic inputs were the main sources for VHOC in the investigated estuaries and correlation of several compounds indicated common anthropogenic sources. In four cases water quality regulations were exceeded. The concentrations of most VHOC show a decrease along the estuary. The results indicate that dilution and degassing to the atmosphere are the dominant processes. However, some compounds revealed an increase with increasing salinity suggesting a natural release even though no definite evidence for this kind of production could be identified.

Further investigations e.g. regarding seasonal variations of VHOC should be conducted to gain insight into processes of formation and degradation of VHOC in estuaries and their general impact on the ocean and the atmosphere. A promising tool for these investigations could be the determination of the isotopic values of the VHOC.

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