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Review

State-of-the-art of gas chromatography-based methods for analysis of anthropogenic volatile organic compounds in estuarine waters, illustrated with the river Scheldt as an example

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Abstract

This review focuses on a number of key procedural steps in the analysis of volatile organic compounds (VOCs) in estuarine waters. The most critical step, from an analytical point of view, is sample preparation. So far, only purge-and-trap and, to some extent, membrane inlet mass spectrometry have successfully been applied in estuarine monitoring of VOCs. The advantages and disadvantages of both techniques are discussed and novel developments are reviewed. Other key elements in VOC analysis and assessment include quality assurance (QA), quality control (QC) and statistical data analysis. This paper gives a brief overview of QA/QC measures of interest in the estuarine monitoring exercise, and provides guidelines for adequate statistical treatment of environmental data. Finally, field measurements of VOCs in estuarine waters are reviewed. Concentrations are reported, and distribution patterns, sources and time-trends are discussed. In addition to literature data, results of a 3-year monitoring survey (May 1998–November 2000) in the Scheldt estuary are presented.

Keywords: Reviews; Water analysis; Sample preparation; Scheldt estuary; Environmental analysis; Volatile organic compounds; Chlorinated hydrocarbons; Monocyclic aromatic hydrocarbons; Chlorinated monocyclic aromatic hydrocarbons

Contents

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1. Introduction

Estuaries are transitions between fluvial and marine environments, and are among the most complex and dynamic ecosystems on earth. They are often subject to intense anthropogenic pressure from nutrients, heavy metals and organic contaminants, and constitute a significant transport route for pollutants from catchment area to coast. The occurrence and spatial-temporal variability of environmental hazards in estuaries have received considerable attention over the past decade. Broadly-based monitoring surveys have improved our understanding of the processes affecting the fate of contaminants in the estuarine environment, and allowed to quantify the in- and output of pollutants in order to assess the impact of river discharges on coastal systems.

Volatile organic compounds (VOCs) constitute up to 10% of total dissolved organic carbon (DOC) in relatively non-polluted waters, and usually represent a greater proportion in estuaries due to pollution [1]. Some of these compounds are of major environmental concern, even at low concentrations, due to their fate and eco-toxicological effects. They feature prominently within several listings of hazardous substances for the marine environment. Short-chain chlorinated hydrocarbons (CHCs), monocyclic aromatic hydrocarbons (MAHs), and chlorinated monocyclic aromatic hydrocarbons (CMAHs) have been classified as "priority" and "priority toxic" pollutants at the 3rd International Conference for the Protection of the North Sea [2]. Recently, several CHCs, MAHs, and CMAHs were proposed by the ICES (International Council for the Exploration of the Sea) Marine Chemistry Working Group for inclusion in the EU Water Framework Directive 2000/60/EC [3], and some CMAHs were listed by the OSPAR (Oslo and Paris) Commission as Chemicals for Priority Action [4].

This paper gives an overview of the literature on recent developments in VOC analysis of estuarine waters. Focus is placed on VOCs listed as priority pollutants for the marine environment, e.g. CHCs, MAHs and CMAHs. The manuscript starts with an overview of key procedural steps in VOC monitoring, from sampling to data assessment, with specific emphasis on sample preparation. Next, field measurements of 27 priority VOCs in estuaries are reported. In addition to literature data, results of a 3-year monitoring survey (May 1998–November 2000) in the Scheldt estuary are presented. This work is a follow-up of an earlier review by Dewulf and Van Langenhove [5] on this subject, and covers the period between 1997 and the present. Significant references that appeared before 1997 have been included if they were not highlighted in Ref. [5].

2. State-of-the-art of VOC analysis in estuarine waters

2.1. General aspects

The analysis and assessment of volatile organic micro-pollutants in estuarine waters involve several distinctive steps as depicted in Fig. 1.

Traditionally, VOC measurements are accomplished by discrete sampling of the water body followed by analysis at the laboratory. Sample preservation is essential to minimize changes during transportation and storage, and to assure the integrity of data. To prevent analyte loss due to volatilization

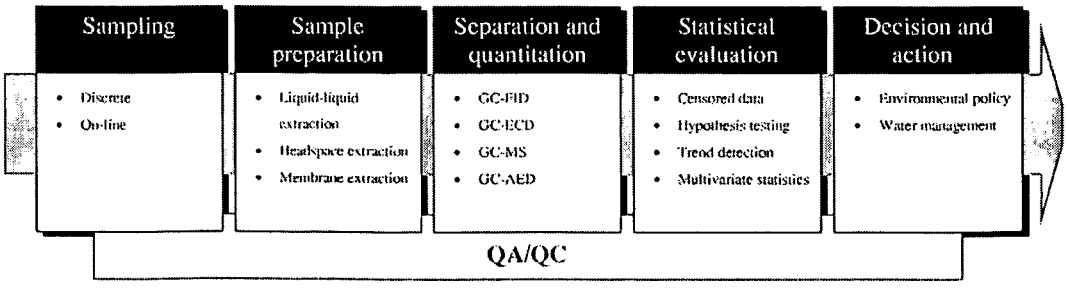

Fig. 1. Steps in estuarine monitoring of VOCs.

or photochemical breakdown, amber glass containers are filled completely without headspace. Refrigeration and pH lowering decrease the rate of chemical and microbial degradation. To alleviate this concern, a significant trend in analytical chemistry is away from the use of laboratory methods and instrumentation, towards in situ, real-time measurements. On-line techniques overcome most of the problems associated with discrete sampling, sample preservation, transportation, storage and sample handling, and enable continuous monitoring of VOCs.

Sample preparation is an important step in the trace analysis of volatile organic pollutants in marine and estuarine waters. Due to the low concentrations, typically ng l^{-1}, analyte enrichment is necessary to obtain low detection limits, and matrix components disturbing the instrumental analysis must be removed. Direct aqueous injection has been attempted, but since the injection volume is limited to a few microliters, it is applicable only to the analysis of samples with high concentrations of volatiles [6,7].

Analyte separation and quantitative determination are usually accomplished by gas chromatography (GC) followed by flame ionization (FID), electron-capture (ECD) or mass spectrometric (MS) detection. Atomic emission detection (AED) has been reported in Refs. [8,9]. Current trends and developments in GC analysis of VOCs have recently been reviewed by Dewulf et al. [10].

Statistical data analysis facilitates the interpretation of field measurements, and provides essential tools to improve our understanding of underlying environmental processes. Unfortunately, statistical methods are often misused, and yield erroneous interpretations instead. Most statistical tests of interest in environmental studies tend to be parametric, premised on the assumption of normally distributed data. They can still be used if the distribution is not normal but can be transformed to normal form. This requires that the underlying distribution is accurately known. Environmental data sets are usually skewed and the lognormal distribution, which is a simple transform of a normal distribution, is commonly employed to fit the data. However, the validity of the lognormal distribution is often questionable, as stated by Reimann and Filzmoser [11]. They have shown that geochemical and environmental data sets, as a rule, are neither normally nor lognormally distributed. Nevertheless, it has become standard practice to ln-transform environmental data prior to statistical analysis. Lack of lognormality is for the most part due to the presence of outliers. Outliers—that is, samples with unusually high concentrations—originate from a population other than the major body of data, and are a matter of course in environmental analysis. One could remove these outlying values and fit the remaining data set to a lognormal or normal distribution. The problem is then how to define outliers—which values should be removed and which should still be included in the calculations? Furthermore, outliers are often interesting results and should not simply be discarded. Since many common statistical methods rely on the basic assumption of (log)normality, their use on non-(log-)normally distributed data sets may lead to faulty or biased results. Other model assumptions, e.g. Weibull, gamma or logit, have been suggested, but as for the lognormal distribution none of them adequately describe environmental data. Non-parametric or robust statistical methods should generally be preferred [11]. Non-parametric methods do not make any assumption about the underlying data distribution, while robust methods are not influenced by outliers. Factor analysis (FA), for instance, is extremely popular in marine and environmental studies. It is routinely used to reduce the dimensionality of a data set while keeping most of the information, and find (hidden) structures or relationships between the different variables. The FA procedure is based on the decomposition of the sample covariance or correlation matrix, and is strongly affected by non-normally distributed data and the presence of outliers. An elegant way to reduce the impact of outlying observations is to apply robust FA. In 1985, Rousseeuw [12] introduced the minimum covariance determinant (MCD) estimator to compute a robust location vector and scatter matrix. Robust FA down-weights the effect of outliers on parameter estimation, and provides a more reliable picture of the majority of the data. MCD-FA has already been successfully applied in geochemical and environmental studies, and has been shown to outperform standard or "classical" FA [13,14].

Statistical processing of environmental data becomes even more tricky if values below the detection limit are present. These so-called "censored" mea-

surements greatly complicate analysis of data. Standard calculation methods fail as only part of the data points are numerically known, while the other fraction is only known to occur within a restricted range of values. Despite the use of sensitive analytical methods, trace level determinations of VOCs in marine waters are often plagued by censored data. Censored data sets can still be a valuable source of information, provided that adequate statistical methods are used. The estimation of summary statistics, for instance, is well documented [15–18]. Huybrechts et al. [16] evaluated several methods to estimate the mean, standard deviation (SD), median and interquartile range (IQR) from censored environmental data sets, using uncensored VOCs from monitoring surveys in the North Sea and Scheldt estuary. The performance of each method was assessed by artificially censoring each uncensored data set, and estimating moments and quantiles at each censoring level. In line with previous considerations, results showed that methods with the least distributional assumptions performed best. The robust bias-corrected restricted maximum likelihood (BRML) method enabled estimation of moments and quantiles up to 80% of censoring with low (5–10%) bias. Similarly, hypothesis testing [19], trend detection [20], and multivariate analysis [21,22] have been shown to yield reliable results up to a certain degree of censoring.

Results of monitoring surveys will eventually be used as a basis for national and international policies. Since inaccurate data may have severe economic and social implications, quality assessment is of paramount importance. Strict quality assurance (QA) and quality control (QC) measures are required to ensure that high quality results are generated in the laboratory. The QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) program provides guidelines to install appropriate QA/QC measures in all steps of the marine monitoring exercise [23]. According to QUASIMEME, QA measures should include field blanks to determine the extent of contamination and/or analyte loss during sampling. Field blanks encompass the contribution of sample container and sampling device to the overall analytical uncertainty. Spiking of samples with known amounts of recovery standards or surrogates enables losses during transportation and storage to be identified. Standard additions and reference materials (RMs) should be analyzed with each batch of samples to continuously assess the analytical performance. Certified RMs are generally preferred over "in-house" laboratory RMs. However, in common with other organic determinants, there are currently no aqueous RMs available which are certified for VOCs. The analytical data for RMs should also be plotted on analytical quality control charts (AQCCs). AQCCs allow the assessment of long-term precision and accuracy, and have been referred to as the heart of a QA/QC program. They provide a graphical way to monitor the method's output and instrumental performance, and enable to detect in time when the analytical method is out of control. Proficiency tests are an additional source of quality control information in support of co-operative monitoring data, and allow a comparable assessment of data quality over a large number of monitoring laboratories. QUASIMEME provides laboratory performance studies (LPS) for a wide range of environmental determinants and marine matrices. Unfortunately, the number of VOCs covered by these inter-laboratory exercises is rather limited. The LPS on volatile organochlorines in seawater includes only six CHCs. Another three VOCs, i.e. trichlorobenzenes, are covered by the LPS on chlorinated pesticides. In addition, the concentrations are of the order of those found in groundwater and drinking water instead of those commonly observed in the marine environment.

From an analytical point of view, sample preparation is the most critical step within the process scheme exemplified in Fig. 1. The following section provides an overview of sample preparation methods commonly used in VOC analysis of water samples. Only techniques that have already been used in marine or estuarine VOC monitoring are considered for further discussion.

2.2. Sample preparation

In spite of several drawbacks, solvent extraction has long been the method of choice for VOC analysis in marine waters [24,25]. However, current challenges in the context of "green" analytical chemistry favor the use of "solvent-free" sample preparation methods. Static headspace extraction and solid-phase

micro extraction (SPME) comply with this requirement, but fall short on trace level analysis of VOCs due to lack of concentrating power. Even so, SPME enables rapid and selective enrichment of organic compounds from aqueous samples. Analytes are sorbed from the headspace or directly from the aqueous phase onto a polymer-coated fiber. The solutes are then thermally desorbed, on-column, in a GC-injector. The most popular coating is polydimethylsiloxane (PDMS). PDMS extracts a broad range of non-polar analytes, and offers superior performance over other polymers. Yet, the small amount of PDMS, typically less than 0.5 μl, limits the applicability of SPME, resulting in low extraction efficiencies for volatiles with low $K_{o/w}$ values ($K_{o/w}$ = octanol–water partition coefficient). Baltussen and co-workers [26] described a new and improved technique of sorptive extraction, known as stir bar sorptive enrichment (SBSE). A stir bar coated with 55–219 μl of PDMS is introduced into an aqueous sample, and extraction takes place during stirring. The stir bar is then removed from the sample, and transferred to a thermal desorption unit to release the analytes into a GC. The higher amount of sorbent allows quantitative extraction at much lower $K_{o/w}$ compared with SPME. Measurements of VOCs in marine waters by SBSE have, to our knowledge, not yet been reported. In contrast, dynamic headspace extraction has gained widespread acceptance and use in marine pollution studies [1,27–35]. The method is highly sensitive and provides reproducible quantitative data. Next to it, membrane extraction is a fast-growing technique for VOC analysis in aqueous samples, and is less cumbersome and time-consuming than dynamic headspace techniques. Membranes with a direct connection to a mass spectrometer have already been successfully applied for on-line and real-time monitoring of VOCs in marine waters [36].

2.2.1. Dynamic headspace techniques

In the dynamic headspace method commonly known as purge-and-trap, VOCs are stripped from water samples by a continuous flow of an inert gas through [1,27–35,37], or above [38,39] the liquid phase. Following the extraction, the volatiles are focused on a sorbent cartridge or a cryotrap. The analytes are then released by thermal desorption and transferred to the GC-column. If sorbent sampling is used, an additional cryogenic refocusing zone is necessary prior to injection in order to obtain sharp chromatographic peaks. The recent application of sorbent micro-traps eliminates the need for cryogenic cooling at the head of the column. Flash heating provides narrow chromatographic peaks as well as high resolution [29,37–39].

Because of its low detection limits and high precision, the purge-and-trap method has emerged as the leading technique for VOC analysis in marine waters [1,27–35]. Purge-and-trap provides reliable data but is time-consuming and labor intensive, particularly when many samples are involved. In addition, it requires complex instrumentation. Hence, purge-and-trap is a priori not a technique with on-line and real-time monitoring capability. On-site measurements have nevertheless been accomplished. An on-line sampling system connected through a purge-and-trap injector to a GC–FID for automatic sampling and analysis of VOCs in the river Meuse (the Netherlands) has been reported by Miermans et al. [34]. Similarly, shipboard analysis of VOCs in seawater by purge-and-trap coupled to a GC–MS enabled on-site measurements of unstable analytes [29]. Christof et al. [31] used a GC equipped with an ECD/FID tandem for direct on-site measurements of halogenated VOCs in estuaries.

Another major drawback of dynamic headspace methods is the high amount of water vapor generated at the purge stage, and the chromatographic problems associated with it. Excess water vapor causes peak distortion and plugging of the cryotrap. Water removal has been carried out using hygroscopic membranes (Nafion), cryotrapping, adsorbent trapping, desiccants or a dry purge stage [40,41].

To allow a higher sample throughput, Leonard et al. [42] used a high-speed gas extraction device interfaced to a commercial cryofocusing inlet system for high-speed gas chromatography. Samples were purged at elevated temperatures and high flow-rates. Exhaustive extraction of BTEX was achieved in a few seconds at an extraction temperature of 90 °C. A reflux condenser was used to minimize water vapor interference. Baykut and Voigt [43] introduced spray-and-trap as an alternative to purge-and-trap. Here, the aqueous sample is gradually pumped through a special spray nozzle into a recipient vessel,

generating a cone of tiny liquid droplets. A low-speed carrier gas flows through the chamber, and acts as a mobile extractor phase. Upon this, analytes are transferred to a sorbent or cryotrap. Spray extraction accelerates gas/liquid partitioning, and offers a continuous analyte flux of constant concentration for optimum trapping conditions. Hence, analysis of halocarbons, BTEX and chlorobenzenes was accomplished within a few minutes at low ng l^{-1} concentrations. Matz and Kesners [44] constructed a simple portable spray-and-trap device with enhanced extraction efficiencies for field use with a mobile GC–MS. In 1997, Lee et al. [45] evaluated purge-and-trap and spray extraction combined with GC–MS and GC–MS–MS for the determination of organochlorine compounds in water. Both methods were convenient for the detection of chlorinated volatiles at low to mid ng l^{-1}. Pulsed spray extraction, however, was capable of monitoring aqueous systems containing surfactants. St-Germain et al. [46] coupled a spray extraction chamber through a helium jet separator directly to an ion trap MS. The inertial spray extraction mass spectrometry interface provided a quick, simple, and reproducible way to analyze VOCs in small volumes of aqueous solutions. A spray extraction system compatible with high-speed gas chromatography was developed by Borgerding and co-workers [47–49]. Quantitative extraction of VOCs at low to mid μg l^{-1} concentrations was accomplished within seconds. Yet, detection limits were too high to enable marine applications of the method.

2.2.2. Membrane inlet mass spectrometry

Membrane extraction enables rapid, simple and solvent-free sample preparation, and is suitable for continuous on-site and on-line monitoring of VOCs in natural waters. Analytes diffuse from the sample matrix through a membrane and are transferred to a chromatographic or mass spectrometric system. Non-porous silicone membranes are preferentially used as the interface between the sample, and stripping gas or vacuum. They allow selective transport of volatile non-polar compounds while keeping water from entering the analytical instrument.

In membrane inlet mass spectrometry (MIMS) solutes permeate directly into the ion source of a mass spectrometer, without chromatographic separation. The membrane inlet system acts both as a sample enrichment and sample introduction device for the MS. Total analysis takes only a few minutes. Hence, unlike purge-and-trap, MIMS allows a high sample throughput, and enables real-time sampling and monitoring of organic compounds in the environment.

In 1993, Harland and Nicholson [36] carried out continuous measurements of chlorinated aliphatics and aromatics at low to mid μg l^{-1} in several British estuaries. The ability to analyze VOCs in seawater matrices was also demonstrated by Bauer and Solyom [50] and Kasthurikrishnan and Cooks [51]. Their allegations, however, relied upon spiked natural water samples instead of real-sample monitoring.

Field measurements of VOCs in marine or estuarine waters have not been reported since [36]. Clearly, in spite of the many advantages over conventional analytical methods such as purge-and-trap, membrane extraction has not yet gained widespread acceptance and usage in marine environmental research.

For one thing, MIMS lacks the sensitivity required in trace and ultra-trace level analysis. Detection limits within a few ng l^{-1} are necessary to adequately measure VOCs in marine waters. Several instrumental upgrades have been reported to lower detection limits from μg l^{-1} to ng l^{-1}. So far, they have only been tested on spiked water samples in the laboratory. Detection of toluene and *trans*-1,2-dichloroethene in water at pg l^{-1} has been achieved by Soni et al. [52] with ion-trap MIMS analysis and applying the stored wave form inverse Fourier transform (SWIFT) method. Trapping was carried out in the course of ionization at relatively long periods of time via selective ejection of all but the analyte ions. Mendes and co-workers [53] inserted a liquid nitrogen trap between the membrane module and the ion source of the mass spectrometer. Detection limits of 10–20 ng l^{-1} were obtained for BTEX and several halocarbons, while 1–2 μg l^{-1} was observed by conventional MIMS. Similarly, Bocchini et al. [54] used a cryofocusing trap based on Tenax adsorption and a Peltier cell to detect trace amounts of organohalogens, e.g. chloroform (8 ng l^{-1}), in water.

Even if detection limits enable quantitative measurements, results may still be jeopardized owing to

MIMS' poor specificity. Since MIMS does not involve chromatography, the resultant mass spectrum is a composite of spectra of all components in the pervaporate. That is, reliable quantification is not possible for isomers or compounds with overlapping mass fragments. Even if measurements are made in the selected ion monitoring (SIM) mode, there is still the possibility to make false assignments. The difficulty of distinguishing between two analytes with the same fragment ions was overcome in a number of ways. Ojala et al. [55] and Kostiainen et al. [56] used the chemometric Solver program as a tool to quantify individual compounds from a mixture mass spectrum. Chang and Her [57] combined rapid chromatographic separation with mass spectrometric detection. A cryofocusing unit and a short GC-column (5 m) were placed between the membrane and the ion source. Discrimination between chloroform and bromodichloromethane in chlorinated drinking water was made possible without losing the on-line monitoring characteristics of MIMS. Ouyang et al. [58] used liquid chromatographic (LC) separation of volatile compounds prior to membrane extraction. Quantification of LC/MIMS is based on two-dimensional identification (retention time and m/z) and provides a tangible approach to the analysis of complex aqueous samples. Furthermore, the dynamic response of silicone membranes was dramatically improved by the addition of an organic co-solvent in the aqueous mobile phase.

3. Field measurements: a literature overview

Concentrations of priority VOCs in estuarine waters, reported in the literature since 1997, are summarized in Tables 1 and 2. Tabulated compounds are analytes targeted in our own research work [30].

From 1993 to 1995, Yamamoto et al. [35] surveyed the levels and distributions of 55 VOCs listed in US EPA method 524.2 within the urban rivers and estuaries of Osaka, an industrialized city of Japan. Several CHCs, MAHs and CMAHs were detected at concentrations ranging from 0.1 to 100 $\mu g\ l^{-1}$ or even more. Exact concentrations were not reported in the manuscript, and are therefore not included in Tables 1 and 2. The analytes present in the estuary and its tributaries resulted from nearby industrial activities. Some of these compounds were used as solvents or intermediates in chemical processing, or as metal cleaning agent. Domestic discharges and sewage effluents were an additional source of volatile organics. Diurnal variations of chloroform, for instance, showed a good correlation with anionic surfactant concentrations and COD (chemical oxygen demand) levels.

The presence and spatial distribution of VOCs in the Southampton Water estuary were studied in 1995 by Bianchi and Varney [1] to reassess measurement results of a first sampling program carried out in 1987/88. Over 100 individual compounds were routinely found in estuarine waters during both surveys. Volatile organohalogens were ubiquitous. The main compounds were dichloromethane, chloroform, 1,1,1-trichloroethane, tetrachloromethane, trichloroethene and tetrachloroethene. According to the authors, these compounds had been among the most widely used in British industry for over 30 years. Their uses and applications ranged from, e.g. degreasing agents, propellants, and solvents to fumigants and dyestuffs. The 1995 data for volatile organohalogens indicated an increase in concentrations over the 1987/88 data, mainly brought about by an apparent increase in the concentrations of chloroform, trichloroethene and tetrachloroethene. This was counteracted by an apparent decrease in concentrations of tetrachloromethane and 1,1,1-trichloroethane, probably as a result of phase-out agreements under the Montreal Protocol. Over 30 volatile aromatic compounds were also identified, predominated by benzene, toluene, and C_2-alkylbenzenes. C_2-alkylbenzenes were invariably present at approximate relative ratios of about 1.4:1.0:3.5:1.9 (ethylbenzene/*p*-xylene/*m*-xylene/*o*-xylene). These ratios are typical of those found in the volatilized fraction of gasolines, light fuels and distillates used in industrial, domestic and marine fuels. A number of industrial operations were also associated with inputs. No significant differences were found between the chronological periods 1987/88 and 1995.

Air/water exchange dynamics of 13 CHCs and MAHs were investigated over a 95 km long section of the Scheldt estuary, between Vlissingen and Antwerp, by Dewulf and co-workers [32,33]. Results showed that a substantial fraction of emitted amounts

Table 1
Concentrations of priority VOCs (CHCs) in estuaries (ng l^{-1})

Location	Year	CHCs												Ref.
		DCE11	CH_2Cl_2	tDCE12	DCA11	$CHCl_3$	TRI111	CCl_4	DCA12	TCE	DCP12	TRI112	PCE	HCB	
Southampton Water (UK)[a]	'95		150–4200			850–15 000	50–4200	50–800		220–4400			180–6700		[1]
Scheldt (B–Neth)[b]	'93–'97	<100	3800	<100	<100	6800	600	300	900	800	<100	600	2300		[34]
Scheldt (B–Neth)[c]	'94				4.2–4.3	44–48	41–56	1.8–2.2	30–40	24–61			63–72		[32]
Scheldt (B–Neth)[d]	'95–'97				<1.1–110[e]	7.4–1300	2.3–720	0.8–34	3.0–370	2.7–330			1.6–1100		[33]
Evros (Gr)	'96–'98					<25[f,g]	<20[f,g]	<25[f,g]		<20[f,g]		<50[f,g]	<20[f,g]	<30[f,g]	[27]
Nestos (Gr)	'96–'98					<25[f,g]	<20[f,g]	<25[f,g]		<20[f,g]		<50[f,g]	<20[f,g]	<30[f,g]	[27]
Strimonas (Gr)	'96–'98					<25[f,g]	<20[f,g]	<25[g]–310[f]		<20[f,g]		<50[f,g]	<20[f,g]	<30[f,g]	[27]
Axios (Gr)	'96–'98					<25[f,g]	<20[f,g]	<25[f,g]		<20[f]–7900[g]		<50[f,g]	<20[f,g]	<30[f,g]	[27]
Rhine (Neth)[h]	'97	<0.1–0.6	6.6–5000	<0.1–0.2	<0.1–1.9	14–100	<0.1–12	<0.1–8.5	0.9–100	<0.1–40		<0.3–2.2	<0.1–19		[31]
Scheldt (B–Neth)[h]	'98	<0.1–1.7	0.3–2900	<0.1–1.4	0.1–7.2	6.2–360	0.1–12	<0.1–1.8	0.1–150	0.1–79		<0.3–17	0.1–93		[31]
Loire (Fr)[i]	'98	<0.1–4.4	1.7–47	<0.1	<0.1–5.7	2.0–36	<0.1–34	<0.1–2.2	1.5–28	0.3–43		<0.3	0.1–1200		[31]
Scheldt (B–Neth)[i]	'98	0.1–4.0	1.4–160	<0.1–2.6	0.1–14	5.4–2900	0.5–17	1.6–72	0.5–91	1.0–170		<0.3–16	0.4–91		[31]
Thames (UK)[h]	'99	0.2–6.4	7.3–160	<0.1–3.8	<0.1–13	2.0–120	2.3–48	0.9–30	1.1–7.0	2.2–100		<0.3	0.7–210		[31]

Abbreviations: DCE11: 1,1-dichloroethene; CH_2Cl_2: dichloromethane; tDCE12: *trans*-1,2-dichloroethene; DCA11: 1,1-dichloroethane; $CHCl_3$: chloroform; TRI111: 1,1,1-trichloroethane; CCl_4: tetrachloromethane; DCA12: 1,2-dichloroethane; TCE: trichloroethene; DCP12: 1,2-dichloropropane; TRI112: 1,1,2-trichloroethane; PCE: tetrachloroethene; HCB: hexachloro-1,3-butadiene.

[a] Samples were taken from seven equidistant stations in the estuary ($n=52$).

[b] Only the highest measured concentrations (>100 ng l^{-1}) for each compound were reported in Ref. [34] ($n=13$ per year).

[c] Samples were taken at one location near the Dutch–Belgian border ($n=2$).

[d] Eight to ten locations were sampled along the trajectory Vlissingen (Netherlands)–Antwerp (Belgium) ($n=72$).

[e] Detection limits are reported in Ref. [59].

[f] Mean concentration observed during the first year of sampling ($n=4$).

[g] Mean concentration observed during the second year of sampling ($n=4$).

[h] Samples were taken along the salinity gradient ($n=15$).

[i] Samples were taken along the salinity gradient ($n=14$).

Table 2
Concentrations of priority VOCs (cyclohexane, MAHs and CMAHs) in estuaries (ng l^{-1})

Location	Year		MAHs					CMAHs							Ref.
		CYCLO	BENZ	TOL	EtBENZ	MPXYL	OXYL	ClBENZ	DCB13	DCB14	DCB12	TCB135	TCB124	TCB123	
Southampton Water (UK)[a]	'95		650–30 000	460–37 000	ΣC_2-MAHs: 370–77 000										[1]
Scheldt (B–Neth)[b]	'93–'97	1600	100	100	<100	200	<100	100	<100	100	200	<100	200	<100	[34]
Scheldt (B–Neth)[c]	'94		13–26	18–34	6.7–21	8.6–32	7.2–32								[32]
Scheldt (B–Neth)[d]	'95–'97		4.8–700	6.9–210	2.6–160	3.1–560	1.8–190								[33]
Evros (Gr)	'96–'98													<40[e,f]	[27]
Nestos (Gr)	'96–'98													<40[e,f]	[27]
Strimonas (Gr)	'96–'98													<40[e,f]	[27]
Axios (Gr)	'96–'98													<40[e,f]	[27]

Abbreviations: CYCLO: cyclohexane; BENZ: benzene; TOL: toluene; EtBENZ: ethylbenzene: MPXYL: *m*/*p*-xylene; OXYL: *o*-xylene; ClBENZ: chlorobenzene; DCB13: 1,3-dichlorobenzene; DCB14: 1,4-dichlorobenzene; DCB12: 1,2-dichlorobenzene; TCB135: 1,3,5-trichlorobenzene; TCB124: 1,2,4-trichlorobenzene; TCB123: 1,2,3-trichlorobenzene.

[a] Samples were taken from seven equidistant stations in the estuary ($n=52$).

[b] Only the highest measured concentrations (>100 ng l^{-1}) for each compound were reported in Ref. [34] ($n=13$ per year).

[c] Samples were taken at one location near the Dutch–Belgian border ($n=2$).

[d] Eight to ten locations were sampled along the trajectory Vlissingen (Netherlands)–Antwerp (Belgium) ($n=72$).

[e] Mean concentration observed during the first year of sampling ($n=4$).

[f] Mean concentration observed during the second year of sampling ($n=4$).

are volatilized before they can be transported to the open sea.

The occurrence of several volatile halocarbons in rivers and lakes of northern Greece was investigated by Kostopoulou et al. [27], and assessed against EU regulations. Six halocarbons were occasionally detected in surface water samples, four of which, i.e. chloroform, tetrachloromethane, trichloroethene and tetrachloroethene, are targeted in this paper. With that, riverine concentrations were higher than the concentrations observed in lakes. The Evros, Nestos, Strymonas and Axios rivers run through an area of intense agricultural and industrial activity before pouring into the Aegean Sea. Trichloroethene, for instance, was never detected above 20 ng l^{-1} in lake water, whereas up to 40 μg l^{-1} was found in the Axios river. Even so, all data, except for trichloroethene, were well below environmental quality standards of the European Community.

Maximum concentrations of CHCs, cyclohexane, MAHs, and CMAHs in the Scheldt estuary were reported by Miermans et al. [34]. Analytes were measured on a regular basis at Schaer van Ouden Doel, near the Dutch-Belgian border, over the period 1993–1997. This study was intended to enable calamities or short-term events to be traced resulting from industrial malfunctions or illegal practices.

Christof et al. [31] identified more than 50 distinct volatile halogenated compounds within the BIOGEST project in the Scheldt, Rhine, Loire and Thames estuaries. Concentrations and distribution patterns were reported for the most commonly found organohalogens. Dichloromethane, chloroform, trichloroethene and tetrachloroethene were the quantitative dominating compounds in all investigated estuaries. Distribution patterns indicated a riverine source with decreasing concentrations at increasing salinities. Anthropogenic inputs from industries and/or water treatment plants were identified as the main sources.

4. A case-study: the Scheldt estuary

A 3-year monitoring survey was undertaken in the Scheldt estuary from May 1998 till November 2000 to assess the present concentrations and spatial-temporal variability of 27 priority VOCs. The Scheldt estuary is situated in northwest Belgium and southwest Netherlands, and is one of the main riverine contributors to the southern North Sea. Its drainage basin covers a very densely populated and highly industrialized region, and provides marine access to the Antwerp harbor. Water samples were taken twice a year from 14 stations located along the trajectory Vlissingen–Temse on board the Dutch research vessel "Luctor" from the "Nederlands Instituut voor Oecologisch Onderzoek (NIOO)" in Yerseke, the Netherlands. The sampling stations are shown in Fig. 2. Eighty-four water samples were analyzed at the laboratory by purge-and-trap combined with high-resolution gas chromatography and detection by mass spectrometry in the SIM mode. A representative chromatogram is shown in Fig. 3. Recoveries of deuterated surrogates ranged from 100±12% for [$^2H_1$]chloroform to 93±18% for [$^2H_8$]toluene and 90±13% in the case of [$^2H_5$]chlorobenzene ($n=84$). Hence, no apparent loss of analytes occurred during storage and sample handling. Furthermore, all data were produced by analyses deemed "in control" by a rigorous QA/QC program, as proposed by QUASIMEME. Detailed information on sampling, sample preparation, analysis, and quality assessment can be found in a previous paper [30].

The concentrations observed during each sampling campaign are shown in Table 3 for all target VOCs, except for benzene and dichloromethane. Both analytes were discarded from the data set for reasons of QA/QC. Similarly, 14 measurements of 1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, hexachloro-1,3-butadiene and 1,2,3-trichlorobenzene, and one data point of 1,2-dichlorobenzene were excluded from tabulation.

Except for 1,1,2-trichloroethane and tetrachloroethene, all analytes were plagued by censored measurements, despite decision limits of 0.4 ng l^{-1} (1,1,1-trichloroethane) to 14 ng l^{-1} (chloroform). The BRML method was used to estimate the mean, SD, median, and IQR for each censored analyte [16]. Estimation of the median and IQR was only required at censoring levels above 50 and 25%, respectively. Summary statistics were not computed for hexachloro-1,3-butadiene as only two data points were numerically known.

Most volatile halogenated hydrocarbons were traceable to a single source in the upper estuary. The

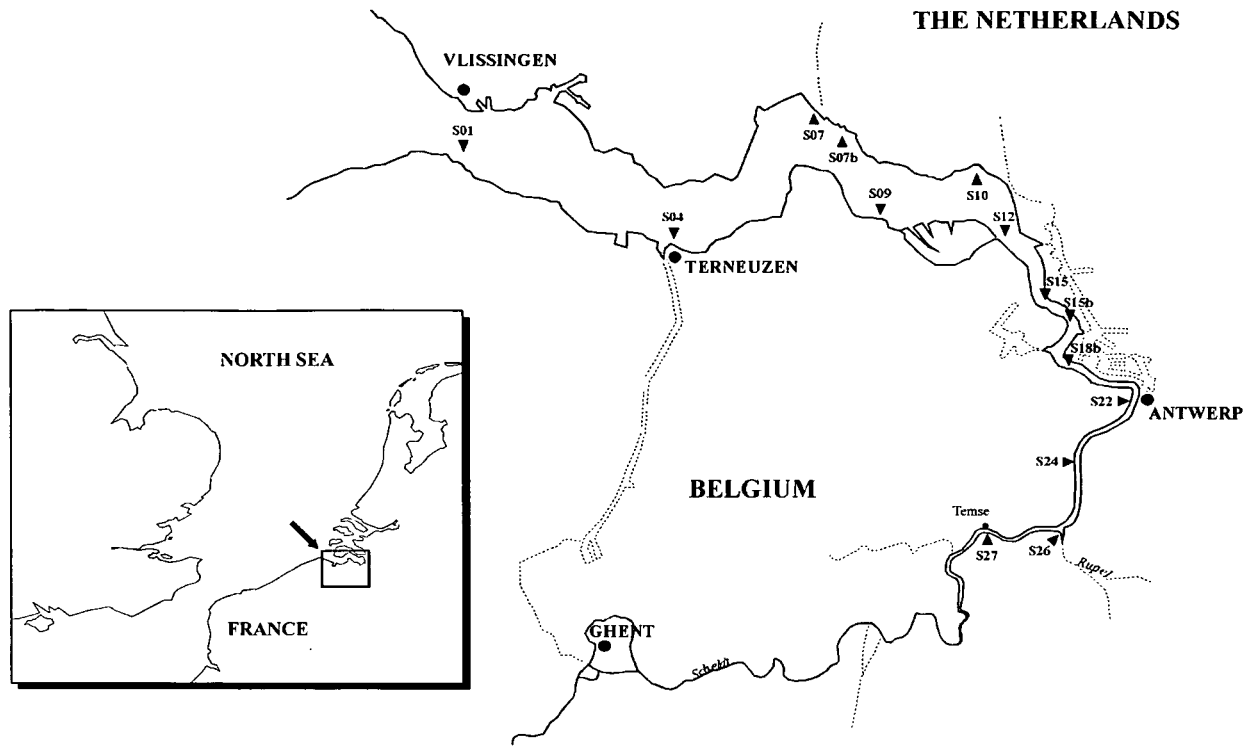

Fig. 2. Sampling locations within the Scheldt estuary: S01 (51°N 24.75, 3°E 34.00); S04 (51°N 20.90, 3°E 49.60); S07 (51°N 26.35, 4°E 1.00); S07b (51°N 25.25, 4°E 2.50); S09 (51°N 22.30, 4°E 5.00); S10 (51°N 23.95, 4°E 12.00); S12 (51°N 20.85, 4°E 15.80); S15 (51°N 18.10, 4°E 17.30); S15b (51°N 17.07, 4°E 19.19); S18b (51°N 15.10, 4°E 19.50); S22 (51°N 13.30, 4°E 23.50); S24 (51°N 10.50, 4°E 19.65); S26 (51°N 7.50, 4°E 18.50); S27 (51°N 7.00, 4°E 14.30).

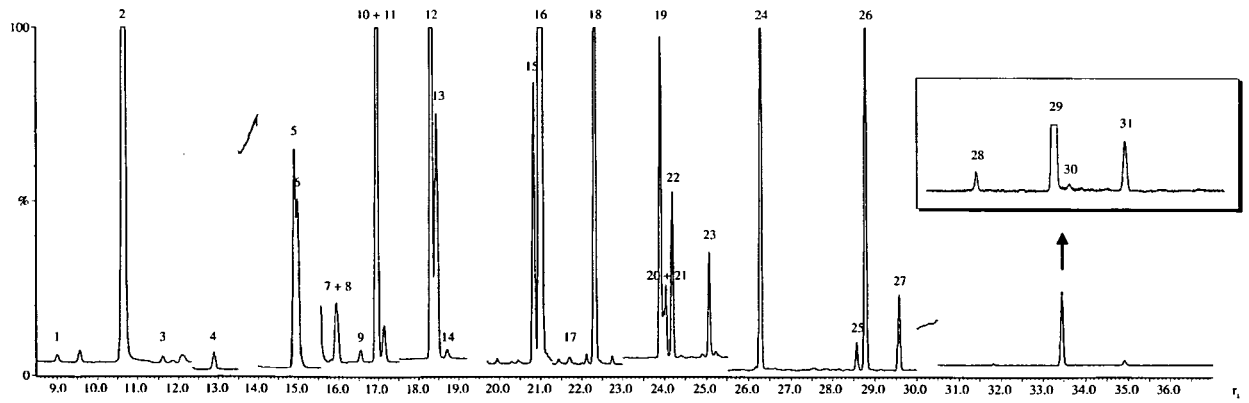

Fig. 3. GC–MS chromatogram in SIM mode of 27 priority VOCs. The sample was taken in the Scheldt estuary at station S26 on 3 April, 2000. 1: DCE11; 2: CH_2Cl_2; 3: tDCE12; 4: DCA11; 5: [$^2H_1$]chloroform (surrogate); 6: $CHCl_3$; 7: TRI111; 8: CYCLO; 9: CCl_4; 10: DCA12; 11: BENZ; 12: TCE; 13: α,α,α-trifluorotoluene (internal standard); 14: DCP12; 15: [$^2H_8$]toluene (surrogate); 16: TOL; 17: TRI112; 18: PCE; 19: [$^2H_5$]chlorobenzene (surrogate); 20: ClBENZ; 21: EtBENZ; 22: MPXYL; 23: OXYL; 24: 4-bromofluorobenzene (internal standard); 25: DCB13; 26: DCB14; 27: DCB12; 28: TCB135; 29: TCB124; 30: HCB; 31: TCB123 (for abbreviations, see Tables 1 and 2). Ions 17 and 18 were added in time windows 13.5–14.0 min and 30.0–30.5 min to verify water background levels.

Table 3
Summary of VOC concentrations observed during six monitoring surveys in the Scheldt estuary (ng l^{-1})

Compound	Concentrations						Summary statistics					
	19–20/05/98	14–15/10/98	11–12/05/99	02–03/11/99	03–04/04/00	13–14/11/00	n	$n_{censored}$	Mean	SD	Median	IQR
DCE11	<1.7–11	<1.7–2.5	<1.7–7.8	<1.7–3.8	<1.7–3.4	<1.7–3.2	84	34	1.9	1.9	1.3	1.9
tDCE12	<1.0–7.4	<1.0–4.5	1.0–12	<1.0–5.4	<1.0–3.5	<1.0–2.9	84	27	2.0	2.3	1.1	2.1
DCA11	<3.1–21	<3.1–17	<3.1–18	<3.1–13	<3.1–21	<3.1–12	84	33	5.2	5.5	2.6	7.2
$CHCl_3$	20–770	<28–170	<28–530	18–75	18–240	<28–89	84	3	81	110	47	68
TRI111	10–73	<0.8–30	2.4–43	1.2–17	2.6–46	<0.8–31	84	2	14	14	9.5	18
CYCLO	2.8–47	<4.3–29	3.9–690	<4.3–460	6.0–92	6.1–79	84	4	46	100	12	26
CCl_4	<2.3–4.3	<2.3–3.1	1.1–4.0	<2.3–4.1	2.3–8.3	1.8–26	84	5	3.3	3.8	2.6	1.5
DCA12	<16–110	<16–92	<16–110	<16–84	<16–140	<16–70	84	8	40	30	32	41
TCE	14–190	<12–420	<12–830	<12–130	9.7–220	6.8–320	84	8	91	130	39	120
DCP12	1.5–9.0	<1.2–230	2.1–8.6	<1.2–2.8	<1.2–43	0.8–23	84	5	6.8	25	2.7	2.6
TOL	<19–70	<19–150	19–400	<19–130	16–370	16–1300	84	4	71	150	36	49
TRI112	12–70	0.3–270	11–74	1.1–79	2.0–56	1.0–55	84	0	27	35	16	27
PCE	2.7–210	1.5–3800	7.9–450	1.6–330	7.9–590	1.4–350	84	0	200	470	85	180
ClBENZ	<7.3–30	<7.3–34	<7.3–22	<7.3–31	5.7–29	4.0–52	84	6	17	12	14	14
EtBENZ	4.6–17	<4.2–27	3.1–30	<4.2–33	4.4–47	2.7–23	84	3	9.0	7.5	7.3	6.8
MPXYL	<11–39	<11–79	9.4–67	<11–100	12–71	8.0–30	84	4	21	18	16	16
OXYL	1.8–27	<3.2–32	3.1–41	<3.2–45	5.1–39	3.6–20	84	2	11	9.6	8.2	8.8
DCB13	<2.8–30	<2.8–8.4	<2.8	<2.8–9.1	<2.8–3.7	<2.7–12	84	30	3.1	3.8	2.0	2.7
DCB14	23–160	<15–46	<15–80	<15–33	<15–56	<15–97	84	32	27	29	16	37
DCB12	<3.7–26	<3.7–27[a]	<3.7–20	<3.7–34	<3.7–27	<3.7–26	83	29	7.4	7.9	4.0	8.9
TCB135	<1.8–640	[a]	<1.8	<1.8	<1.8–2.6	<1.8–2.0	70	48	22	110	0.2	1.1
TCB124	<5.8–25	[a]	<5.8	<5.8	<5.8	<5.8–86	70	40	5.2	12	2.2	3.2
HCB	<4.8–7.5	[a]	<4.8	<4.8	<4.8	<4.8	70	68	[b]	[b]	[b]	[b]
TCB123	<6.6–560	[a]	<6.6	<6.6	<6.6	<6.6–7.8	70	57	17	82	0.2	1.6

Abbreviations: DCE11: 1,1-dichloroethene; tDCE12: *trans*-1,2-dichloroethene; DCA11: 1,1-dichloroethane; $CHCl_3$: chloroform; TRI111: 1,1,1-trichloroethane; CYCLO: cyclohexane; CCl_4: tetrachloromethane; DCA12: 1,2-dichloroethane; TCE: trichloroethene; DCP12: 1,2-dichloropropane; TOL: toluene; TRI112: 1,1,2-trichloroethane; PCE: tetrachloroethene; ClBENZ: chlorobenzene; EtBENZ: ethylbenzene: MPXYL: *m*/*p*-xylene; OXYL: *o*-xylene; DCB13: 1,3-dichlorobenzene; DCB14: 1,4-dichlorobenzene; DCB12: 1,2-dichlorobenzene; TCB135: 1,3,5-trichlorobenzene; TCB124: 1,2,4-trichlorobenzene; HCB: hexachloro-1,3-butadiene; TCB123: 1,2,3-trichlorobenzene; n = number of measurements; $n_{censored}$ = number of measurements below the detection limit; SD = standard deviation; IQR = interquartile range.

[a] Measurement results have been discarded for reasons of QA/QC (see Ref. [30]).

[b] Number of censored data is too high for parameter estimation [16].

distribution profile in Fig. 4a, for instance, indicates a major input of 1,1-dichloroethane between S24 and S27, possibly from the tributary at S26. Concentrations decreased exponentially with distance to the mouth of the estuary owing to dilution and volatilization. Similar patterns were observed for 1,1,1-trichloroethane, 1,2-dichloroethane, trichloroethene, 1,1,2-trichloroethane and tetrachloroethene with concentration maxima between S18b and S27. The other CHCs, such as chloroform, entered the estuary from multiple sources.

Apart from a few outliers, which could refer to occasional spills, volatile aromatic data were almost uniformly distributed along the salinity gradient, with concentrations varying within a relatively small range of values. The occurrence of alkylbenzenes clearly resulted from contributions of a wide spectrum of sources spread within the estuary, as shown for ethylbenzene in Fig. 4b.

Chlorobenzene was ubiquitous in the Scheldt estuary, and displayed a bell-shaped distribution pattern (Fig. 4c). Concentration maxima between S15 and S18b were indicative of an input source close to these stations. Dichlorobenzenes, with the exception of 1,2-dichlorobenzene, displayed a rather irregular pattern along the salinity gradient, whereas

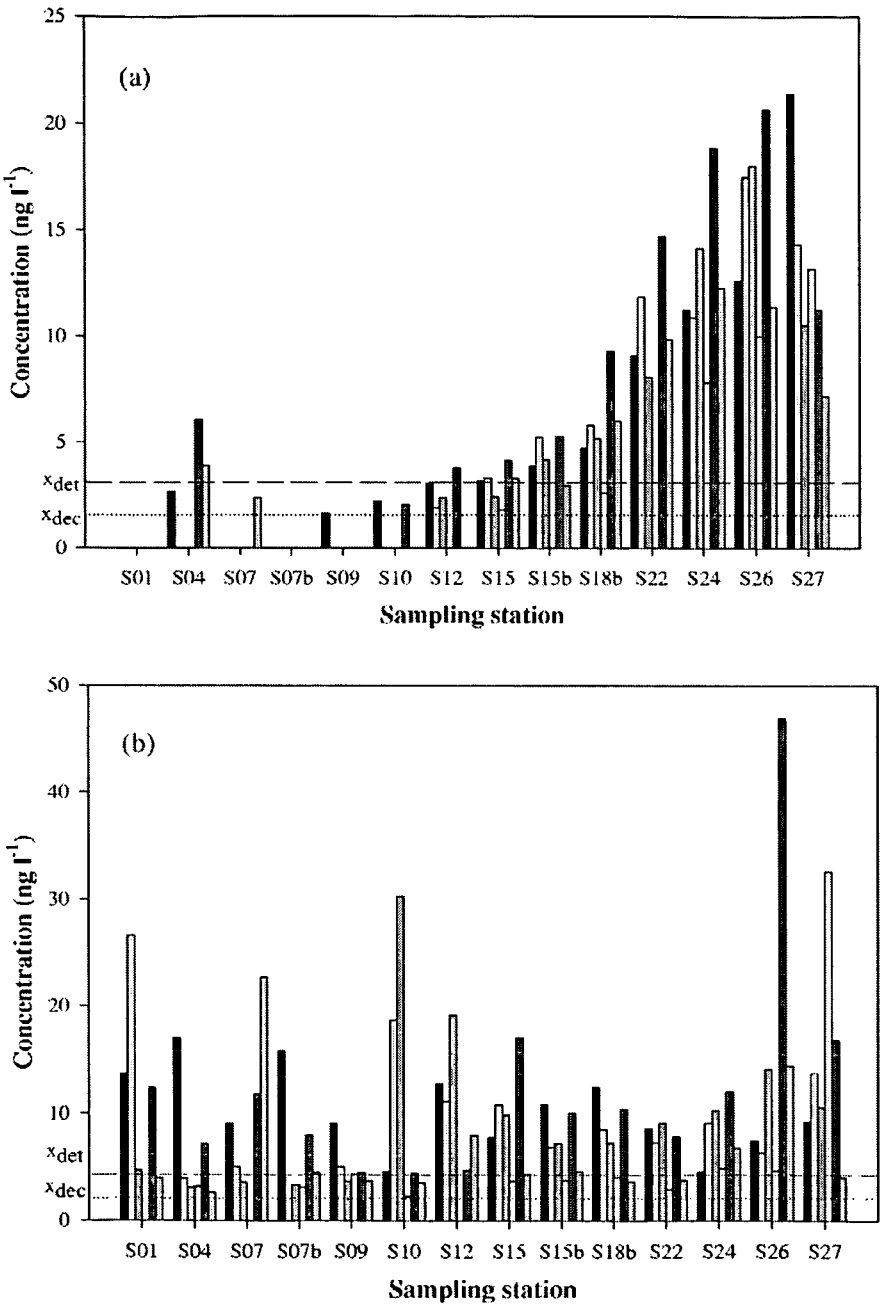

Fig. 4. Distribution patterns of (a) 1,1-dichloroethane, (b) ethylbenzene, and (c) chlorobenzene within the Scheldt estuary. Censored observations are left blank. ■, 19–20/05/98; □, 14–15/10/98; ▣, 11–12/05/99; ▢, 02–03/11/99; ▣, 03–04/04/00; ▣, 13–14/11/00; x_{dec} = decision limit; x_{det} = detection limit (for a comprehensive discussion of x_{dec} and x_{det}, see Ref. [60]).

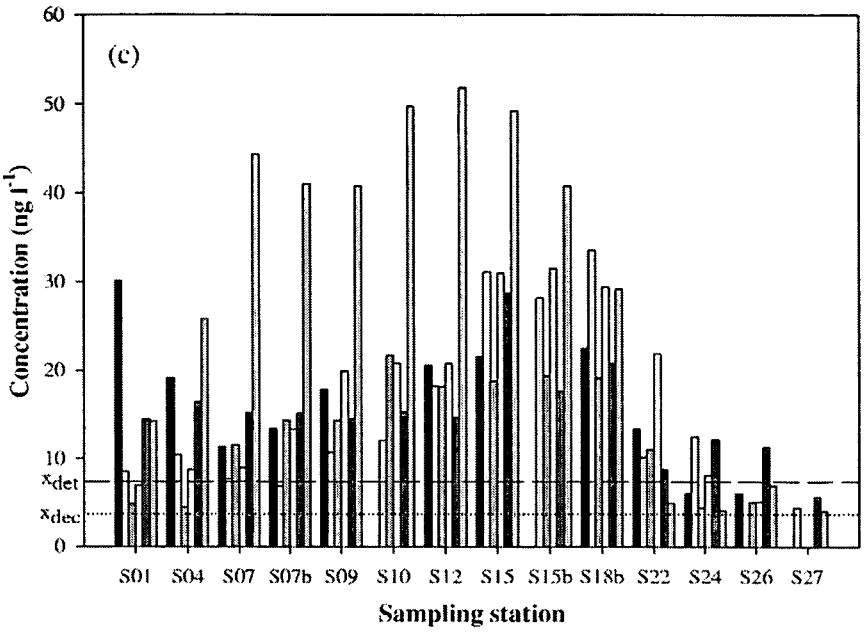

Fig. 4. (*continued*)

trichlorobenzenes were found on an intermittent basis with concentrations mostly below detection limits.

5. Conclusion

Analysis of priority VOCs in estuarine waters requires adequate sample preparation to enable quantitative measurements down to a few ng l^{-1}. Despite a number of drawbacks, purge-and-trap remains the method of choice for VOC enrichment in marine and estuarine water samples. Promising new techniques have been proposed such as membrane inlet mass spectrometry, but most of these methods require further improvements to enable trace and ultra-trace level analysis.

Other key elements in VOC analysis and assessment are QA/QC and statistical data analysis. As marine monitoring data are used to formulate quality guidelines, it is essential that field measurements are published with demonstrable evidence of QA/QC in all aspects of the monitoring exercise.

Statistical data analysis facilitates the interpretation of field measurements and improves our understanding of underlying environmental processes, provided that adequate statistical methods are used. Environmental data distributions are often skewed, contain outliers and are plagued by censored data. Statistical methods that overcome these problems exist, but are generally unknown by environmental analysts.

Purge-and-trap combined with high-resolution gas chromatography and detection by mass spectrometry was used to survey 27 priority VOCs in the Scheldt estuary from May 1998 to November 2000. Monitoring data showed clear differences between CHCs, MAHs, and CMAHs within concentrations, input sources, and fate processes. Considering the overall concentrations of VOCs in other estuaries, the Scheldt estuary can be considered as moderately polluted.

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