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Intercompartment distribution of monocyclic aromatic hydrocarbons and C_1-C_2 organochlorines in the North Sea environment

Part I
Literature study

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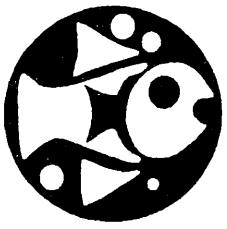

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I. LITERATURE STUDY

I.1. AIR

I.1.1. SAMPLING AND ANALYSIS

Only these methods which have been used to analyse real world samples are discussed. More recent developments like hollow fiber sampling or solid phase microextraction which have been evaluated mostly on running lab samples are not considered in this overview.

I.1.1.1. SAMPLING

Since atmospheric concentrations of volatile organic compounds (VOCs) are low, air samples generally have to be preconcentrated before they can be analysed. Preconcentration can be done either in the field or at the laboratory. Two sampling techniques include on-site preconcentration: sorbent sampling and cryogenic sampling. This latter sampling technique is usually followed by analysis on the same location because of difficult storage and transport of the preconcentrated sample. Canister sampling does not include the preconcentration of the VOCs but it collects the whole air matrix, which is then transported to the laboratory.

I.1.1.1.1. Sorbent sampling

Several types of commercially available sorbents are used in order to concentrate chlorinated C_1- and C_2-hydrocarbons (CHCs) and monocyclic aromatic hydrocarbons (MAHs) among other VOCs. Tenax-TA, Tenax-GC, Tenax-GR, Carbotrap B, Carbotrap C and Carbosieve SIII are widely used. Tenax sorbent is a 2,6-diphenyl-p-phenylene oxide polymer whereas Tenax-GR contains in addition graphitized carbon. The Carbotrap sorbents are also carbon-based materials, Carbosieve SIII is a carbon molecular sieve. Other sorbents like divinylbenzene polymer (Hayesep D, ...) combined with Carbosphere (carbon molecular sieve) (Frank et al., 1991b) and spherical macroporous resins of linked polystyrene/divinylbenzene (XAD-2) (Von Düszeln and Thiemann, 1985) are used in air sampling. A summary of used sorbents with their properties is given in Table I.1.1.

Table I.1.1. Characteristics of sorbents used for sampling CHCs and MAHs at remote sampling sites

Sorbents	Type	Surface area ($m^2.g^{-1}$)	Temperature limit (°C)	Reference
Polymer type				
Tenax-TA	2,6-diphenyl-p-phenylene oxide polymer	35	300	Camel and Caude (1995)
Tenax-GR	77% Tenax TA + 23% graphite carbon		350	Camel and Caude (1995)
Hayesep D	Divinylbenzene polymer	795	290	Camel and Caude (1995)
Chromosorb 102	Styrene/divinylbenzene polymer	350	250	Camel and Caude (1995)
XAD-2	Styrene/divinylbenzene polymer	300	200	Camel and Caude (1995)
Carbon based				
Carbotrap B	Graphitized carbon black	100		Matisová and Škrabáková (1995)
Carbotrap C	Graphitized carbon black	10-12	400	Matisová and Škrabáková (1995); Camel and Caude (1995)
Molecular sieve				
Carbosieve SIII	Carbon molecular sieve	820-1000	400	Matisová and Škrabáková (1995); Camel and Caude (1995)

Generally, air is pumped through the adsorption tube but for CHCs measurements with electron capture detection, sampling with 50 to 60mL syringes filled with sorbent is reported too (Frank and Frank, 1990a; Frank et al., 1991a).

Four points have to be considered in the selection of a sorbent. First of all, the retention of the VOCs must be as high as possible in order to avoid breakthrough. Breakthrough volumes are determined for different Tenax-GC/sorbate combinations (Brown and Purnell, 1979). However, Walling et al. (1986) mentioned that the retention volumes in practice sometimes differ greatly from literature values. Frank and Frank (1990b) determined breakthrough volumes of some CHCs for sorbents like a styrene-divinylbenzene polymer (Chromosorb 102), a spherical divinylbenzene polymer (Hayesep D), graphitized carbon black (Graphtrap 5), charcoal (SK4) and a spherical carbon molecular sieve (Carbosphere). The trapping efficiency increases with decreasing temperature as shown for the cryogenic sampling in the -20 to -180°C range on Tenax TA and Chromosorb 101 (Cao and Hewitt, 1992). Ventura et al. (1993) found higher retention volumes for Tenax-GR than for Tenax-TA and Tenax-GC. Helmig and Greenberg (1994) tested several individual adsorbents and multistage combinations of adsorbents for air analysis with VOCs at pptv levels. They concluded that charcoal-based adsorbent traps showed higher trapping efficiencies than Tenax-TA or Tenax-GR. Among the different trapping systems tested, the multi-adsorbent trap containing Carbotrap C, Carbotrap B and Carbosieve SIII gave the best results because of the wide range of compounds that could be trapped. Moreover, the preferred combination showed low levels of blanks and artifacts.

Secondly, the sorbent itself may not produce any artifacts. Helmig and Greenberg (1994) found Carbotrap B, Carbotrap C and Carbosieve SIII to be the most resistent adsorbents to degradation whereas Tenax TA and Tenax GR adsorbents showed some significant artifact formation like benzaldehyde, acetophenone, phenol and benzonitrile. Similarly Walling et al. (1986) reported that chemical reactions during sampling and thermal desorption are common for Tenax. The authors suggested oxidizing reactions to explain the degradation products.

Further on, the sorbents must be free of contamination before and after sampling. Usually sorbents are thermally cleaned by heating and flushing clean gas (Helium) over the sorbent before sampling. In addition extraction of the sorbent can be done, like n-pentane extraction (Class and Ballschmiter, 1987a) or Soxhlet extraction with n-hexane (Frank and Frank, 1988). In order to avoid contamination or losses during transport and storage, the tubes are closed with end-caps. Some authors report flamesealing before and after sampling (Class and

Ballschmiter, 1986b; Class and Ballschmiter, 1987a; Wiedmann et al., 1994). In this way Class and Ballschmiter (1987a) found no CHCs losses after 1 year or more.

Finally, the water retention on the sorbent material has to be as low as possible. Since water retained on the sampling tube interfered with the following GC analysis, Helmig and Greenberg (1994) had to limit the cooling of the sorbent during sampling. McCaffrey et al. (1994) mentioned that carbon tubes adsorb more water than Tenax tubes. This water retention resulted in the blocking of the cryogenic trap during the desorption stage owing to ice formation. Since Carbosieve SIII retained relative high amounts of water, Ciccioli et al. (1993) preferred Carbotrap C and Carbotrap B without Carbosieve SIII to sample hydrocarbons and halocarbons at remote sites. Boudries et al. (1994) dehydrated the air stream before the sorbent preconcentration. This was performed by Nafion tubes (Perma Pure Products, Inc.). These dryers are tubular hygroscopic ion-exchange membranes removing water vapour selectively form mixed gas streams (McClenny et al., 1984).

Many applications of sorbent sampling at remote sites are reported. Tenax is reported for sampling of CHCs at oceanic sites (Kirschmer and Ballschmiter, 1983; Class and Ballschmiter, 1986a; Class and Ballschmiter, 1986b; Class and Ballschmiter, 1987a), in forest areas (Frank and Frank, 1990a) and at several remote sites (Wiedmann et al., 1994), whereas a Tenax TA/ charcoal combination was used at urban, coastal and oceanic sites by Frank et al. (1991a).

CHCs measurements at coastal urban sites and over the Atlantic using XAD-2 resins are reported by Von Düszeln and Thiemann (1985).

A multistage combination of Carbotrap C, Carbotrap B and Carbosieve SIII was frequently used like for estuarine air (Bianchi and Varney, 1993), for coastal sites (Boudries et al., 1994) or for marine sites (Helmig and Greenberg, 1994). Two stage combinations at remote sites are reported as well, e.g. Carbotrap C/ Carbotrap B (Ciccioli et al., 1993) and Carbotrap B/ Carbosieve SIII (Dewulf et al., 1995).

I.1.1.1.2. Canister sampling

Canister sampling involves the collection of the whole air matrix in a precleaned evacuated cylinder. This canister can be filled up to atmospheric pressure by grab sampling in which the valve is just opened and closed (Rudolph et al., 1984) or the canister can be pressurized up to 4-5 bar by means of a pump (Rudolph et al., 1984; Lightman et al., 1990; Penkett et al.,

1993). Several canister sampling volumes are reported: 1L (Cronn and Nutmagul, 1982), 1.6L (Lightman et al., 1990; Penkett et al., 1993), 2L (Rudolph et al., 1984), 4L (Greenberg and Zimmerman, 1984), 6L (Cronn and Nutmagul, 1982) and 10L (Rudolph et al., 1984). Before sampling the canister can be flushed with air (Cronn and Nutmagul, 1982; Lightman et al., 1990; Penkett et al., 1993).

Greenberg et al. (1992) made a comparison of hydrocarbons measurements over the Pacific with canister sampling and in situ cryogenic sampling. Individual canister and in situ sample results did not allow direct intercomparison. However, median and interquartile ranges of measurements and data could be compared.

Though the canister sampling method is simple, some aspects have to be considered. Before use the inner wall of the canister must be cleaned intensively (EPA Compendium Method TO-14, 1988; Coutant, 1992). Greenberg et al. (1992) reported cleaning by purging overnight humidified air of 100°C before sampling over the Pacific. The inner wall has to be inactive in order to minimise sorption effects. Therefore, canisters are electropolished (Summa-passivated). The inner surface is minimised and covered by a CrO_2-layer. It is also shown that the humidity of the sampled air does influence the stability of the VOCs in the canister (Gholson et al., 1990; Hsu et al., 1991; Coutant, 1992). This is due to the competition effect of water sorbing on the inner wall. Coutant (1992) applied the Dubinin-Radushkevich isotherm in order to estimate the sorbed fraction of VOCs. A high relative humidity proved to be necessary. On the other hand condensation has to be avoided (Greenberg et al., 1992).

Atmospheric measurements of MAHs and CHCs with canister sampling are reported, not only for urban sites (Sweet and Vermette, 1992; Farmer et al., 1994) but for remote continental and marine atmospheres as well (Cronn and Nutmagul, 1982; Singh et al., 1983; Rudolph et al., 1984; Greenberg and Zimmerman, 1984; Lightman et al., 1990; Penkett et al., 1993; Wofsy et al., 1994).

I.1.1.1.3. Cryogenic sampling

Air can be concentrated in sampling loops which are kept at cryogenic temperatures by means of liquid oxygen or nitrogen. In this way air volumes from 100-200mL (Khalil et al., 1983) over 1L (Greenberg et al., 1992) to 1.5-4L (Koppmann et al., 1993; Koppmann et al., 1994) were concentrated cryogenically. Some sampling loops are filled with glass beads (Khalil et al., 1983), others with porous glass beads (Koppmann et al., 1993; Koppmann et al., 1994).

A more complex cryogenic trapping method, established for the analysis of non-methane hydrocarbons (NMHCs) at pptv levels, is the double cryogenic trapping system of Greenberg et al. (1994) (See Figure I.1.1). In this sampling technique, a first cryogenic trap is heated slowly after sampling up to 80°C in 3 minutes in order to transfer the trapped VOCs to a second cryogenic trap but to minimize the transfer of water vapour. The second trap is then heated to 80°C in approximately 15 seconds to transfer the sample to the analytical column.

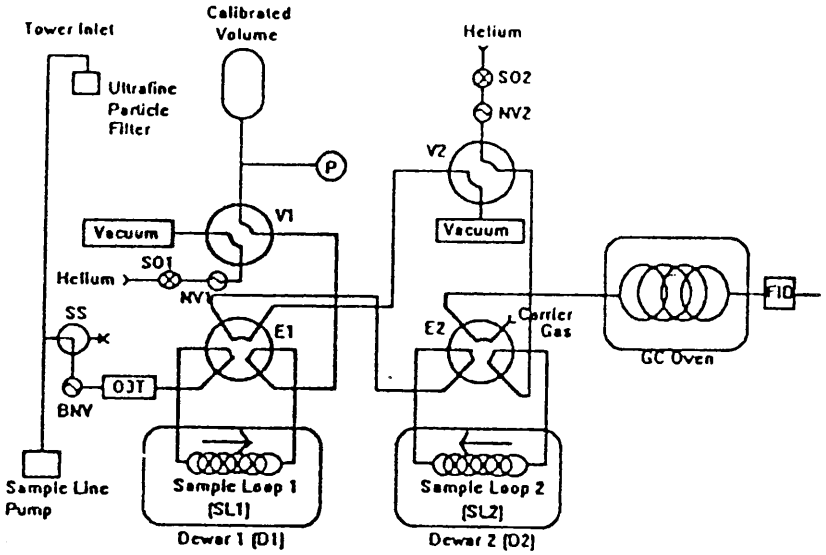


Figure I.1.1. Scheme of the sample collection/introduction system of Greenberg et al. (1994) (in collection mode). Abbreviations: V1 and V2: 4-port direction valves; E1 and E2: 6-port sample trap valves; SS: 3-port stream selector valve; BNV: stainless steel bellows needle valve; NV1 and NV2: stainless steel needle valves; SO: stainless steel bellows pneumatic shut-off valves; P: pressure measurement; SL1: first stage cryogenic sample trap packed with 0.18-0.23mm diameter glass beads; SL2: second stage cryogenic sample trap packed with 60/80 mesh glass beads; D1 and D2: liquid nitrogen dewars; O3T: ozone trap.

CHCs measurements at oceanic sites (Khalil et al., 1993; Koppmann et al., 1993; Koppmann et al., 1994) and in the stratosphere (Fabian and Gömer, 1984) are reported, whereas marine benzene and toluene measurements were carried out by Greenberg et al. (1992) and by Greenberg et al. (1994).

I.1.1.2. ANALYSIS

I.1.1.2.1. Injection of the sample

I.1.1.2.1.1. Injection of VOCs preconcentrated on adsorbent tubes

Generally VOCs, preconcentrated on adsorbents, are thermally desorbed. Only Von Düszeln and Thiemann (1985) reported n-pentane extraction of CHCs after sampling on XAD-2, followed by GC-electron capture detection.

Direct injection after thermal desorption is rarely done. Frank et al. (1991b) directly injected CHCs from Hayesep D at 200°C. The high heating rate of the trap ($20K.s^{-1}$) provided a narrow band injection and so good chromatographic separation and detection could be achieved. Most of the reported thermal desorption procedures are combined with cryogenic refocussing after the desorption because of the slow thermal release of the compounds from the adsorbent (Kirschmer and Ballschmiter, 1983; Class and Ballschmiter, 1986a; Class and Ballschmiter, 1986b; Class and Ballschmiter, 1987a; Ciccioli et al., 1993; Wiedmann et al., 1994).

Some researchers use cryofocussing traps filled with adsorbent materials like Chromosorb 106 (Bianchi and Varney, 1993), Al_2O_3/KCl (Boudries et al., 1994) or Gas Chrom Q (Frank and Frank, 1988; Frank and Frank; 1990a; Frank et al., 1991a). A special refocussing technique is the trapping of the VOCs onto the column head, e.g. at -60°C (Helmig and Greenberg, 1994). Also desorption combined with a (second) adsorption after water removal, followed by desorption with cryofocussing is reported (Dewulf et al., 1995).

I.1.1.2.1.2. Injection of VOCs sampled in canisters

When the canister is transferred to the laboratory, a preconcentration still has to be done, i.e. by cryoconcentration. The air from the canister is led through a cryogenic trap which is subsequently placed on-line with the GC-system in order to inject the compounds by fast heating of the cold trap. Several applications for remote sampling sites are reported (Singh et al., 1983; Greenberg and Zimmerman, 1984; Greenberg et al., 1992; Greenberg et al., 1994). The cryofocussing trap can be filled with glass beads (Rudolph et al., 1984; Lightman et al., 1990; Penkett et al.,1993). Lai et al. (1993) applied double trapping for urban air

samples: cryotrapping and cryofocussing where the cryofocussing trap is ballistically heated. Hsu et al. (1991) analysed canister samples on an automated Tekmar system. The procedure included cryotrapping, sorbent trapping followed by a final cryofocussing.

I.1.1.2.1.3. Injection of VOCs after cryogenic preconcentration

The cryogenic preconcentration allows direct injection of the VOCs after sampling, provided that the sampling system together with the analytical instrumentation is on the sampling site. The VOCs are injected by heating the cryogenic trap, immediately after sampling.
The technique is applied for NMHCs including MAHs at the Pacific (Greenberg et al., 1992), for chloroform over tropical oceans (Khalil et al., 1983) and for CHCs over the Atlantic (Koppmann et al., 1993; Koppmann et al., 1994).

I.1.1.2.1.4. Direct injection of an air sample

Some researchers use a 3 to 5mL sample loop which can be switched on-line with the analytical instrument, equipped with a packed column for separation (Hunter-Smith et al., 1983; Hisham and Grosjean, 1991). Since a limited sampling volume is taken, a sensitive detector like the ECD-detector, is needed.

I.1.1.2.2. Separation

Capillary as well as packed columns are reported for the gas chromatographic separation of MAHs and CHCs. Oftenly used are 100% poly (dimethylsiloxane) capillary columns (Kirschmer and Ballschmiter, 1983; Greenberg and Zimmermann, 1984; Von Düszeln and Thiemann, 1985; Bianchi and Varney, 1993; Ciccioli et al., 1993; Greenberg et al., 1994; Helmig and Greenberg, 1994). Other capillary columns have stationary phases like poly (5%-diphenyl-95%-dimethylsiloxane), poly (7%-cyanopropyl-7%-phenylmethyl-86%-dimethylsiloxane) (Class and Ballschmiter, 1986a; Class and Ballschmiter, 1986b) or Carbowax type polymers (Lightman et al., 1990). Some studies report the use of poly (dimethylsiloxane) capillary columns next to packed columns (Cronn and Nutmagul, 1982; Rudolph et al., 1986). Poly (phenylmethylsiloxane) type stationary phases are also used (Frank and Frank, 1988; Frank and Frank, 1990a; Frank et al., 1991a; Frank et al., 1991b; Koppmann

et al., 1993; Koppmann et al., 1994). Specific types of stationary phases to separate a wide range of compounds are reported. Hsu et al. (1991) separated a wide range of NMHCs, including CHCs and MAHs, on a Supelco VOCOL column, while Dewulf et al. (1995) analysed CHCs and MAHs in rural air samples on a RTX 502.2 column. Finally capillary columns with Al_2O_3/KCl stationary phases are reported by Boudries et al. (1994) and by Penkett et al. (1993).

The compounds can be separated on packed columns too, like on n-octane/Porasil (spherical silica packing material) (Cronn and Nutmagul, 1982) and dimethylsilicone on Chromosorb (polymer type packing material) (Hunter-Smith et al., 1983; Fabian and Gömer, 1984) or on Supelcoport (Khalil et al., 1983; Singh et al., 1983). Finally Carbowax 400 (on Chromosorb) for 1,1,1-trichloroethane and tetrachloroethylene analysis in urban and background site samples is reported (Hisham and Grosjean, 1991).

I.1.1.2.3. Detection

Several detector types are applied in the measurement of CHCs and MAHs from remote sampling sites. When only chlorinated (halogenated) compounds are detected, the sensitive electron capture detector (ECD) (Lovelock et al., 1971) is preferable. But, because of the selectivity, the range of detectable compounds is limited. A lot of reports with application of this detector can be found. Marine air samples (Kirschmer and Ballschmiter, 1983; Class and Ballschmiter, 1986a; Class and Ballschmiter, 1987a; Frank et al., 1991a; Frank et al., 1991b; Hunter-Smith et al., 1983; Khalil et al., 1983; Koppmann et al., 1993; Koppmann et al., 1994; Singh et al., 1983; Wiedmann et al., 1994), rural and mountain forest air samples (Frank, 1991a; Frank and Frank, 1990a; Frank et al., 1991a; Wiedmann et al., 1994), coastal air samples (Frank et al., 1991a; Von Düszeln and Thiemann, 1985; Wiedmann et al., 1994) and Antarctic air samples (Rasmussen et al., 1981) were analysed in this way. Class and Ballschmiter (1987a) used mass spectrometry to identify the CHCs while the quantification was done by ECD.

Flame ionization detectors (FID) allow a wider range of detectable compounds (Cronn and Nutmagul, 1982; Greenberg and Zimmermann, 1984; Penkett et al., 1993; Boudries et al., 1994; Greenberg et al., 1994). Bianchi and Varney (1993) splitted the separated NMHCs, including MAHs and CHCs, from estuarine air samples into two streams: 50% to FID detection and 50% to ion trap mass spectrometer detection in order to assure identification and

quantification.

Further on, mass spectrometry provides identification as well as quantification for a wide range of compounds (Penkett et al. 1982; Ciccioli et al., 1993; Helmig and Greenberg, 1994, Dewulf et al., 1995).

A very sensitive detection system with a wide range of detectable VOCs is the system described by Rudolph and Jebsen (1983) and by Rudolph et al. (1986). Rudolph et al. (1984) applied this system for Atlantic air samples. It consists of three detectors placed in series with in front two non-destructive detectors (photoionization detector, PID, followed by ECD) and at the end of the analytical line a FID. The PID guarantees a high sensitivity for aromatic compounds and alkenes, the ECD provides low detection limits for CHCs and chlorofluorocarbons (CFCs) while the FID detector assures the wide range of compounds.

I.1.1.2.4. Limits of detection and reproducibility

I.1.1.2.4.1. Limits of detection

The limit of detection (LOD, defined as a signal to noise ratio of three) depends on three factors of the analytical procedure. The first factor determining the LOD is the volume of the sample which can be concentrated and introduced in the GC-detection system. This volume is limited by the capacity of the sampling system and of the preconcentration system, and by the moisture content which may be introduced in the analytical tool. Further on, the sensitivity of the detector determines the LOD. Finally the blank result of the whole procedure, including sampling and analysis, limits the LOD.

Some reported LODs are presented in Table I.1.2. With a combination of preconcentration and ECD-detection, very low detection levels of 0.1-5pptv are obtained for CHCs (Fabian and Gömer, 1984; Class and Ballschmiter, 1987a; Koppmann et al., 1993; Rudolph et al., 1986; Rudolph et al., 1984; Wiedmann et al., 1994). PID-detection of MAHs allowed measurements of 0.2-3ppt concentrations (Rudolph et al., 1986; Rudolph et al., 1984). Mass spectrometry is reported for detection of both CHCs and MAHs. The LOD ranges from about 1pptv (Helmig and Greenberg, 1994; Dewulf et al., 1995) to 200-800pptv (Hsu et al., 1991), depending on the preconcentrated volumes, the compounds, the background levels and the detection modes (e.g. single ion monitoring versus full scan detection in quadrupole type MS systems.

I.1.1.2.4.2. Reproducibility

Some reproducibility data are presented in Table I.1.2. In general, relative standard deviations (%SD) less than 10% are achievable. Reproducibilities decrease for measurements in the low ppt range, where relative standard deviations can be up to 20 (Wiedmann et al., 1994) or 30% (Class and Ballschmiter, 1987a; Dewulf et al., 1995).

I.1.1.2.5. Calibration techniques

A simple way to calibrate air samples is the direct injection of a liquid solution in the GC-injector. Wiedman et al. (1994) applied external liquid calibration with standard solutions in n-pentane for the quantification of tetrachloroethylene in air samples taken at remote sites in both hemispheres. A lot of publications where VOCs in air are measured do not mention a calibration method (Cronn and Nutmagul, 1982; Khalil et al., 1983; Frank and Frank, 1990a; Frank et al., 1991; Ciccioli et al., 1993; Helmig and Greenberg, 1994). Probably calibration in these investigations is done by external calibration by means of direct liquid injection.
In the gravimetric preparation of gas standard mixtures, VOCs are weighted accurately and subsequently diluted with a clean gas in a closed system (Frank et al., 1991b; Hisher and Grosjean, 1991; Hsu et al., 1991; Koppmann et al., 1993; Bianchi and Varney, 1993; Boudries et al., 1994; Koppmann et al., 1994).
In a third method, commercially available cylinders containing certified gas calibration mixtures are used. They are at ppmv or ppbv concentrations. If pptv concentrations are necessary dilutions of the ppmv or ppbv mixtures have to be done (Greenberg et al., 1994).
Finally, the permeation tube technique (Berezkin and Drugov, 1991), the dynamic vapour pressure method (Schoene and Steinhanses, 1991) and the closed two phase system method (Dewulf et al., 1995) have to be mentioned as usefull calibration methods.

Table I.1.2. Reported limits of detection (LODs, in pptv) and relative standard deviations (%SD, in %) values for several analytical methods determining CHCs and MAHs concentrations.[1]

VOCs	Sampling / preconcentration	Detection	LOD	%SD	Reference
CHCs + MAHs	Sorbent/CF	50%FID/50%MS	0.025-0.1	10	Bianchi and Varney, 1993
Benzene	Sorbent/CF	FID	13	6	Boudries et al., 1994
Toluene	Sorbent/CF	FID	11	3	Boudries et al., 1994
CCl_4, TTCE	Cryosampling	ECD	0.1-3	5-10	Fabian & Gömer, 1984
TTCE	Sorbent/CF	ECD	0.1-5	10-15/<30[2]	Class & Ballschmiter, 1987a
1,2-DCE	Sorbent/CF	ECD	1-5	10-15/<30[2]	Class & Ballschmiter, 1987a
CHCs+MAHs	Sorbent/CF	MS	0.47-1.25	0.6-7.3/21-39[3]	Dewulf et al., 1995
MAHs	Canister/CF	FID	25	-	Greenberg & Zimmerman,1984
Benzene	Cryosampling	FID	0.3	5-7	Greenberg et al., 1994
Toluene	Cryosampling	FID	0.3	5-7	Greenberg et al., 1994
CHCs+MAHs[4]	Sorbent/CF	MS	1.9-222	-	Helmig & Greenberg, 1994
TRI	Sample loop	ECD	500	4.1-4.5[5]	Hisham & Grosjean, 1991
TTCE	Sample loop	ECD	200	4.1-4.5[5]	Hisham & Grosjean, 1991
CHCs+MAHs	Canister/CF	MS	400-800	2-5	Hsu et al., 1991
TCE, TTCE	Cryosampling	ECD	0.1	<10	Koppmann et al., 1993
MAHs	Canister/CF	FID	2-5[6]	-	Penkett et al., 1993
Aromatics	Canister/CF	PID[7]	0.2-2	±5	Rudolph et al., 1986
CHCs	Canister/CF	ECD[7]	0.1-0.5	±5	Rudolph et al., 1986
Benzene	Canister/CF	PID[7]	0.3-3	3-15	Rudolph et al., 1984
CHCs	Canister/CF	ECD[7]	0.1-1	3-15	Rudolph et al., 1984
TTCE	Sorbent/CF	ECD	0.2-1	20	Wiedmann et al., 1994

[1] Abbreviations: TTCE: tetrachloroethylene; 1,2-DCE: 1,2-dichloroethane; TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; CF: cryofocussing; [2] 10-15% at 10pptv; to 30% below 10pptv; [3] 0.6-7.3% at 30-350pptv; 21-39% at 7-19pptv; [4] Chloroform, tetrachloromethane, 1,1,1-trichloroethane, tetrachloroethylene, benzene and toluene; [5] on slope of calibration curve; [6] blanks: benzene 8pptv, toluene 27pptv; [7] in PID-ECD-FID configuration

I.1.2. MEASUREMENT RESULTS

I.1.2.1. CHCs

I.1.2.1.1. CHCs in coastal, bay and estuarine air samples

Data on CHCs concentrations in coastal, bay and estuarine air are presented in Table I.1.3. Levels of tetrachloroethylene at the Atlantic coast south of Lisbon are elevated, two to three times higher than at remote sites like Madeira (Frank et al., 1991a). Differences in trichloroethylene levels were even more pronounced since the atmospheric lifetime of this compound is only about one week. 1,1,1-trichloroethane levels exhibited only marginal differences. Chloroform levels, being high in comparison with non-coastal remote sites, suggest natural biotic or abiotic sources, as already mentioned by Class and Ballschmiter (1987b). Khalil et al. (1983) reported similar observations. They stated that atmospheric chloroform may be largely natural in origin, rather than only anthropogenic as previously thought.

The measurements of CHCs in the coastal city Bremen showed concentration levels similar to those of other West German cities. Concentrations were some factors higher than those over the Atlantic, except for tetrachloromethane (Von Düszeln and Thiemann, 1985). Various local sources were identified for the CHCs, except for tetrachloromethane.

The highest reported CHCs concentrations at coastal sites are the data for 1,1,1-trichloroethane and tetrachloroethylene at the semi-industrialized Southampton estuary (Bianchi & Varney, 1993). The Southampton estuary accomodates a wide range of industries and activities including a large petrochemical complex and an electric power generating plant. The winter and summer concentrations of the CHCs are similar, whereas for MAHs a significant difference is noticed.

Table I.1.3. CHCs in coastal, bay and estuarine air samples (pptv) [1]

Location	Date	$CHCl_3$	CCl_4	TRI	TCE	TTCE	Reference
Atl. Coast (Portugal)	3/85					25	Class & Ballschmiter, 1987a
Atl. Coast (Portugal)	88-89	19 - 875	30 - 226	52 - 350	18 - 265	14 - 280	Frank et al., 1991a
Coast of Bretagne (Fr.)	9/85					19	Class & Ballschmiter, 1987a
Coast of Bretagne (Fr.)	9/85					19	Wiedmann et al., 1994
German Bay	7/82					20	Class & Ballschmiter, 1987a
Californian Coast (U.S.)	'87-'88					8 - 26	Wiedmann et al., 1994
Near Melbourne (Austr.)	11/81	21 ± 3					Khalil et al., 1983
Bremen, urban coast (Ger)	9/81-9/82	52	62	410	141	470	Von Düszeln & Thiemann,1985
Southampton Est. (Eng.)	Sum. '91			35 - 14900		14 - 3400	Bianchi & Varney, 1993
Southampton Est. (Eng.)	Wint. '91			174 - 15700		56 - 4700	Bianchi & Varney, 1993

[1] Abbreviations: TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene.

I.1.2.1.2. CHCs in island air samples

A lot of data on tetrachloroethylene measurements at island locations are available (Table I.1.4). The tetrachloroethylene concentration levels are low, within the 2-28pptv range except higher levels for Madeira (Frank et al., 1991a) and for the San Nicolas Island (Hisham and Grosjean, 1991), where concentrations up to 700pptv are observed. Similar concentrations are noticed for chloroform, 1,2-dichloroethane and trichloroethylene. Higher concentrations are reported for tetrachloromethane on island sampling sites (45-160pptv), whereas for 1,1,1-trichloroethane 70-208pptv levels are observed, including those measured at Madeira by Frank et al. (1991a). However, the measurements at San Nicolas Island (Hisham and Grosjean, 1991) showed again elevated concentration.

I.1.2.1.3. CHCs in remote continental air samples

Some CHCs measurements at remote continental sites are presented in Table I.1.5. The data for chloroform at a German forest (Ciccioli et al., 1993), in the German Alps (Kirschmer and Ballschmiter, 1983), at a remote Belgian rural site (Dewulf et al., 1995), at remote Canadian sites (Wofsy et al., 1994) and at the South Pole (Khalil et al., 1983) are in the same low concentration range as those over open seas (Table I.1.6), in the free troposphere (Table I.1.7) or at some islands (Table I.1.4).

Higher concentrations are reported for some German forests (Frank and Frank, 1990a; Frank et al., 1991a) and at the foot of the Everest (Ciccioli et al., 1993) though the authors considered the anthropogenic sources at the latter site as non-existent.

Except the 4.5-101pptv concentrations at the foot of the Everest (Ciccioli et al., 1993), the tetrachloromethane concentrations (44-151pptv) are similar to those measured over open seas (Table I.1.6), in the free troposphere (Table I.1.7) and at Island locations (Table I.1.4). 1,1,1-trichloroethane and trichloroethylene showed concentrations of 64-157 and 64-159pptv at all sites, except for the Black Forest where concentrations up to 696 and 353pptv were measured respectively (Frank and Frank, 1990a; Frank et al., 1991a). Tetrachloroethylene shows similar data but with some lower concentrations at the German Alps (Kirschmer and Ballschmiter, 1983) and at remote Canadian sites (Wofsy et al., 1994).

Table I.1.4. CHCs concentration on islands (pptv) [1]

Location	Date	$CHCl_3$	CCl_4	DCE	TRI	TCE	TTCE	Reference
Azores	3/82	32	160	16	208	16	16	Class & Ballschmiter, 1986a
Azores	6/82	13	106		138	<5	13	Kirschmer & Ballschmiter,1983
Azores	6/82						22	Class & Ballschmiter, 1987a
Azores	6/82						22	Wiedmann et al., 1994
Madeira	3/84, 8/84	13 - 36	130 - 145	<3 - 29	150 - 196	<3 - 29	7 - 22	Class & Ballschmiter, 1986a
Madeira	3/82, 6/82	19 - 21	95 - 103		139 - 148	<2 - 13	9 - 26	Kirschmer & Ballschmiter,1983
Madeira	'82, '84						4 - 28	Class & Ballschmiter, 1987a
Madeira	'88, '89	39 - 390	45 - 120		70 - 174		<70 - 700	Frank et al., 1991a
Tenerife	10/85						7 - 20	Class & Ballschmiter, 1987a
Tenerife	10/85						7 - 24	Wiedmann et al., 1994
Maldives	3/86						2 - 8	Class & Ballschmiter, 1987a
Maldives	3/86						2 - 8	Wiedmann et al., 1994
Bermuda	7/85	12	120	<3	132	<3	<3	Class & Ballschmiter, 1986a
Bermuda	7/85						2	Class & Ballschmiter, 1987a
Mauna Loa	7/88						3	Wiedmann et al., 1994
Mauna Loa	8/92	9.7	105		146		2.9	Helmig & Greenberg, 1994
Moorea Island	3/89						2.0	Wiedmann et al., 1994
Reunion (Indic)	3/87						2.2	Wiedmann et al., 1994
San Nicolas	6-9/87				550 - 570		420 - 700	Hisham & Grosjean, 1991

[1] Abbreviations: DCE: 1,2-dichloroethane; TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene.

Table I.1.5. CHCs in remote continental air (pptv) [1]

Location	Date	$CHCl_3$	CCl_4	DCE	TRI	TCE	TTCE	Reference
Black Forest (Ger.)[2]	'86 - '88	68 - 88	75 - 90		217 - 263	79 - 97	154 - 168	Frank & Frank, 1990a
Black Forest (Ger.)	'88 - '89	<19 - 390	45 - 151		52 - 696	17.7 - 353	42 - 1260	Frank et al., 1991a
Pine forest (Ger.)	7/91	23	44		85		42	Ciccioli et al., 1993
Wooded area (It.)	2/92		47		110		63	Ciccioli et al., 1993
Alps (Ger.)	1/82	19	80		86	6	15	Kirschmer & Ballschmiter,1983
Nukerke, rural site (Bel.)	2/95	13.5 - 18.5	66 - 72	6.8 - 8.9	99 - 144	145 - 159	31 - 33	Dewulf et al., 1995
Remote sites (Can.) [3]	'90	5.1			155		12	Wofsy et al., 1994
Foot of Everest, 5050m	9-10/91	43 - 272	4.5 - 101		64 - 157	64	224	Ciccioli et al., 1993
South Pole	'75 - '80		120 - 135		45 - 102			Rasmussen et al., 1981
South Pole	1/79, 1/81	16 ± 2						Khalil et al., 1983

[1] Abbreviations: DCE: 1,2-dichloroethane; TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene.

[2] For chloroform 90-percentile concentration range of 4 sites; for other CHCs mean concentration range of 4 sites.

[3] Remote sites in Canada: Hudson Bay lowlands, Ontario, Labrador, Quebec and coastal areas

Frank and Frank (1990a) occasionally measured relatively high atmospheric chloroform levels although the anthropogenic emissions were known to be small. The authors suggested other sources like biogenic formation or anthropogenic precursors. Concentrations being 25-150 times the atmospheric concentrations were detected in soil air and indicated that some of the atmospheric chloroform originated there. It has been suggested that chloroform arises from decarboxylation of trichloroacetic acid (Frank et al., 1989).

I.1.2.1.4. CHCs concentrations at open sea areas

Measured data on CHCs concentrations at open seas are presented in Table I.1.6. Chloroform data are all within a 8.8-45pptv range except the north-eastern Atlantic measurements in 1972 with levels below 1pptv (Murray and Riley, 1973). Tetrachloromethane data are similar to other remote air concentrations (71-154pptv) except some higher measurements of Hunter-Smith et al. (1983) for the Atlantic, and the extreme low data for the NE Atlantic reported by Murray and Riley (1973). The tetrachloromethane concentrations of Lovelock et al. (1973) over the Atlantic are lower than the other values, probably due to lower anthropogenic inputs at that time.

A similar concentration range is reported for 1,1,1-trichloroethane. The levels for trichloroethylene and tetrachloroethylene vary much more with data below 1 or about 1pptv up to 22pptv for trichloroethylene and up to 20-40pptv for tetrachloroethylene. The lower trichloroethylene concentrations reflect the short atmospheric lifetime, as suggested by Koppmann et al. (1993).

I.1.2.1.5. CHCs in the free troposphere and in the stratosphere

Measurements of CHCs in the free troposphere are presented in Table I.1.7. The data for chloroform, tetrachloromethane, 1,1,1-trichloroethane and trichloroethylene are all within a factor of 2, whereas for tetrachloroethylene concentrations from 4 to 167pptv are reported.

Table I.1.6. CHCs concentrations over open seas (pptv) [1]

Location	Date	$CHCl_3$	CCl_4	DCE	TRI	TCE	TTCE	Reference
NE Atlantic	7-8/72	0.14 - 0.91	0.03 - 0.11			0.18 - 3.89	0.14 - 1.26	Murray & Riley, 1973
Atlantic, N. hemisphere	'83		84		111	<18	27	Von Düszeln&Thiemann,1985
N. Atlantic	3/85						18 - 25	Wiedmann et al., 1994
N. Atlantic	3/85	24	140	28	179	7	27	Class & Ballschmiter, 1986a
N. Atlantic	3/85						18	Class & Ballschmiter, 1987a
Atlantic, N. hemisphere	8-9/89					0.3 - 15	<1 - 10	Koppmann et al., 1993
S. Atlantic	3/85	14	140	<3	141	<3	11	Class & Ballschmiter, 1986a
S. Atlantic[2]	3/85						8	Class & Ballschmiter, 1987a
S. Atlantic[3]	3/85						2.3	Class & Ballschmiter, 1987a
S. Atlantic [4]	3/85						2.3 - 13	Wiedmann et al., 1994
Atlantic, S. hemisphere	8-9/89					0.6 ± 0.1	2.7 ± 0.1	Koppmann et al., 1993
Atlantic	'71 - '72		71.2 ± 6.9					Lovelock et al., 1973
Atlantic (48N - 65 S)	9-11/81		135-240					Hunter-Smith et al., 1983
Atlantic (35 N)	-	31.4 ± 6.0	82 ± 5		73.5 ± 7.2	6.0 ± 4.7	34.2 ± 8.3	Penkett, 1982
Atlantic (77S - 45 N)	'82 - '83						±1 - 35	Rudolph et al., 1984
NW Pacific (45N)	'75 - '80		130 - 154		87 - 156			Rasmussen et al., 1981
NW Pacific	3/76	8.8 ± 2.7	122 ± 13.1		94.5 ± 8.2	20 ± 3.9	15.6 ± 4.6	Cronn et al., 1977
E Pacific, N. hemisphere	12/81	21	135		156	12	29	Singh et al., 1983
E Pacific, S. hemisphere	12/81	11	128		116	<3	5	Singh et al., 1983
Cape Meares Oregon(45N)	'77 - '82	45 ± 5						Khalil et al., 1983
Barrow, Alaska (72 N)	2-12/81	39 ± 2						Khalil et al., 1983
Cape Kumukahi, Hawaii	2-7/81	32 ± 4						Khalil et al., 1983
Marshall Islands (10N)	7-10/81	26 ± 6						Khalil et al., 1983
Samoa (20 S)	2-12/81	21 ± 2						Khalil et al., 1983
Biskaya	3/85	42	140	42	214	22	38	Class & Ballschmiter, 1986a
N. Sea (W. of Denmark)	7/82						20	Wiedmann et al., 1994

[1] Abbreviations: DCE: 1,2-dichloroethane; TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene; [2] Influenced by South Africa; [3] Inner tropical Convergence; [4] Influenced by South Africa: industrial Cape region

Table I.1.7. CHCs concentrations in the free troposphere (pptv) [1]

Location	Date	$CHCl_3$	CCl_4	TRI	TCE	TTCE	Reference
N. Atlantic	'87		91 - 107	180 - 233			Penkett et al., 1993
N. Atlantic	'87		109 - 134	156 - 209		4 - 23	Penkett et al., 1993
N. Atlantic	'87		120 - 135	157 - 283		15 - 167	Penkett et al., 1993
Pacific	11/78-1/79			134 ± 14			Cronn & Nutmagul, 1982
N. hemisphere	'78	29 ± 7			117 ± 4	56 ± 11	Rasmussen & Khalil, 1982
S. hemisphere [2]	11/81	14 - 20	141 - 147	123 - 127		8 - 14	Rasmussen et al., 1982
S. hemisphere	'78	29 ± 4			90 ± 3	14 ± 4	Rasmussen & Khalil, 1982

[1] Abbreviations: TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene

[2] 30-40S, 138-146E, 0-4km

Rasmussen et al. (1982) found declining chloroform concentrations with increasing height (0-4km). The observed gradient was explained by a one-dimensional steady state model based on a diffusion equation and on a lifetime of four months. For compounds like tetrachloromethane, 1,1,1-trichloroethane and tetrachloroethylene, there was no difference in the concentrations in the boundary layer and those above the boundary layer. The authors explained this by the better atmospheric stability of these compounds. On the contrary, Rasmussen and Khalil (1982) found strong evidence that 1,1,1-trichloroethane, tetrachloroethylene and chloroform were all significantly more abundant in the boundary layer than above it in the tropical region.

The results of Rasmussen and Khalil (1982) for the northern and southern hemisphere were consistent with global sources and life times of the trace gases.

Tetrachloromethane and 1,1,1-trichloroethane concentration profiles from 0 to 26km were measured by Fabian and Gömer (1984). They found exponential decrease in concentration with increasing height, starting with ground levels of ±150 and 100-180pptv and ending with concentrations of ±0.1-1 and ±1pptv above 20km, respectively.

I.1.2.2. ATMOSPHERIC MAHS IN THE FREE TROPOSPHERE, AT OCEANIC, COASTAL, ESTUARINE AND REMOTE CONTINENTAL SITES

Measurement of atmospheric MAHs in the free troposphere, at oceanic, coastal, estuarine and remote continental sites are presented in Table I.1.8. The lowest concentrations are those in the free troposphere and over oceans (from 1.8 to 203pptv, except some benzene concentrations in the free troposphere over the North Atlantic in 1989 (Penkett et al., 1993)). The data on concentrations at coastal and estuarine sites show a wide range with low benzene and toluene concentrations at the Pacific coast (Robinson et al., 1973) and with some extreme concentrations in winter 1991 above 100ppbv for all individual compounds (Bianchi and Varney, 1993).

Remote continental atmospheric MAHs measurements revealed concentrations typically in the 40-1000pptv range. Only toluene showed some higher concentrations at the foot of the mount Everest (Ciccioli et al., 1993).

Table I.1.8. Atmospheric MAHs at different sampling sites (pptv)

Location	Date	Benzene	Toluene	Et-benzene	o-Xylene	m/p-Xylene	Reference
1. Free troposphere							
Near and above Britain	'82-'86	79 - 203					Lightman et al., 1990
North Atlantic	'88	9 - 195	2 - 164		<5 - 54	<5 - 52	Penkett et al., 1993
North Atlantic	'89	90 - 302	9 - 181		<5 - 29	<5 - 56	Penkett et al., 1993
2. Oceanic sites							
Atlantic (35N)	-	66 ± 32	16.8 ± 10.4				Penkett, 1982
Atlantic (77S-45N)	'82-'83	10 - 160	<3 - 140				Rudolph et al., 1984
Pacific (Mauna Loa)	5-6/88	11 - 24	3 - 12				Greenberg et al., 1992
Pacific[1]	5/87	20 - 40					Greenberg et al., 1992
Pacific (Mauna Loa)	8/92	8.3	1.8				Helmig & Greenberg, 1994
3. Coasts, estuaries							
Pacific coast, Washington	-	25	5				Robinson et al., 1973
Bretagne coast (Fr.)	2/92-2/93	71 - 360	160 - 650	24 - 290	18 - 180	37 - 410	Boudries et al., 1994
Southampton Est.	summ. '91	330 - 15850	1160 - 19400	263 - 14880	504 - 17050	990 - 18500	Bianchi & Varney, 1993
Southampton Est.	winter '91	1600-148500	2600 -238400	1160-174700	1230-175400	1700-196300	Bianchi & Varney, 1993
4. Remote continental sites							
Storkow, pine forest (Ger.)	7/91	161	472	103	90	169	Ciccioli et al., 1993
Wooded area (It.)	2/92	917	1015	145	208	337	Ciccioli et al., 1993
Foot of Mount Everest[2]	9-10/91	80 - 593	35 - 7920	110 - 458	204	436 - 763	Ciccioli et al., 1993
Nukerke, rural site (Bel.)	2/95	220 - 231	307 - 347	95 - 98	94 -95	148 - 152	Dewulf et al., 1995
Background, Brazil	'79-'80	310 - 720	40 - 190	510 - 1010	40 - 140	40 - 280	Greenberg & Zimmermann,1984
Remote sites (Can.)[3]	Summ. '90	56					Wofsy et al., 1994

[1] 400km northwest of Honolulu; [2] at 5050m; [3] remote sites: Hudson Bay Lowlands, Ontarion, Labrador, Quebec and coastal areas

Penkett et al. (1993) observed a pronounced seasonal variation for benzene and toluene over the northern Atlantic, with a summer maximum and a winter minimum. The positive correlation between the winter to summer concentration ratio and the reaction rate constant with the OH-radical strongly suggested that the hydroxyl chemistry is responsible for the seasonal cycle.

Boudries et al. (1994) divided the air masses at the coast of Brittany in France in five classes, based on meteorological data. They defined continental air masses, North Sea air masses, England air masses, stagnant oceanic air masses moving slowly to the coast and oceanic air masses, moving fastly to the coast. For the continental air masses high winter and low summer NMHCs concentrations were observed. This was explained by higher summer OH-radical concentrations and confirmed by a plot of winter to summer concentration ratios of the organic compounds as a function of their OH-radical rate constant.

The composition of the North Sea air masses were close to the composition of the continental air masses. The sources suggested were oil drilling platforms, natural emissions by the sea for some compounds, mixing with land emissions along the trajectory, marine traffic exhausts and possible local contamination over the site itself.

The England air masses, staying for one day or more above England and for an average time of 6 hours above the English Channel before reaching the coast, show concentrations of the same order of magnitude as in the case of continental air masses. The air parcels can be loaded as well by English urban regions as by sea emissions or marine traffic exhaust. The concentrations showed a similar winter to summer ratio.

The stagnant oceanic air masses exhibited lower concentrations than England air masses, which was explained by the absence of continental contamination. However, levels were higher than for oceanic air masses. Two hypotheses were made. Diffusion of polluted air from the continent can explain these concentrations. Secondly, the long over-ranging of the air masses above the ocean under stable atmospheric conditions can lead to the accumulation of oceanic emissions in the boundary layer.

The oceanic air masses, with high winter and low summer concentrations showed the lowest levels. The alkane chemistry demonstrated the long-range transport of light alkanes from the American continent. The most reactive alkanes showed now the lowest winter to summer ratios. The rapid decrease in concentrations during summer from the high reactive compounds reaching the background level (since the ocean acts as a buffer) explained the negative correlation between the winter to summer ratio and the OH-radical rate constant. Since the

OH-radical rate constants for MAHs are of the same order of magnitude as those for alkanes, a similar long-range transport of MAHs can be supposed.

I.1.3. SOURCES AND FATE

I.1.3.1. SOURCES

In general all mentioned CHCs and MAHs are from anthropogenic activities like the winning of oil, production of chemicals, marine and continental transport or from their applications and uses of the compounds.

Chloroform has known marine natural sources. Penkett (1982) suggested natural sources for chloroform because of equal distribution in both hemispheres, even though it should be removed by atmospheric oxidation and because of its rather small anthropogenic release. Another source could be larger indirect anthropogenic sources. Khalil et al. (1983) concluded that tropical oceans are a source of chloroform to the atmosphere. The estimated magnitude of the flux is uncertain but probably greater than $0.15 Tg.yr^{-1}$, and estimated as $0.35 Tg.yr^{-1}$. At higher latitudes, colder water and smaller supersaturations of chloroform coupled with uncertainties in determining the flux made it impossible to prove that regions of the ocean there also release chloroform to the atmosphere. Nightingale et al. (1995) explained the production of chloroform by marine macroalgae by the presence of a chloroperoxydase enzyme.

Besides the marine source of chloroform, the decarboxylation of trichloroacetic acid in forest soil air is already mentioned (Frank et al., 1983).

I.1.3.2. FATE

Based on emission data Wiedmann et al. (1994) applied a three box model in order to investigate the environmental fate for tetrachloroethylene. The model is presented in Figure I.1.2. Emissions were proposed for anthropogenic halocarbons as 95% for the 30-60°N latitudes, as 2% for the 30°N-30°S latitudes and as 3% for the 30-40°S latitudes. Exchange times for the flux from troposphere to stratosphere were calculated as 10 year for 30-90°N,

2.5 year for 15°S-30°N and no flux for the 15-90°S box. Washout fluxes for tetrachloroethylene were considered to be negligible in comparison to other tropospheric fluxes. The oceans were supposed to be in equilibrium with the troposphere, whereas the atmospheric inputs (479kt .yr^{-1}) were estimated to be removed by tropospheric degradation (441kt.yr^{-1}) and by stratospheric sink (38kt.yr^{-1}).

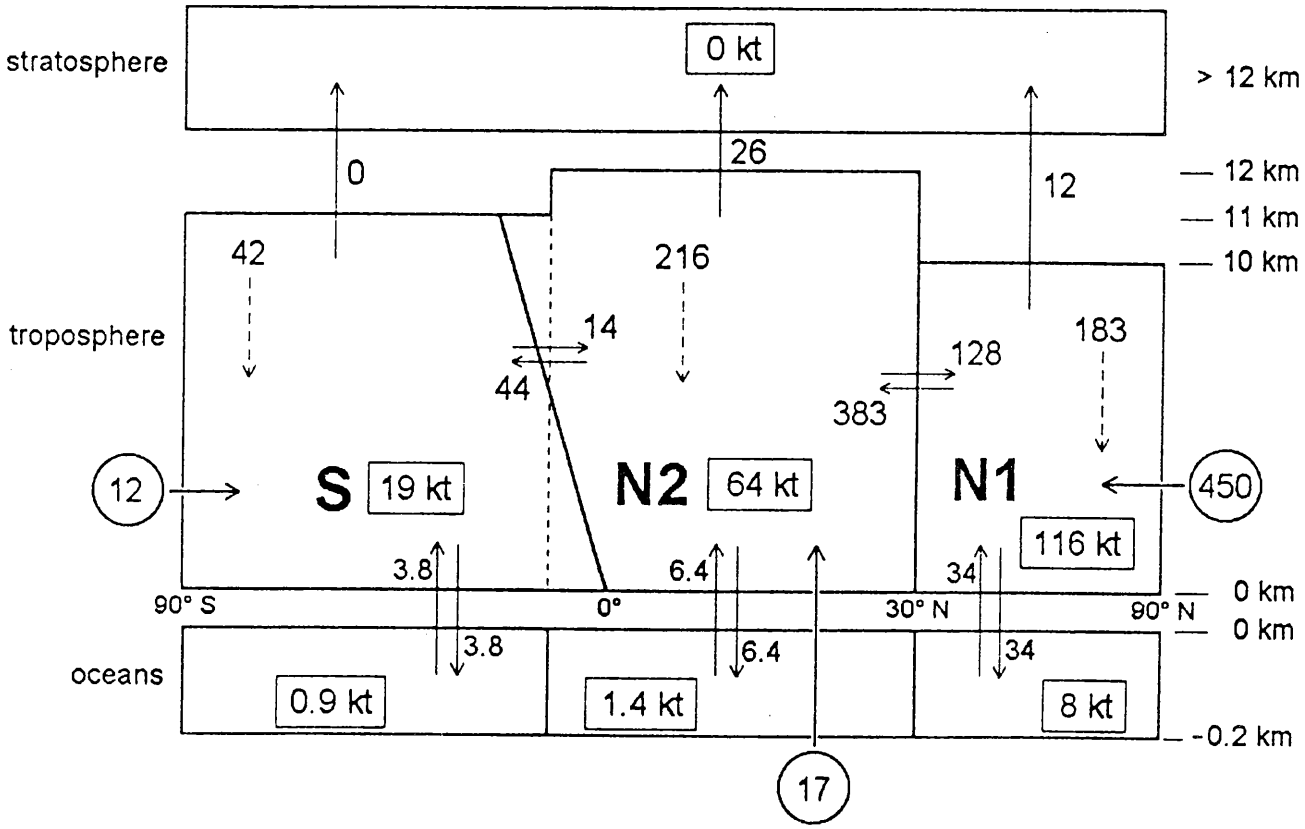


Figure I.1.2. Global model for tetrachloroethylene with estimations of intercompartment mass fluxes (Wiedmann et al., 1994). The model boxes are the three tropospheric compartments S (0-90°S), N1 (30-90°N) and N2 (0-30°N), three oceanic boxes with a mixing depth of 200m and one stratospheric box. Encircled figures are input data for the three tropospheric model boxes (kt.yr^{-1}). Figures in rectangular boxes represent the burdens (kt) in each model box. Arrows indicate the fluxes between all model boxes (kt.yr^{-1}). Dashed arrows represent the losses by degradation in the tropospheric model boxes (kt.yr^{-1}).

The major input in the atmosphere is the 30-90°N section (450kt.yr^{-1}) where 183kt.yr^{-1} is degraded and 12kt.yr^{-1} is exchanged with the stratosphere. After exchange with the 0-30°N compartment the major sink is localized in this latter section (216kt.yr^{-1} tropospheric degradation and 26kt.yr^{-1} exchange to the stratosphere), while 42kt.yr^{-1} is degraded in the 15-90°S box where no stratospheric exchange occurs. In conclusion, atmospheric breakdown by photoreactions is the most important removal process for volatile compounds with characteristics like tetrachloroethylene. About 90% of the anthropogenically produced tetrachloroethylene is photochemically degraded.

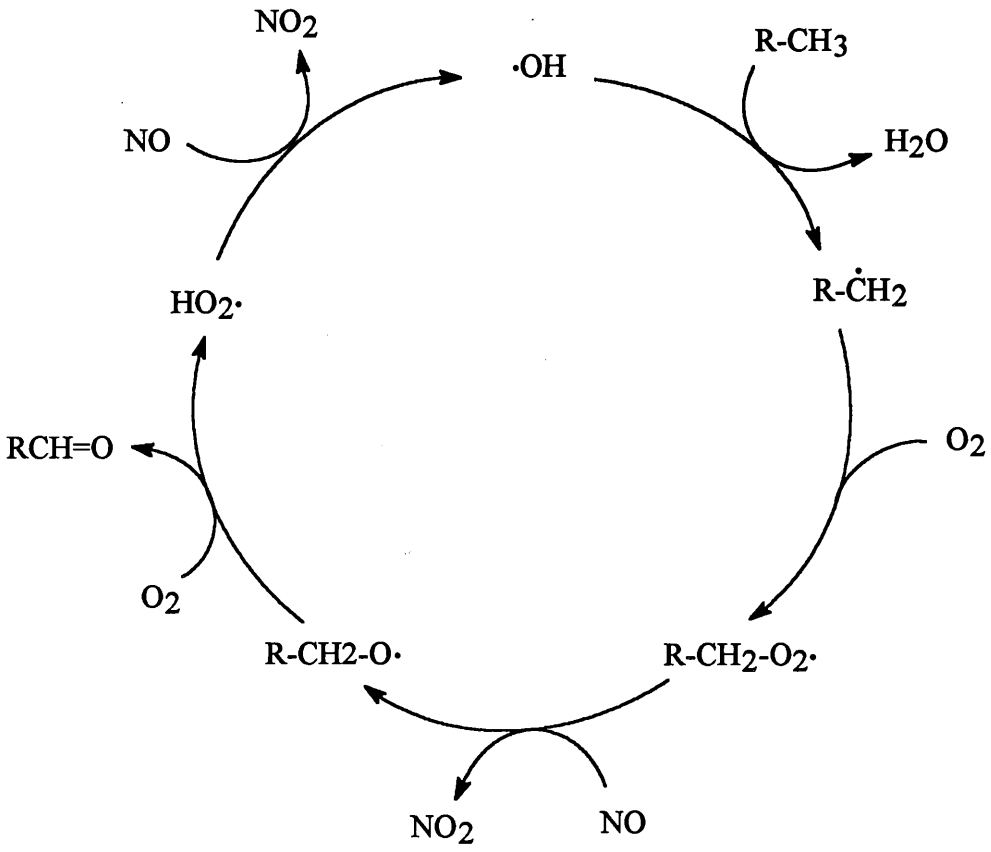
I.1.3.2.1. Photochemical degradation

I.1.3.2.1.1. Photochemical stability of MAHs

In the seventies the first experiments were carried out in order to investigate the atmospheric stability of monocyclic aromatic hydrocarbons. Davis et al. (1975) showed that the reaction of benzene and toluene with OH-radicals was an important removal process. Later on, it was proved that reactions of MAHs with atmospheric oxidants such as O_3 and nitrate radicals (during the night time) were much slower. In this respect, the reaction with OH-radicals is almost the only reaction to be considered (Table I.1.9). Further degradation processes depend on the presence of atmospheric compounds, especially NO_x species. When NO_x are present, the following oxidation cycle for alkylated compounds can be drawn.

Table I.1.9. Reaction rate constants of MAHs with some atmospheric species at normal temperature and pressure.

Species	k ($cm^3.molecule^{-1}.s^{-1}$)	Reference
OH·	$1.59\ 10^{-12}$ (benzene)	Davis et al., 1975
	$6.11\ 10^{-12}$ (toluene)	
O_3	$< 1.10^{-20}$	Atkinson & Carter, 1984
NO_3·	$1\ 10^{-17}$ - $1\cdot 10^{-16}$	Atkinson, 1989



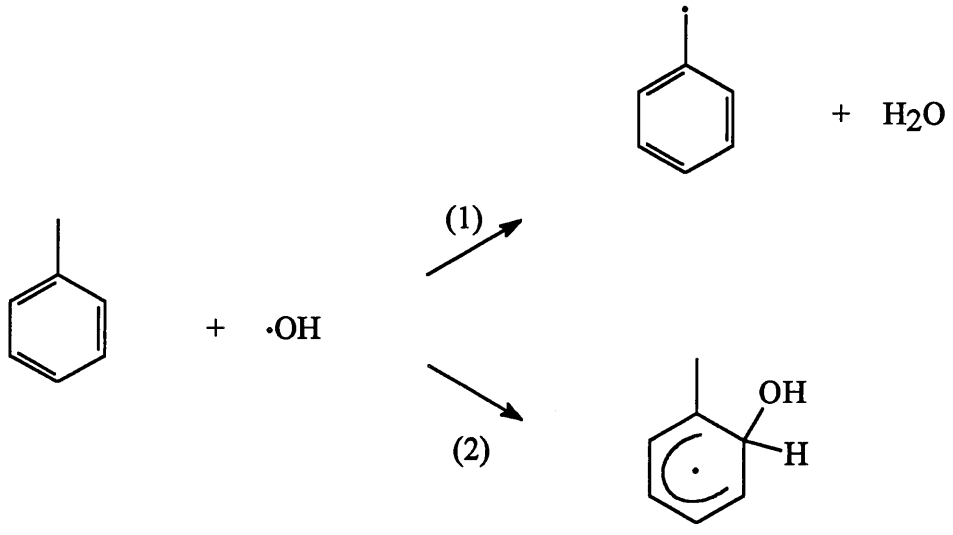
The degradation reaction of MAHs with OH-radicals is a first order reaction in the MAHs and in the OH-radical (Carter, 1990):

$$v = - \frac{d[MAH]}{dt} = k'.[MAH].[OH\cdot]$$

When the degradation at one location is considered, an average OH-radical concentration can be assumed, whether daily, seasonally or yearly averaged. Hence, the degradation reaction can be written as a first order reaction in the MAH concentration:

$$\frac{d[MAH]}{dt} = - k \, . \, [MAH]$$

Two mechanisms occurs: hydrogen radical abstraction and an OH-radical addition:



(1) H-radical abstraction
(2) OH-radical addition

I.1.3.2.1.1.1. Hydrogen atom abstraction

By the reaction of MAHs with OH-radicals producing water, a side chain-H is abstracted from the substituted MAHs. For benzene a ring-H has to be abstracted. This reaction obviously is slower. The temperature dependancy of these reactions is determined by the Arrhenius equation (Table I.1.10):

$$k_1 = A_1 \cdot e^{-E_1 / R.T}$$

The velocity of the reaction is decreasing with decreasing temperature.

Table I.1.10. Arrhenius constants for H-abstraction of MAHs by reaction with OH-radicals (Perry et al., 1977).

MAH	A_1 ($cm^3.molecule^{-1}.s^{-1}$)	E_1 ($kJ.mol^{-1}$)
Benzene	$39.8\ 10^{-12}$	16.7
Toluene	$5.01\ 10^{-12}$ *	3.76 *
o-Xylene	$5.01\ 10^{-12}$	1.25
m-Xylene	$50.1\ 10^{-12}$	9.61
p-Xylene	$63.1\ 10^{-12}$	10.0

*According to Zetsch et al. (1989) $A_1 = 2\ 10^{-12}$ and $E_1 = 3.28$.

I.1.3.2.1.1.2. OH-radical addition

The reaction of MAHs with OH-radicals producing OH-adducts, gives an unstable intermediair. The energy-rich OH-adduct can split again into the former MAH and the OH-radical or it is stabilized (thermalized) (Atkinson et al., 1979).
In this reaction the kinetics were studied using the Arrhenius equation (Perry et al., 1977) (Table I.1.11):

$$k_2 = A_2 \cdot e^{-E_2 / R.T}$$

It is remarkable that for all MAHs, except benzene, the reaction is increasing with decreasing temperature since chemical reactions usually go faster at higher temperatures.

Table I.1.11. Arrhenius parameters for OH-radical addition reactions of MAHs with OH·. (Perry et al., 1977).

MAH	A_2 (cm^3/molecule.s)	E_2 (kJ/mol)
Benzene	$5.01\ 10^{-12}$, $2.3\ 10^{-12}$ *	+3.77, 1.30*
Toluene	$3.16\ 10^{-13}$, $1.9\ 10^{-13}$ *	-6.69, -8.65*
o-Xylene	$3.98\ 10^{-12}$	-2.93
m-Xylene	$20.08\ 10^{-12}$	-0.42
p-Xylene	$6.31\ 10^{-12}$	-2.51

*According to Zetsch et al., 1989

I.1.3.2.1.1.3. Global reaction velocity with OH-radicals

The global reaction velocity of MAHs with OH-radicals consists of two pseudo-first order reactions:

$$k = k_1 + k_2$$

with k_1 and k_2 the first order reaction rate constants of the H-abstraction and the OH-radical addition reaction, respectively.

It is clear from the Arrhenius equations that the OH-addition is the most important reaction at environmental temperatures (Table I.1.12). Only at higher temperatures H-abstraction is important. This was shown by Perry et al. (1977) by comparison of the toluene-d8 degradation rate constants with those of toluene. At room temperature the k value for toluene-d8 is within 5% of that for toluene, while for higher temperatures (159°C) the rate is a factor 2.5 lower. Within a temperature range like 0-25°C the reaction velocity varies only slightly. E.g. the k_2 value for toluene at 25°C ($4.7\ .10^{-12}$ $cm^3.molecule^{-1}.s^{-1}$) is 80% of the rate constant at 0°C ($6.0\ .10^{-12}$ $cm^3.molecule^{-1}.s^{-1}$). More recent data indicate a temperature independance for C_2-MAHs (Atkinson, 1990). In Table I.1.13 an overview of experimentally determined rate constants is given.

Table I.1.12. Rate r = fraction H-abstraction/ (fraction H-abstraction+fraction OH-addition) for the reaction of MAHs with OH-radicals at room temperature (298K) (Atkinson et al., 1990)

MAH	r
Benzene	0.05
Toluene	0.12
o-Xylene	0.10
m-Xylene	0.04
p-Xylene	0.08

Table I.1.13. Experimental rate constants for the reaction of OH-radicals with MAHs at 298±5K.

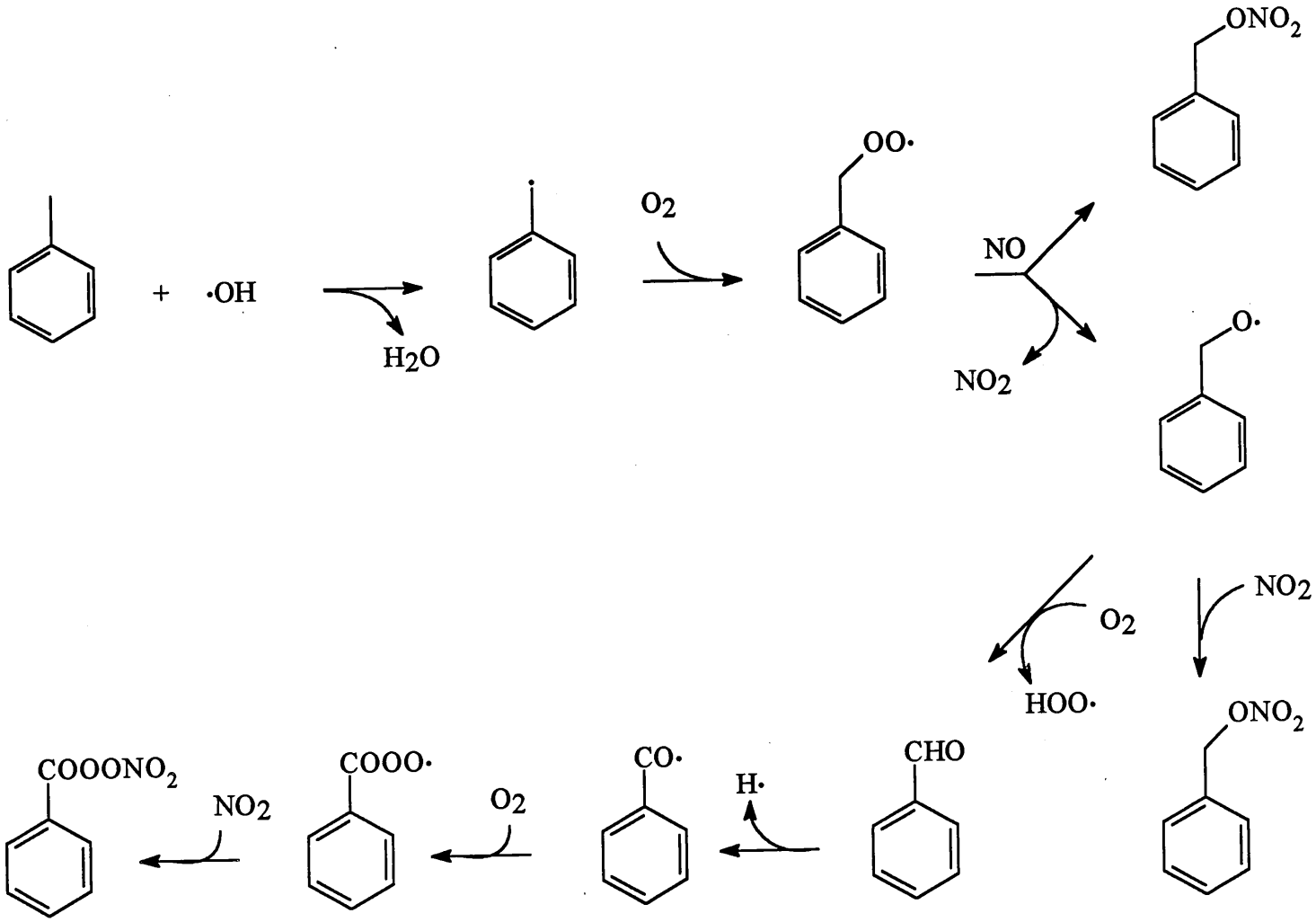
MAH	k ($cm^3.molecule^{-1}.s^{-1}$)	reference
Benzene	$1.59 .10^{-12}$	Davis et al., 1975
	$1.24 .10^{-12}$	Hansen et al., 1975
	$<2.6 .10^{-12}$	Doyle et al., 1975
	$1.20 .10^{-12}$	Perry et al., 1977
	$0.80 .10^{-12}$	Cox et al., 1980
	$1.24 .10^{-12}$	Tully et al., 1981
	$0.93 .10^{-12}$	Barnes et al., 1982
	$1.16 .10^{-12}$	Lorenz & Zellner, 1983
	$0.88 .10^{-12}$	Wahner & Zetsch, 1983
	$1.02 .10^{-12}$	Rinke & Zetsch, 1984
	$1.53 .10^{-12}$	Ohta & Ohyama, 1985
	$1.22 .10^{-12}$	Edney et al., 1986
	$1.05 .10^{-12}$	Witte et al., 1986
	$1.29 .10^{-12}$	Wallington et al., 1987
	$1.11 .10^{-12}$	Knispel et al., 1990
	$1.17 .10^{-12}$	Semadini et al., 1995

(continued)

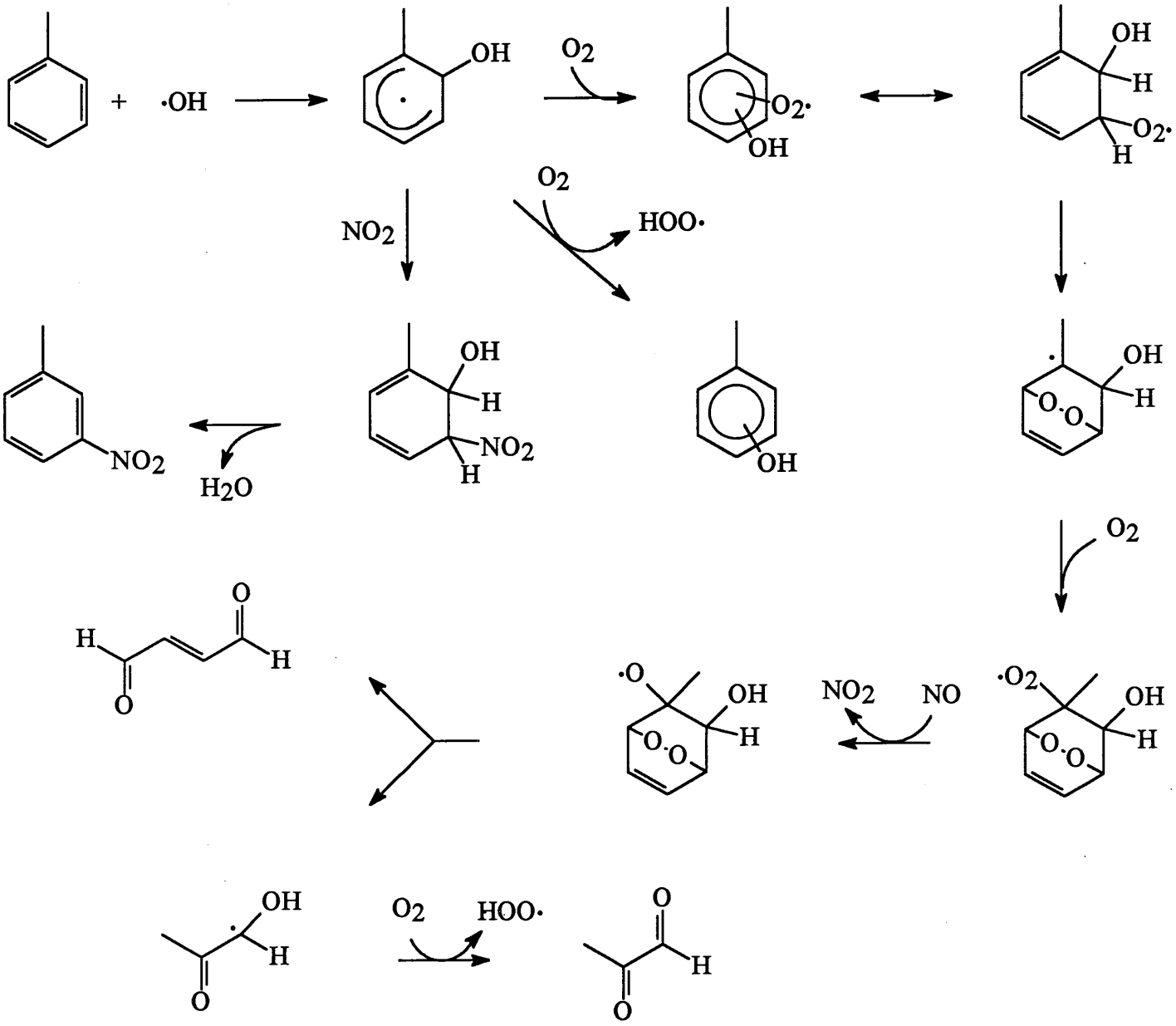
Toluene	$6.11 .10^{-12}$	Davis et al., 1975
	$5.78 .10^{-12}$	Hansen et al., 1975
	$3.7 .10^{-12}$	Doyle et al., 1975
	$6.40 .10^{-12}$	Perry et al., 1977
	$7.2 .10^{-12}$	Cox et al., 1980
	$6.36 .10^{-12}$	Tully et al., 1981
	$6.37 .10^{-12}$	Ohta & Ohyama, 1985
	$5.44 .10^{-12}$	Edney et al., 1986
	$5.48 .10^{-12}$	Atkinson & Aschmann, 1989
	$6.66 .10^{-12}$	Knispel et al., 1990
	$6.00 .10^{-12}$	Finlayson-Pitts et al., 1993
	$6.03 .10^{-12}$	Semadini et al., 1995
Et-benzene	$7.95 .10^{-12}$	Ravishankara et al., 1978
	$6.84 .10^{-12}$	Ohta & Ohyama, 1985
o-Xylene	$15.3 .10^{-12}$	Hansen et al., 1975
	$14.3 .10^{-12}$	Perry et al., 1977
	$12.4 .10^{-12}$	Ravishankara et al., 1978
	$13.3 .10^{-12}$	Cox et al., 1980
	$13.2 .10^{-12}$	Ohta & Ohyama, 1985
m-Xylene	$23.6 .10^{-12}$	Hansen et al., 1975
	$24.0 .10^{-12}$	Perry et al., 1977
	$20.6 .10^{-12}$	Ravishankara et al., 1978
	$18.6 .10^{-12}$	Cox et al., 1980
	$23.4 .10^{-12}$	Ohta & Ohyama, 1985
p-Xylene	$12.2 .10^{-12}$	Hansen et al., 1975
	$15.3 .10^{-12}$	Perry et al., 1977
	$10.5 .10^{-12}$	Ravishankara et al., 1978
	$13.6 .10^{-12}$	Ohta & Ohyama, 1985

I.1.3.2.1.1.4. Further degradation processes

The further degradation processes of the MAHs after reaction with OH-radicals are not fully clear but a series of degradation products are identified (Carter, 1990). For toluene for instance, approximately 10% of the degradation occurs by H-atom abstraction to form benzaldehyde and benzyl nitrate in the presence of NO (Atkinson, 1990). Cresols account for 25% of the overall OH-radical reactions and glyoxal plus methylglyoxal, together with their co-products, account for approximately 25% of the reaction, although the co-products are not known. The remaining reaction products, accounting for approximately 40% of the overall OH-radical reaction, are not quantitatively known, although a variety of ring-cleavage products have been observed (Atkinson, 1990).



Several breakdown pathways are proposed. After H-abstraction the formed radical (toluene radical for instance) reacts with oxygen to produce a toluene peroxy-radical (Atkinson et al., 1979). This radical reacts with NO to benzyl nitrate or to a new oxygen-radical. This latter radical undergoes a reaction with NO_2 or with oxygen to produce benzyl nitrate or benzaldehyde respectively. The benzaldehyde can further transform into peroxybenzoyl nitrate when NO_x species are present.



The OH-adduct (toluene for instance) undergoes several reactions. A first reaction with oxygen results in cresol after H-abstraction by oxygen. A second reaction pathway, with oxygen, gives rise to an oxygen adduct. This new radical undergoes different ring openings. Degradation to 2-oxo-propanal and 2-butene-1,4-dial are occurring (Carlier et al., 1988). Finally, NO_2 addition at the OH-adduct of toluene followed by loss of water produces 3-nitrotoluene.

The reaction kinetics of the OH-adduct with N-oxides and with oxygen are presented in Table I.1.14.

The atmospheric degradation and halflife times of MAHs depend on the OH-radical concentrations. This radical rises from fotochemical reactions. Several estimations of the MAHs half life times are made in literature and they are listed in Table I.1.15. The reported half life times are mainly based on k values and on estimated atmospheric OH-radical concentrations.

Table I.1.14. First order reaction constants ($cm^3.molecule^{-1}.s^{-1}$) for OH-adducts of benzene, toluene and p-xylene with N-oxides and oxygen.

MAH	k_{NO}	k_{NO2}	k_{O2}	T (K)	Reference
Benzene			$<1 .10^{-15}$		Perry et al., 1977
			$\leq 2 .10^{-16}$		Zellner et al., 1985
	$1. 10^{-14}$	$2.75 .10^{-11}$	$5.4 .10^{-16}$	300-319	Knispel et al., 1990
	$<3 .10^{-14}$	$2.5 .10^{-11}$	$3.0 .10^{-16}$	300	Koch et al., 1993
Toluene	$3 .10^{-14}$	$3.6 .10^{-11}$	$1.88 .10^{-16}$	299-333	Knispel et al., 1990
	$<3 .10^{-14}$	$3.6 .10^{-11}$	$5.5 .10^{-16}$	300	Koch et al., 1993
p-Xylene	$<10 .10^{-14}$	$3.2 .10^{-11}$	$8 .10^{-16}$	300	Koch et al., 1993

Table I.1.15. Estimated atmospheric halflife times of MAHs.

MAH	$t_{1/2}$ (days)	Reference	Remarks
Benzene	1.75	Ravishankara et al., 1978	30°N,Summer,[OH]=4.10^{6}molec.cm^{-3}
	7.0	Ravishankara et al., 1978	30°N,Winter,[OH]=1.10^{6}molec.cm^{-3}
	3.5	Ravishankara et al., 1978	70°N,Summer,[OH]=2.10^{6}molec.cm^{-3}
	15.5	Semadini et al., 1995	277K, relative to 1,1,1-trichloroethane
	3.9	Singh et al., 1985	[OH]=2.5 .10^{6}molec.cm^{-3} at day (16h)
	4.8	Greenberg & Zimmerman, 1984	tropic [OH]=2 .10^{6}molec.cm^{-3} (24h)
	15	Greenberg & Zimmerman, 1984	global [OH]=6.5 .10^{5}molec.cm^{-3} (24h)
	10	Greenberg et al., 1992	[OH] =1.10^6 molec.cm^{-3}
Toluene	8.3	Singh et al., 1981	[OH] =2.10^6 molec.cm^{-3} (12h)
	0.5	Ravishankara et al., 1978	30°N,Summer,[OH]=4.10^{6}molec.cm^{-3}
	2.0	Ravishankara et al., 1978	30°N,Winter,[OH]=1.10^{6}molec.cm^{-3}
	1.0	Ravishankara et al., 1978	70°N,Summer,[OH]=2.10^{6}molec.cm^{-3}
	2.7	Semadini et al., 1995	277K, relative to 1,1,1-trichloroethane
	40	Zetsch et al., 1989	300K, 100ppt NO_2
	4	Zetsch et al., 1989	300K, 30ppb NO_2
	3	Zetsch et al., 1989	273K, 30ppb NO_2
	0.8	Singh et al., 1985	[OH]=2.5 .10^{6}molec.cm^{-3} at day (16h)
	0.9	Greenberg & Zimmerman, 1984	tropic [OH]=2 .10^{6}molec.cm^{-3} (24h)
	2.8	Greenberg & Zimmerman, 1984	global [OH]=6.5 .10^{5}molec.cm^{-3} (24h)
	1.8	Greenberg et al., 1992	[OH] =1.10^6 molec.cm^{-3}
Ethylbenzene	0.33	Ravishankara et al., 1978	30°N,Summer,[OH]=4.10^{6}molec.cm^{-3}
	1.42	Ravishankara et al., 1978	30°N,Winter,[OH]=1.10^{6}molec.cm^{-3}
	0.71	Ravishankara et al., 1978	70°N,Summer,[OH]=2.10^{6}molec.cm^{-3}
	0.58	Singh et al., 1985	[OH]=2.5 .10^{6}molec.cm^{-3} at day (16h)
	1.4	Singh et al., 1981	[OH] = 2.10^6 molec.cm^{-3} (12h)
o-Xylene	0.23	Ravishankara et al., 1978	30°N,Summer,[OH]=4.10^{6}molec.cm^{-3}
	0.92	Ravishankara et al., 1978	30°N,Winter,[OH]=1.10^{6}molec.cm^{-3}
	0.46	Ravishankara et al., 1978	70°N,Summer,[OH]=2.10^{6}molec.cm^{-3}
	0.38	Singh et al., 1985	[OH]=2.5 .10^{6}molec.cm^{-3} at day (16h)
	0.8	Singh et al., 1981	[OH] = 2.10^6 molec.cm^{-3} (12h)
m-Xylene	0.15	Ravishankara et al., 1978	30°N,Summer,[OH]=4.10^{6}molec.cm^{-3}
	0.58	Ravishankara et al., 1978	30°N,Winter,[OH]=1.10^{6}molec.cm^{-3}
	0.29	Ravishankara et al., 1978	70°N,Summer,[OH]=2.10^{6}molec.cm^{-3}
	0.21	Singh et al., 1985	[OH]=2.5 .10^{6}molec.cm^{-3} at day (16h)
	0.5	Singh et al., 1981	[OH] = 2.10^6 molec.cm^{-3} (12h)
p-Xylene	0.27	Ravishankara et al., 1978	30°N,Summer,[OH]=4.10^{6}molec.cm^{-3}
	1.08	Ravishankara et al., 1978	30°N,Winter,[OH]=1.10^{6}molec.cm^{-3}
	0.54	Ravishankara et al., 1978	70°N,Summer,[OH]=2.10^{6}molec.cm^{-3}
	0.42	Singh et al., 1985	[OH]=2.5 .10^{6}molec.cm^{-3} at day
	0.9	Singh et al., 1981	[OH]=2.10^6 molec.cm^{-3} (12h)

I.1.3.2.1.2. Photochemical stability of CHCs in the atmosphere

I.1.3.2.1.2.1. Reaction kinetics

The basic atmospheric reaction of CHCs is the reaction with OH-radicals. Franklin (1994) reports the reaction rate constants of tetrachloroethylene with several atmospheric oxidants: k_{OH}=1.2 10^{-13}cm^3.molec.$^{-1}$.s^{-1}, k_{O3}<2 10^{-23}cm^3.molec.$^{-1}$.s^{-1}, k_{NO3}<5.2 10^{-17}cm^3.molec.$^{-1}$.s^{-1}, k_{OH2}<1 10^{-17}cm^3.molec.$^{-1}$.s^{-1}. Some reported data on the atmospheric reaction rates of trichloroethylene and tetrachloroethylene with NO_3 en O_3 are presented in Table I.1.16. These figures illustrate the low reaction rates versus the reaction rates with OH-radicals. For chloroform, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane the reaction is a H-atom abstraction by which a halogenated alkyl radical and water is formed (Atkinson et al., 1979):

$$R\text{-}H + HO\cdot \rightarrow R\cdot + H_2O$$

Table I.1.16. Reaction rate constants of trichloroethylene and tetrachloroethylene with NO_3 and O_3 [1]

	k (cm^3.molecule^{-1}.s^{-1})	Reference
TCE + NO_3	2.9 .10^{-16}	Atkinson et al., 1992
	2.81 .10^{-16}	Atkinson, 1991
TCE + O_3	< 5 .10^{-20}	Atkinson et al., 1992
TTCE + NO_3	< 1 .10^{-16}	Atkinson et al., 1992
	< 5.2 .10^{-17}	Atkinson, 1991
	< 5.2 .10^{-17}	Franklin, 1994
TTCE + O_3	< 1 .10^{-21}	Atkinson et al., 1992
	< 2 .10^{-23}	Franklin, 1994

[1] Abbreviations: TCE: trichloroethylene; TTCE: tetrachloroethylene.

For trichloroethylene and tetrachloroethylene, addition of the OH-radical to the double bound gives an OH-adduct (Tuazon et al., 1988; Itoh et al., 1994):

$$Cl_2C{=}CCl_2 + HO\cdot \rightarrow HO\text{-}CCl_2\text{-}\cdot CCl_2$$

The reaction rate constant in both cases is to be considered as an Arrhenius function:

$$k = A \cdot e^{-E/R.T}$$

with A the Arrhenius constant (cm^3. $molecule^{-1}$. s^{-1}) and E the activation energy ($J.mole^{-1}$). Table I.1.17 summarizes results of experimental k, A and E determinations.

Table I.1.17. Experimental determinations of A, E and k values for the reaction of CHCs with OH-radicals (k at ±298K)[1]

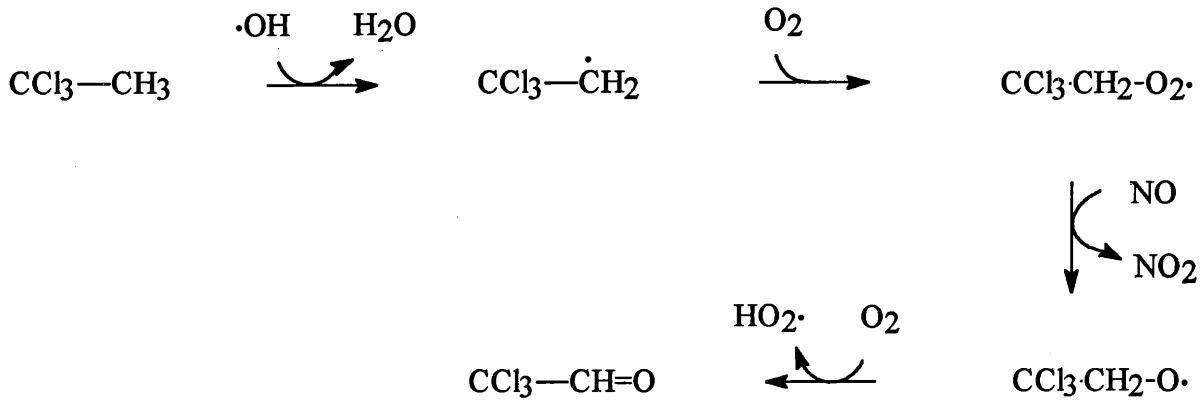
CHC	k (cm^3.$molecule^{-1}$.s^{-1})	A (cm^3.$molec.^{-1}$.s^{-1})	E ($kJ.mole^{-1}$)	Reference
$CHCl_3$	$10.1.\ 10^{-14}$			Howard & Evenson, 1976
	$18.0\ .10^{-14}$			Cox et al., 1976
	$11.4\ .10^{-14}$	$4.69\ .10^{-12}$	9.44	Davis et al., 1976
	$10.0\ .10^{-14}$	$3.3\ .10^{-12}$	8.56	Atkinson et al., 1992
CCl_4	$<0.4\ .10^{-14}$			Howard & Evenson, 1976
	$<0.01\ .10^{-14}$			Cox et al., 1976
	$<0.26\ .10^{-14}$			Barnes et al., 1982
	$<0.05\ .10^{-14}$	$1\ .10^{-12}$	2.26	Atkinson et al., 1992
1,1-DCE	$26.0.\ 10^{-14}$			Howard & Evenson, 1976
1,2-DCE	$22.0.\ 10^{-14}$			Howard & Evenson, 1976
TRI	$1.5.\ 10^{-14}$			Howard & Evenson, 1976
	$3.0\ .10^{-14}$			Cox et al., 1976
	$1.59.10^{-14}$	$3.72\ .10^{-12}$	13.55	Watson et al., 1977
	$0.95\ .10^{-14}$	$1.20\ .10^{-12}$	11.97	Atkinson et al., 1992
	$0.95\ .10^{-14}$	$1.75\ .10^{-12}$	12.89	Talukdar et al., 1992
	$1.09\ .10^{-14}$			Nelson et al., 1990
TCE	$220\ .10^{-14}$			Pearson, 1982
	$286\ .10^{-14}$			Edney et al., 1986
	$220\ .10^{-14}$	$0.5\ .10^{-12}$	3.70	Atkinson et al., 1992
TTCE	$17\ .10^{-14}$			Pearson, 1982
	$12\ .10^{-14}$			Franklin, 1994
	$17\ .10^{-14}$	$9.4\ .10^{-12}$	9.98	Atkinson et al., 1992

[1] Abbreviations: 1,1-DCE: 1,1-dichloroethane; 1,2-DCE: 1,2-dichloroethane; TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene.

I.1.3.2.1.2.2. Reaction mechanisms

I.1.3.2.1.2.2.1. H-atom abstraction: 1,1,1-trichloroethane

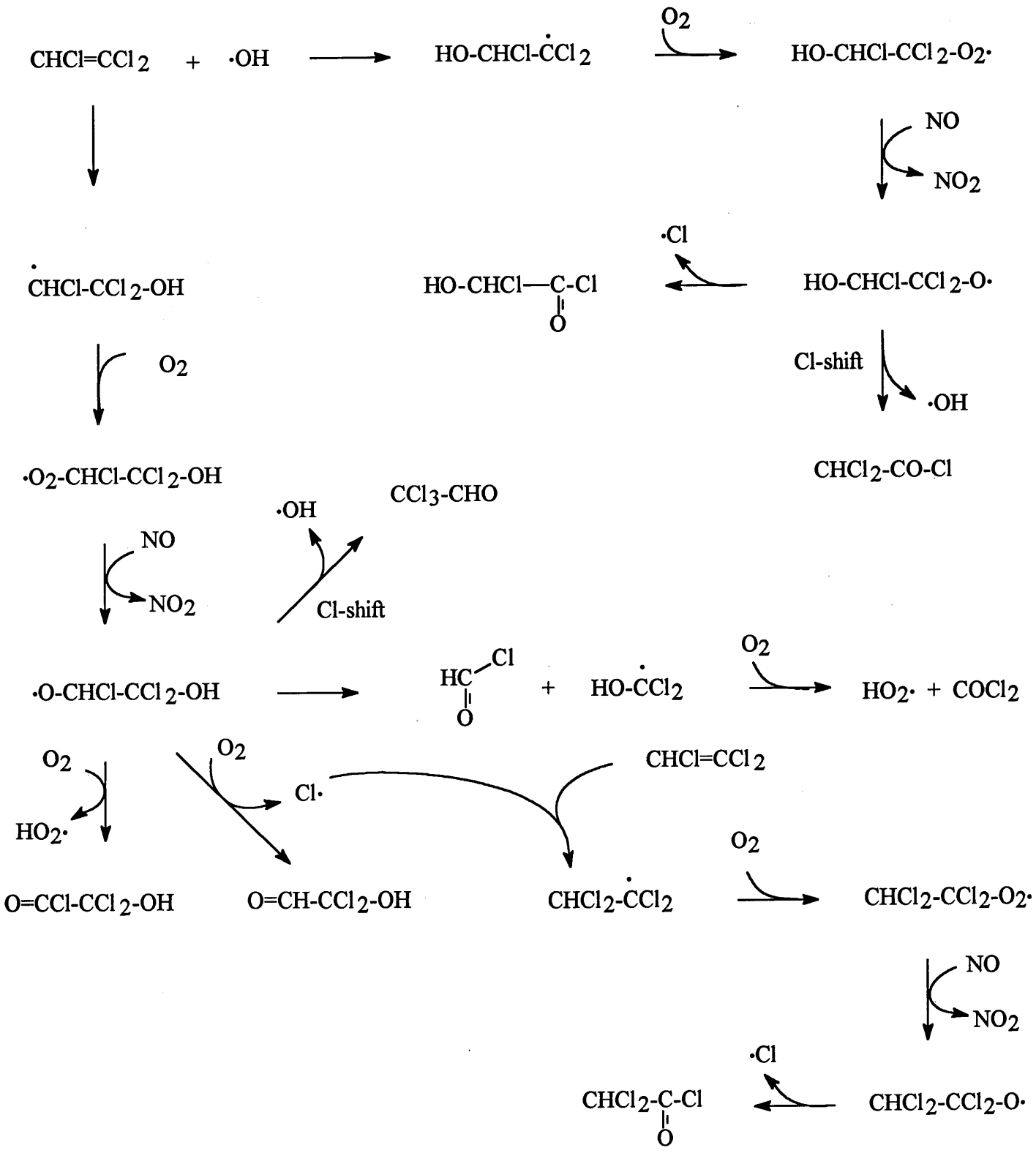
After H-atom abstraction by an OH-radical, the formed radical undergoes oxygen addition within 1μs (Platz et al., 1995). The $CCl_3CH_2O_2$-radical rapidly reacts with NO to produce NO_2 and a CCl_3CH_2O-radical. With a reaction constant of about $6.1.10^{-12}$ $cm^3.molecule^{-1}.s^{-1}$. together with a NO concentration of $2.5.10^{-8}$ $molecules.cm^{-3}$, the lifetime of the CCl_3CH_2O-radical was calculated to be less than 11 minutes (Platz et al., 1995). After reaction with oxygen, finally trichloroacetaldehyd is produced. The stability of trichloroacetaldehyde for the reaction with OH-radical is 290h, but in global, the atmosphere lifetime is considered to be a few hours (Barry et al., 1994).



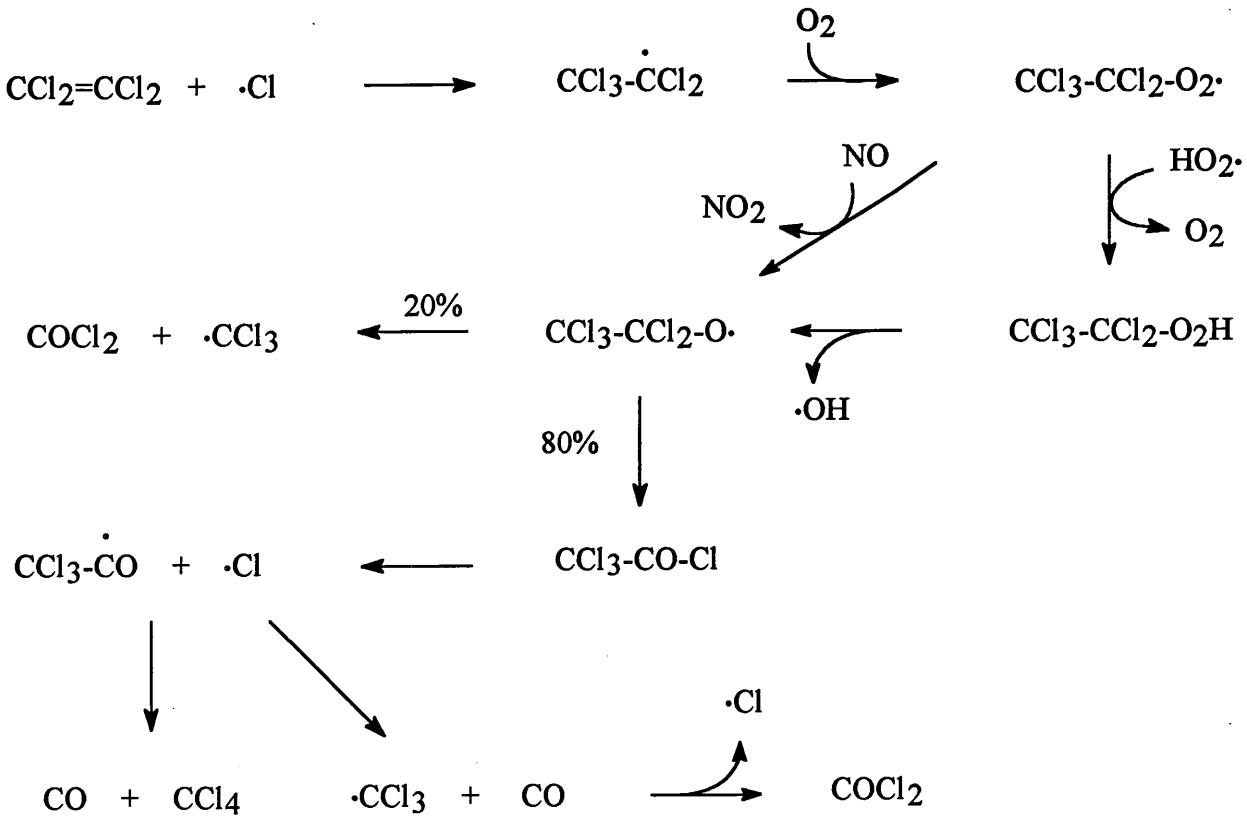
I.1.3.2.1.2.2.2. OH-radical addition: tetrachloroethylene

Tetrachloroethylene and trichloroethylene undergo a sequence of reactions in the atmosphere, starting with an OH-radical addition. The reactions are the same for both trichloroethylene and tetrachloroethylene (Itoh et al., 1994). CO, CO_2 and phosgene are produced from the two compounds, while dichloroacetyl chloride and chloroform are formed by degradation of trichloroethylene, where trichloroacetyl chloride and tetrachloromethane are reaction products of tetrachloroethylene.

Tuazon et al. (1988) proposed the following atmospheric reaction mechanism for trichloroethylene:



The formation of tetrachloromethane and phosgene from tetrachloroethylene (and chloroform and phosgene from trichloroethylene) are explained by the reaction of the compound itself with chlorine radicals (Itoh et al., 1994).



Itoh et al. (1994) found tetrachloromethane to be maximally 0.1% of tetrachloroethylene where Singh et al. (1975) found 8%. Trichloroacetyl chloride was confirmed to be the precursor of tetrachloromethane. In contrast to the closed reactor study, the Cl-atom attack on the OH-adduct of tetrachloroethylene is less probable in the atmosphere since the Cl-atom will be scavenged by other chemicals. Franklin (1994) concluded that the yield of tetrachloromethane from tetrachloroethylene in the troposphere has to be estimated much less than 0.2%.

I.1.3.2.1.2.3. Atmospheric half life times

Some literature data on estimated half-life times of CHCs are presented in Table I.1.18. The half life time ranges from about one week for trichloroethylene, over a few months for 1,1-di- and 1,2-dichloroethane, chloroform and tetrachloroethylene to years for 1,1,1-trichloroethane and tetrachloromethane.

Table I.1.18. Atmospheric half life times of CHCs [1]

CHCs	$t_{1/2}$	Reference	Remarks
$CHCl_3$	386d/39d	Class and Ballschmiter, 1986a	[OH]= 3.10^{-6}, and $0.3.10^{-6}$ cm^{-3}
	116d	Singh et al., 1981	[OH]=2.10^{-6} (12h)
CCl_4	$>10^4/>10^3$d	Class and Ballschmiter, 1986a	[OH]=3.10^{-6}, and $0.3.10^{-6}$ cm^{-3}
	>11600d	Singh et al., 1981	[OH]=2.10^{-6} (12h)
1,1-DCE	44d	Singh et al., 1981	[OH]=2.10^{-6} (12h)
1,2-DCE	175d/18d	Class and Ballschmiter, 1986a	[OH]= 3.10^{-6}, and $0.3.10^{-6}$ cm^{-3}
	53d	Singh et al., 1981	[OH]=2.10^{-6} (12h)
TRI	5.7±0.7y	Derwent et al., 1989	
	3215d/321d	Class and Ballschmiter, 1986a	[OH]= 3.10^{-6}, and $0.3.10^{-6}$ cm^{-3}
	6±1y	Midgley, 1989	
TCE	57d/6d	Class and Ballschmiter, 1986a	[OH]= 3.10^{-6}, and $0.3.10^{-6}$ cm^{-3}
	7d	Koppmann et al., 1993	
TTCE	227d/23d	Class and Ballschmiter, 1986a	[OH]= 3.10^{-6}, and $0.3.10^{-6}$ cm^{-3}
	0.4y	Koppmann et al., 1993	
	155d	Wiedmann et al., 1994	
	68d	Singh et al., 1981	[OH]=2.10^{-6} (12h)
	0.33y	Franklin, 1994	

[1] Abbreviations: 1,1-DCE: 1,1-dichloroethane; 1,2-DCE: 1,2-dichloroethane; TRI: 1,1,1-trichloroethane; TCE: trichloroethylene; TTCE: tetrachloroethylene.

I.1.3.2.2. Other processes

It is clear that other processes like water exchange, stratospheric exchange and long range advective transport (especially for more stable compounds) will determine the atmospheric concentrations, besides the photodegradation. However, the quantification of these processes

is difficult. But as already discussed, Wiedmann et al. (1994) estimated the importance of these processes for tetrachloroethylene by a global modelling.

I.1.4. CONCLUSIONS

Sorbent sampling, canister sampling as well as cryogenic sampling enable the determination of atmospheric CHCs and MAHs concentrations at remote sites. These sampling techniques combined with GC-analysis allow the detection of these VOCs at concentrations of about 1pptv.

In general, chloroform concentrations at coastal, bay and estuarine sites, on islands, in remote continental air, over open seas and in the free troposphere, concentrations are in the range of 10-50pptv. Exceptions are data presented by Frank and Frank (1990a), Frank et al. (1991a) and of Ciccioli et al. (1993). Most measured tetrachloromethane concentrations vary between 60 and 160pptv. Data on 1,2-dichloroethane are limited and show lower concentrations, i.e. in a 6.8-42pptv range. Concentrations of 1,1,1-trichloroethane at different sites are generally 50 to 300 pptv. The lowest trichloroethylene levels reported are those over open seas and at island sites (<1-30pptv), whereas in the free troposphere, at remote continental sites and at coastal sites concentrations of more than 100pptv are reported. The 1,1,1-trichloroethane concentrations are in general higher than those of other CHCs. This could be due to the higher production of 1,1,1-trichloroethane (e.g. 678 10^6kg in 1988 (Midgley, 1989)) and/or its lower atmospheric degradation rate. Tetrachloroethylene concentrations are generally between 1 and 40pptv, but some researchers measured concentrations higher than 150pptv at remote sites, like in the free troposphere above the North Atlantic (Penkett et al., 1993), in the Black Forest (Frank and Frank, 1990a; Frank et al., 1991a), at the foot of the Everest (Ciccioli et al., 1993) and at coastal sites (Frank et al., 1991a; Von Düszeln and Thiemann, 1985).

Less data are available on MAHs concentrations at remote sites. Levels below 10pptv are observed in the free troposphere (Penkett et al., 1993) and at oceanic sites (Greenberg et al., 1992; Helmig and Greenberg, 1994), but at the same sites and at coastal, estuarine, forest and rural sites levels above 100pptv are found (Penkett et al., 1993; Rudolph et al., 1984). Remote continental sites never showed levels below 40pptv for individual MAHs.

An important removal process of the mainly anthropogenic CHCs and MAHs is the reaction with photochemically produced OH-radicals, besides exchange with the stratosphere, as illustrated for tetrachloroethylene by Wiedmann et al. (1994). The reaction with OH-radicals

show atmospheric halflife times for MAHs estimated to be from below 1 day to a few days. CHCs have a better atmospheric stability, with halflife times from about one week (trichloroethylene) over a few months (chloroform, 1,1-dichloroethane, 1,2-dichloroethane, tetrachloroethylene) to several years (1,1,1-trichloroethane, tetrachloromethane).

I.1.5. REFERENCES

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I.2. WATER

I.2.1. SAMPLING AND ANALYSIS

Only these methods which have been used to analyse real river and marine water samples are discussed. More recent developments like solid phase microextraction and membrane introduction mass spectrometry, which have been evaluated mostly on running lab samples, are only briefly mentioned in this overview.

I.2.1.1. SAMPLING, PRETREATMENT AND STORAGE

I.2.1.1.1. Sampling equipment and contamination originating from the sampling material

Sampling techniques have to fulfill two main conditions. They have to enable technically the sampling on the site at the desired depth and the sample taken must be transferred without any loss or contamination to a further subsample device or directly to the analytical unit. Contamination generated outside the equipment and contamination generated from the sample equipment itself must be avoided.

I.2.1.1.1.1. Sampling equipment

Surface waters can be sampled by hand. This is done directly into glass bottles (Kummert et al., 1978; Comba and Kaiser, 1983) or 40mL EPA glass vials (Dawes and Waldock, 1994), usually at the side of a (rubber) boat, up to depths of 0.5m (Rogers et al., 1992). This sampling method avoids further transfer to subsamples for storage.
In order to take water samples at lower sampling depths several systems are commercially available. Some of them are presented in Figure I.2.1. Frequently used for chlorinated C_1- and C_2-hydrocarbons (CHCs) sampling are Teflon lined Niskin sampling bottles and Go Flo bottles (Krysell, 1992; Abrahamsson and Ekdahl, 1993; Dewulf and Van Langenhove, 1995). Sampling in this way to depths of 3000m is reported (Wallace et al., 1992). Usually 10L samplers are in use but 2.5L Niskin bottles (Fogelqvist, 1985) and 30L Niskin bottles

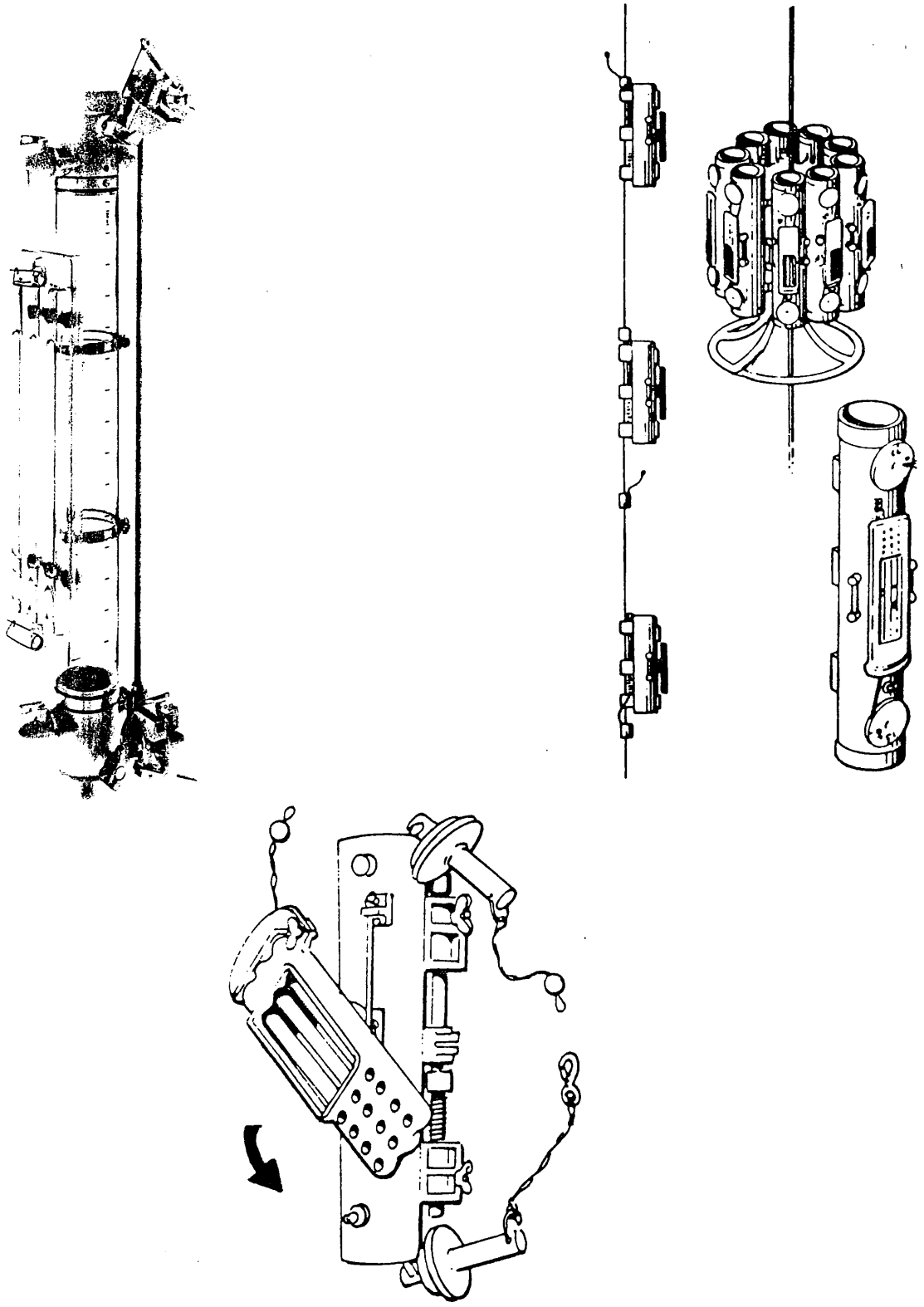

Figure I.2.1. Commercially available water samplers applied for measurements of CHCs and MAHs in river and marine waters. (a) Transparent Plastic Nansen (TPN) water sampler from Hydrobios. (b) Go-Flo sampling bottle from General Oceanics, presented individually, in a serial position and mounted on a Rosette. The bottle is initially loaded closed, is then opened hydrostatically and is subsequently closed. (c) Niskin water sampling bottle from General Oceanics, provided with a 3-thermometer reversing assembly. This type allows free-flushing until activation with a messenger.

(Gschwend et al., 1980) are reported too. This type of bottles can be mounted on a rosette sampler that allows simultaneous measurement of environmental parameters as salinity, temperature and pH (Fogelqvist, 1985; Krysell and Nightingale, 1994). Sauer et al. (1978), Sauer (1980), Brooks et al. (1981) and Dewulf and Van Langenhove (1995) reported the use of this samplers for monocyclic aromatic hydrocarbons (MAHs) measurements.

Transparent Plastic Nansen (TPN) water samplers from Hydro-Bios (FRG) are used by Swedish researchers (Fogelqvist et al., 1982; Fogelqvist, 1985; Fogelqvist and Krysell, 1986; Krysell et al., 1994). A few British researchers take water samples in Winchester bottles (Harper et al., 1992; Rogers et al., 1992; Dawes and Waldock, 1994). They seal the bottles with a poly tetrafluoroethylene (PTFE) stopper which can be lifted by means of a second cord when the sampler is at the required depth. Afterwords the stopper is reseated in the sample bottle neck by a spring (Law et al., 1988). A similar system is used by Petty (1981) for the sampling of marine waters to measure benzene at ppt concentrations. A 1-L glass bottle is evacuated and subsequently connected to a glass tube. After positioning this evacuated system at the desired depth a messenger breaks the sealed-glass tube and the bottle is filled.

I.2.1.1.1.2. Contamination generated by sampling materials

Since all sampling techniques are based on a closed system contamination only arises from the sampling system itself. Sauer (1980) measured 1.6ng.L^{-1} benzene and 1.5ng.L^{-1} toluene in deep water samples (1000m). This indicated that the Niskin bottles used did not contribute to higher contamination than the levels found. Similarly Brooks et al. (1981) did not report any difference between samples taken with a submersible pumping system, Go Flo bottles or Bodman bottles for MAHs at ng.L^{-1} levels in shelf sea waters. (For n-C_6 and n-C_7 compounds Sauer et al. (1978) found higher levels in samples from Go Flo bottles than in samples taken with glass bottles.)

On the contrary Fogelqvist (1985) stated that samples taken with Niskin bottles resulted in 10 to 20% higher concentrations than those from a TPN sampler at levels below 1ng.L^{-1} and 2ng.L^{-1} tetrachloromethane and 1,1,1-trichloroethane, respectively. Moreover, at the same concentrations trichloroethylene measurements were impossible with Niskin bottles, due to contamination. Measurements from samples taken with a pumping system were only possible after installing an appropiate pump since a first pump caused contamination.

Krysell and Wallace (1988) reported Arctic Ocean samples with 1,1,1-trichloroethane below the detection limit (0.053ng.L^{-1}). They concluded that contamination during sampling was negligible, but the sampling apparatus, probably Niskin or TPN materials, are not mentioned. In addition, Wallace et al. (1992) held Niskin bottles with Arctic Ocean water on-deck for 6 hours. No changes of 1,1,1-trichloroethane and tetrachloromethane were found.
In conclusion, no MAHs contamination from usual sampling materials is reported, where for some CHCs at extreme low levels (<1ng.L^{-1}), like in polar seas, contamination problems arising from the sampling equipment are reported, e.g. from Niskin sampling bottles and from a pumping system.

I.2.1.1.2. Pretreatment and storage

Ones the water sample is taken it is transferred to a subsample bottle for storage until analysis. The sampling bottle itself can be stored, especially in case of surface water samples taken by hand (Kummert et al., 1978; Sauer et al., 1978; Schwarzenbach et al., 1979; Comba and Kaiser, 1983; Gomez-Belinchon et al., 1991; Harper et al., 1992; Rogers et al., 1992). Because of the volatility of the compounds samples need to be stored in bottles without any headspace to avoid air-water partitioning (Brooks et al., 1981; Czuczwa et al., 1988).
For short storage times (≤ 1 day), e.g. when the analysis of CHCs with electron capture detection is done on board of a research vessel, no sample pretreatment is done (Rogers et al., 1992; Krysell, 1992; Abrahamsson and Ekdahl, 1993; Krysell and Nightingale, 1994; Krysell et al., 1994). For such short storage times, no losses are expected without any pretreatment since Petty (1981) found losses of benzene to be insignificant after three days storage without any pretreatment.
For longer storage times photochemical, chemical and microbiological breakdown have to be considered. Photochemical degradation can be prevented by storage in dark glass bottles. Microbiological degradation is slowed down by chilling at 4°C (Schwarzenbach et al., 1979; Czuczwa et al., 1988; Gomez-Belinchon et al., 1991; Dawes and Waldock, 1994). Khalil et al. (1983) reported storage at 0°C for CHCs samples. Storage at -30°C in stainless steel containers was applied by Zoccolillo and Rellori (1994) for Arctic surface water. Chemical products avoiding microbial breakdown like sodium azide (Sauer et al., 1978; Brooks et al., 1981; McDonald et al., 1988; Kristiansen et al., 1992), mercury dichloride at 67µM mercury (Gschwend et al., 1980) or hydrogen chloride (Dewulf and Van Langenhove, 1995) are added

to the sample to avoid losses. This latter technique, in which the pH is decreased to a value of 2, is recommended by the U.S. Environmental Protection Agency (Slater and Ho, 1989). Maskarinec et al. (1990) extensively studied the effects of the storage temperature and the effect of preservation agents on the stability of several CHCs and MAHs during storage. Without acidification they found dehydrohalogenation reactions of 1,1,2,2-tetrachloroethane to trichloroethylene and of 1,1,2-trichloroethane to dichloroethylene. Simultaneously degradation of aromatic compounds like toluene and ethylbenzene was observed after 28 days. But, the use of hydrochloric acid (pH=2), sodium bisulfate ($NaHSO_4$, pH=1.92) or ascorbic acid (pH=2.98) and storage at 4°C clearly increased the stability. Maximum holding times of at least 56 days are reported. The authors concluded to prefer sodium bisulfate or ascorbic acid since these acids are noncorrosive, inexpensive, easy available and nonvolatile.
The recovery of CHCs and MAHs during storage at 4°C with hydrogen chloride acidification was illustrated by addition of surrogates (Dewulf and Van Langenhove, 1995). Immediately after sampling chloroform-d and toluene-d8 were injected in the storage flasks to a final concentration of 96.2 and 60.5ng.L^{-1}, respectively. Mean recoveries after a one year storage period were 108.3±20.6 and 102.3±25.1% (n=4).

I.2.1.2. PRECONCENTRATION TECHNIQUES

The preconcentration technique to be chosen depends on the concentration levels of the VOCs in marine or river waters and on the limit of detection (LOD) of the detector.

I.2.1.2.1. Extraction

The extraction technique is widely applied for the determination of CHCs in marine waters. The disadvantage of the extraction method, i.e. only a fraction of the extracting solvent can be introduced in the gas chromatograph (GC), is compensated by the low LOD of the electron capture detector (ECD). In order to determine MAHs this preconcentration technique is not suitable.
Pentane is often used as extraction solvent (Eklund et al., 1978; Fogelqvist et al., 1982; Fogelqvist, 1985; Fogelqvist and Krysell, 1986; Krysell and Wallace, 1988; Dyrssen et al., 1990; Klick, 1992; Krysell, 1992; Rogers et al., 1992; Wallace et al., 1992; Abrahamsson and Ekdahl, 1993; Kristansen et al., 1994). Extraction with n-hexane is reported too (Desideri et

al., 1994; Zoccolillo and Rellori, 1994). Finally Adachi and Kobayashi (1994) extracted CHCs from rain water with o-xylene.

Frequently the extraction solvent contains an internal standard, bromotrichloromethane is often used as internal standard (Fogelqvist et al., 1982; Fogelqvist, 1985; Fogelqvist and Krysell, 1986; Fogelqvist et al., 1986; Krysell and Wallace, 1988; Klick, 1992; Krysell, 1992; Wallace et al., 1992; Abrahamsson and Ekdahl, 1993) though 1,2-dibromopropane is reported too (Rogers et al., 1992). In order to enhance the extraction efficiency the water sample can be enriched with salts like sodium chloride (Kristiansen et al., 1994).

The injection onto the capillary column can be done by a valve with a sample loop of e.g.11.5μL (Fogelqvist et al., 1986; Dyrssen et al., 1990), 15μL (Abrahamsson and Klick, 1990; Klick, 1992; Abrahamsson and Ekdahl, 1993) or 25μL (Krysell and Wallace, 1988; Wallace et al., 1992). 100μL of the extraction solvent was injected by Fogelqvist and Larsson (1983) and Fogelqvist (1985). Desideri et al. (1984) and Desideri et al. (1994) improved the limits of detection by cold evaporation of a 2-5mL n-hexane extract down to 50-100μL under N_2 flow. However, this evaporation showed losses of 36-38 (2mL extract) and 43-46% (5mL extract) for the xylenes.

A special mechanized extraction procedure is developed by Fogelqvist et al. (1986) and applied by Fogelqvist and Krysell (1986) (See Figure I.2.2). The extraction system is coupled on-line to an on-column injector. The CHCs are extracted from the water sample with pentane in a liquid/liquid segmented flow in a glass coil. By the hydrophobic thin layer coating in this glass coil, a film of the organic phase is formed along the wall drastically increasing the contact area between the liquids. After the extraction the phases are separated with the aid of a hydrophobic membrane supported by a screen coated with Teflon. Finally the organic phase is fed to a loop injector.

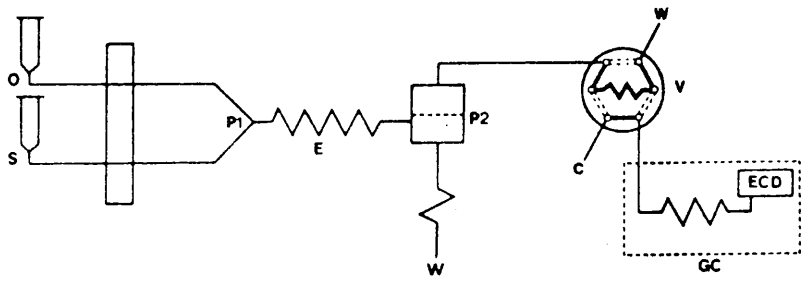

Figure I.2.2. Mechanized on-line liquid/liquid extraction system of Fogelqvist et al. (1986). O: 50mL glass syringe with extraction solvent; S: 50mL glass syringe with water sample; P1: phase segmentor; E: polymer-coated glass extraction coil with length 5m and i.d. 0.7mm; P2: phase separator with Teflon membrane, pore size 0.2μm; W: waste; V: rotary valve with variable loop (in load position); C: carrier gas inlet; GC: gas chromatograph; ECD: electron capture detector.

I.2.1.2.2. Purge and trap

The purge and trap technique is a commonly used method in the determination of VOCs in water samples. Kinetics of the purge step are well examined (Mackay et al., 1979; Lin et al., 1993). The technique developed by Grob (1973) and Grob and Zürcher (1976) consisted of a purging step with charcoal as sorbent in a closed loop system (CLS) and carbon disulphide desorption of the volatiles from the adsorbent. Gschwend et al. (1980) reported 2ng.L^{-1} LOD for saturated and unsaturated hydrocarbons and alkylated benzenes with this method whereas Marchand and Caprais (1983) reported 1ng.L^{-1} LODs for alkylbenzenes. The technique is further used by Schwarzenbach et al. (1979); Gschwend et al. (1982), Mantoura et al. (1982) and Kristiansen et al. (1992). Czuczwa et al. (1988) detected in the same way CHCs, MAHs and PAHs (polyaromatic hydrocarbons) in rain water. Gomez-Belinchon and Albaigés (1987) and Gomez-Belinchon et al. (1991) used a similar technique.

Further developments of trapping the volatiles are the application of thermally desorbable adsorbents or cryogenic trapping. These techniques allow quantitative transfer of all the volatiles from the purging vessel to the GC. Due to the slow release of the compounds during thermal desorption from the adsorbents the volatiles need to be refocused cryogenically before entering the GC in order to inject them in a discrete band by fastly heating the cryogenic trap. Tenax is widely used as trap material (Sauer et al., 1978; Sauer, 1980; Brooks et al., 1981;

Petty, 1981; McDonald et al., 1988). Other adsorbent materials are Chromosorb 106 and Sphericarb (Bianchi et al., 1989) and more recently Carbotrap B, Carbotrap C and Carbosieve SIII are reported in the analysis of river water, ground water, rain water and sea water (Yamasaki et al., 1992; Dewulf and Van Langenhove, 1995).

Cryogenic trapping of the compounds at -100°C during purging is reported by Dawes and Waldock (1994) and at -150/-160°C by Krysell and Nightingale (1994) and Krysell et al. (1994).

In most purge and trap applications, a water trap had to be inserted between the purging vessel and the adsorbent or cryogenic trap. This wet trap can be a simple condensing trap (Sauer et al., 1978; Rosen and Pankow, 1991; Plass et al., 1991; Dewulf and Van Langenhove, 1995) or an adsorbing material like Nafion tubing (Krysell and Nightingale, 1994).

I.2.1.2.3. Other techniques

Harper et al. (1992) measured chloroform in an estuary at levels >500ng.L^{-1} by static headspace analysis after saturation of the sample with sodium sulphate. Helz and Hsu (1978) analysed CHCs at levels >10μg.L^{-1} in river samples by static headspace analysis at 60°C. Static headspace applications in combination with electron capture detection are reported by Singh et al. (1983) and by Herzfeld et al. (1989). A special headspace technique is reported by Comba and Kaiser (1983). Essentially the technique is a vacuum distillation with cryogenic trapping of the distillate. Further on, Kummert et al. (1978) detected tetrachloroethylene in natural waters with high pressure liquid chromatography - UV detection (HPLC-UV). Benfenati et al. (1992) measured xylenes in river water after extraction of the water sample with C18-columns and elution with dichloromethane. Finally, van Zoest and van Eck (1991) determined estuarine CHCs among other compounds by preconcentration on XAD-4 resins followed by dichloromethane extraction.

I.2.1.2.4. New techniques

New techniques not yet currently applied in field sample analysis, have to be mentioned. Their low limits of detection and simplicity show their capability of analysing CHCs and MAHs in environmental water samples in the future.

In the Solid Phase Micro Extraction (SPME) technique a polydimethylsiloxane fiber is brought into the sample and the apolar volatiles are sorbed into the fiber. The VOCs are directly injected in the GC since the fiber is mounted on a syringe and can be brought entirely in the injector. Arthur et al. (1992) measured MAHs in ground water by SPME while Potter and Pawliszyn (1992) developed the technique, combined with GC-ion trap mass spectrometry for the detection of MAHs at ng.L^{-1} levels. Chai et al. (1993) developed the method for CHCs detection in water with 1-100ng.L^{-1} LODs. A modification of the SPME technique is the headspace SPME (Zhang and Pawliszyn, 1993). This method shortens the extraction time and is illustrated with the detection of PAHs at 0.3-2.0ppb.

The Membrane Introduction Mass Spectrometry (MIMS) completely avoids preconcentration steps (Bauer and Solyom, 1994). The ion trap mass spectrometer is configured to accept an insertion capillary membrane probe through an accessory vacuum lock assembly installed in the GC transfer line inlet port. Soni et al. (1995) illustrated the possibilities of MIMS for toluene and trans-1,2-dichloroethene at 0.5ppt.

Finally, Xu and Mitra (1994) developed the Membrane Extraction MicroTrap (MEMT) method. Water samples are passed through a hollow fiber membrane into a gas stream. The volatiles are trapped on a microtrap in front of the GC and are subsequently thermally injected onto the GC column.

I.2.1.3. ANALYSIS: SEPARATION, DETECTION, LIMITS OF DETECTION AND REPRODUCIBILITY

For the separation of the volatiles, commercially packed but mainly capillary gas chromatographic columns with stationary phases like poly (5%-diphenyl-95%-dimethylsiloxane), poly (14%-cyanopropylphenyl-86%-dimethylsiloxane) and poly (6%-cyanopropylphenyl-94%-dimethylsiloxane) are used. (Only Kummert et al. (1978) used HPLC separation for the determination of tetrachloroethylene.) Researchers only investigating CHCs use electron capture detectors (ECD) (Lovelock, 1971) because of their excellent sensitivity. To detect a wider range of volatiles in environmental samples detection with flame ionization detectors (FID) is reported. Mass spectrometry (MS), either in full scan mode or in selected ion monitoring mode, allows the detection of a wide range of volatiles.

Several limits of detection (LODs) and reproducibility data reported in applied and applicable methods are given in Table I.2.1.

Table I.2.1. Limits of detection (LODs, ng.L^{-1}) and analytical relative standard deviations in % (%SD) reported in methods for CHCs and MAHs in environmental waters (field samples) and for techniques like the solid phase microextraction and the membrane extraction microtrap techniques (lab samples).[1]

Compounds	Preconcentration technique	Detection	LOD	%SD	Reference
CHCs	Headspace[2]	ECD	0.8 - 80	12 - 27	Comba and Kaiser, 1983
CHCs	Static headspace	ECD	1 - 20		Herzfeld et al., 1989
CHCs	Liquid/liquid extraction	ECD	0.030 - 2	3 - 12	Abrahamsson and Klick, 1990
CHCs	Mechanized liq/liq extraction	ECD	0.020 - 0.480	10	Fogelqvist et al., 1986
CHCs	Purge and trap	ECD	0.010 - 0.200		Krysell and Nightingale, 1994
CCl_4	Liquid/liquid extraction	ECD	0.015	± 10	Krysell and Wallace, 1988
CH_3CCl_3	Liquid/liquid extraction	ECD	0.053	±10	Krysell and Wallace, 1988
CHCs	XAD-concentration/extract.	MS	10-50		van Zoest and van Eck, 1991
CHCs and MAHs	Purge and trap	MS	0.48 - 4.93	± 10	Dewulf and Van Langenhove, 1995
MAHs, among others	Liq/liq extr. + solv. evaporation	FID	5	5-10	Desideri et al., 1994
MAHs, among others	Purge and trap	FID	1	± 12	Sauer et al., 1978
MAHs, among others	Purge and trap	FID/MS	2	10	Schwarzenbach et al., 1978
MAHs, among others	Purge and trap	FID	± 1	3 - 5	Gomez-Belinchon et al., 1991
Alkylbenzenes	Purge and trap	FID	1.0		Marchand and Caprais, 1983
Alkylbenzenes	Purge and trap	FID/MS	± 10		Kristiansen et al., 1992
Alkylbenzenes	Purge and trap	FID/MS	3 - 169	1.3 - 48	Eganhouse et al., 1993
MAHs	SPME	MS	1.5 - 15	5.5 - 7.3	Potter and Pawliszyn, 1992
Toluene	MEMT	FID	42		Xu and Mitra, 1994
Trichloroethane	MEMT	FID	280		Xu and Mitra, 1994

[1] Abbreviations: SPME: solid phase microextraction; MEMT: membrane extraction microtrap; XAD: styrene/divinylbenzene resin; ECD: electron capture detector; MS: mass spectrometer; FID: flame ionization detector; [2] Essentially the headspace technique is a vacuum distillation with cryogenic trapping of the distillate.

Generally the reproducibility is satisfactory (relative standard deviations (%SD) below 12%) although some relative standard deviations are higher (Comba and Kaiser, 1983; Eganhouse et al., 1993). From Table I.2.1. it is clear that LODs for CHCs are extremely low with ECD detection with the lowest reported data of 10pg.L^{-1} for tetrachloromethane, bromodichloromethane and tetrachloroethylene using purge and trap-GC-ECD (Krysell and Nightingale, 1994) and 20pg.L^{-1} tetrachloromethane for mechanized liquid/liquid extraction-GC-ECD (Fogelqvist et al., 1986).

For the FID detection of volatiles, including MAHs, combined with liquid/liquid extraction with cold evaporation of the solvent extract, Desideri et al. (1994) reported detection limits of 5ng.L^{-1}.

Comparable LODs (1ng.L^{-1}) are found by Sauer et al. (1978) and by Gomez-Belinchon et al. (1991) with purge and trap preconcentration.

The new techniques (SPME and MEMT) showed to be able to detect compounds at ng.L^{-1} concentrations, e.g. SPME-GC-MS analysis of MAHs with 1.5 to 15ng.L^{-1} as detection limits (Potter and Pawliszyn, 1992).

I.2.2. MEASUREMENTS OF CHCS AND/OR MAHS IN ENVIRONMENTAL WATERS

I.2.2.1. ESTUARIES

I.2.2.1.1. Concentration levels

Estuarine concentration levels for CHCs and MAHs are given in Table I.2.2 and Table I.2.3, respectively. It can be seen that samples were frequently taken in British estuaries because this work was a part of the British National Monitoring Programme. This Programme was started as a consequence of the Final Declaration of the Third International Conference on the Protection of the North Sea (The Hague, 1990).

Table I.2.2. CHCs concentrations in estuaries ($ng.L^{-1}$).[1]

Estuary	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Humber (UK)	1992	<10-16.2	<25	<25	<10-49.5	<10-40.6	51.1-274	Dawes & Waldock, 1994
Tees (UK)	1992	<10-11500	<25-29.4	720-4020	<10-602	<10-269	<10-175	Dawes & Waldock, 1994
Tyne (UK)	1992	<10-239	<25	<25	<10-89.2	<10-43.7	<25-42.5	Dawes & Waldock, 1994
Wear (UK)	1992	<10-199	<25-102	<25	<10-64.3	<10-132	<25-72	Dawes & Waldock, 1994
Tweed (UK)	1992	<10	<25	<25	<10	<10	<25	Dawes & Waldock, 1994
Forth (UK)	1990	<500						Harper et al., 1992
Humber (UK)	1990		13-18				8-15	Krysell & Nightingale, 1994
Mersey (UK)	1987-89	200-5200	<500-44000		200-2750	250-4200	100-2000	Rogers et al., 1992
Rhine (Neth.)	1990	3-10	0.6-2				0.6-1.5	Krysell & Nightingale, 1994
Scheldt (Neth/BE)	1987-89	<10-1640	<10-290		<10-5190	<10-1570	<10-3520	van Zoest and van Eck, 1991
Scheldt (Neth/BE)	1993	42.6	3.0	48.0	101.6	54.7	52.9	Dewulf and Van Langenhove, 1995
Elbe (FRG)	1986	<2000	<260		<35	<700	<400	Dyrssen et al., 1990
Back river (US)	2/1977	<120-49000	<154-28000			<132-30000	<166-60500	Helz & Hsu, 1978
Back river (US)	5/1977	120-12500	<154-2100			260-13800	<166-8200	Helz & Hsu, 1978
Brazos river (US)	1981-82		<10-3650	9-51	10-257	6-280	<2-600	McDonald et al., 1988

[1] 1,2-DCE = 1,2-dichloroethane; TRI = 1,1,1-trichloroethane; TCE = trichloroethylene; TTCE = tetrachloroethylene.

I.2.2.1.1.1. CHCs

Chloroform

The highest chloroform levels in British estuaries are reported by Dawes and Waldock (1994) for the Tees estuary (11500ng.L^{-1}) and by Rogers et al. (1992) for the Mersey estuary (5200ng.L^{-1}). For the Humber, the Tyne, the Wear and the Tweed estuaries concentrations were below 250ng.L^{-1} (Dawes and Waldock, 1994) while Harper et al. (1992) observed levels below 500ng.L^{-1} in the Forth estuary.

The sources suggested by Dawes and Waldock (1994) are industrial use of chloroform in manufacturing fluorocarbons and for solvent purposes. It is also produced during the manufacturing of chlorinated bulk chemicals like 1,2-dichloroethane, trichloroethylene and tetrachloroethylene. Further on, chloroform is produced by the chlorination of drinking water. Finally, they suggest natural production since McConnell and Fenical (1976) found chloroform production from the tropical marine red algae *Asparagopsis armata* and therefore natural inputs are considered as possible.

For non-British estuaries, the lowest observed concentrations are 3-10ng.L^{-1} in the Rhine estuary (Krysell and Nightingale, 1994). The highest reported levels are reported by van Zoest and van Eck (1991) for the Scheldt estuary (up to 1640ng.L^{-1}), by Dyrssen et al. (1990) for the Elbe estuary (up to 2000ng.L^{-1}) and by Helz and Hsu (1978) for the Back river estuary (up to 49000ng.L^{-1}).

Tetrachloromethane

Except in the case of the Mersey estuary, levels below 100ng.L^{-1} tetrachloromethane are reported for British estuaries. The tetrachloromethane sources were considered as inputs from the manufacture of chlorofluorocarbons (CFC12 and CFC11) and from the use as metal degreaser (Dawes and Waldock, 1994). The levels below the LOD of 25ng.L^{-1} observed in 1992 by Dawes and Waldock (1994) for the Humber estuary are confirmed by the measurements of Krysell and Nightingale (1994) in 1990. They found 13 to 18ng.L^{-1} tetrachloromethane in the same estuary. Lower levels were found in the Rhine estuary (0.6-2ng.L^{-1}). It was concluded that the Humber is a pronounced source of tetrachloromethane for the North Sea while the Rhine is considered to be a moderate source.

Higher levels are found in the Elbe estuary (<260ng.L^{-1}) (Dyrssen et al., 1990) and in the Scheldt estuary (<290ng.L^{-1}) (van Zoest and van Eck, 1991). µg.L^{-1} concentrations are found in the Back River estuary (Helz and Hsu, 1978), at the Brazos river mouth (McDonald et al., 1988) and in the Mersey estuary, generally considered as one of the most polluted estuaries in Europe (Rogers et al., 1994).

1,2-Dichloroethane

Only in the Tees estuary of the examined British estuaries 1,2-dichloroethane was detected above the 25ng.L^{-1} LOD (720 to 4020ng.L^{-1}) (Dawes and Waldock, 1994). The highest levels measured were from a station near an industrial area where 1,2-dichloroethane and the vinylchloride monomer are produced. 1,2-Dichloroethane is used in the industrial production of vinylchloride and polyvinylchloride.

1,1,1-trichloroethane

1,1,1-Trichloroethane, used in metal degreasing and as industrial solvent, was measured by Dawes and Waldock (1994) in British estuaries at levels from below 10 to 600ng.L^{-1}. Concentrations in the Elbe estuary are below 35ng.L^{-1} (Dyrssen et al., 1990). On the contrary Rogers et al. (1992) found 200-2750ng.L^{-1} in the Mersey estuary, McDonald et al. (1988) measured concentrations up to 257ng.L^{-1} in the Brazos estuary and levels up to 5190ng.L^{-1} were detected in the Scheldt estuary by van Zoest and van Eck (1991).

Trichloroethylene

Trichloroethylene, a metal degreasing solvent, was measured in the <10-269ng.L^{-1} concentration range for British estuaries, the Mersey estuary excepted (Dawes and Waldock, 1994). Similar concentration levels are observed by McDonald et al. (1988) for the Brazos river mouth. Levels up to 700ng.L^{-1} are reported for the Elbe estuary (Dyrssen et al., 1990), up to 1570ng.L^{-1} for the Scheldt estuary (van Zoest and van Eck, 1991), up to 4200ng.L^{-1} for the Mersey estuary (Rogers et al., 1992) and up to 30000ng.L^{-1} for the Back River estuary (Helz and Hsu, 1978).

Tetrachloroethylene

Tetrachloroethylene, a dry cleaning solvent, was measured in five British estuaries at concentrations from <10 up to 274ng.L^{-1}.

The Humber estuarine concentrations of 8-15ng.L^{-1} in 1990 observed (Krysell and Nightingale, 1994) are lower than those in 1992, reported by Dawes and Waldock (1994). Still lower concentrations are detected in the Rhine estuary (0.6-1.5ng.L^{-1}) (Krysell and Nightingale, 1994). Similar to tetrachloromethane the authors concluded that the Humber has to be considered as a pronounced source of tetrachloroethylene in the North Sea, where the Rhine has to be regarded rather as a moderate source.

Similarly to trichloroethylene higher levels are reported for the Elbe estuary (<400ng.L^{-1}) (Dyrssen et al., 1990), for the Brazos river mouth (<600ng.L^{-1}) (McDonald et al., 1988), for the Scheldt estuary (<3520ng.L^{-1}) (van Zoest and van Eck, 1991) and for the Mersey estuary (100-2000ng.L^{-1}) (Rogers et al., 1992), while the highest levels reported are for the Back River estuary (<60.5µg.L^{-1}) (Helz and Hsu, 1978).

I.2.2.1.1.2. MAHs

In the British estuaries, Dawes and Waldock (1994) did not detect MAHs above the LOD (10ng.L^{-1} for benzene, toluene, ethylbenzene, 25ng.L^{-1} for o-xylene) except in two cases. In the Wear estuary benzene was found at levels up to 29.6ng.L^{-1}. For the Tees estuary toluene end ethylbenzene were found at concentrations up to 60.7 and 46.3ng.L^{-1} respectively. High o-xylene concentrations (720-4020ng.L^{-1}) were detected in the same estuary. All these MAHs were considered to be generated by petrochemical sources. Additionally the authors assume that toluene can originate from biogenic production since Juttner and Henatsch (1986) found biogenic toluene in eutrophic lakes. In these lakes phenylalanine is suggested to be the biogenic source of toluene. The high o-xylene concentrations were explained by the use of o-xylene as intermediate in the production of phthalic anhydride.

Individual MAHs concentrations in the Scheldt estuary were below 46.4ng.L^{-1} (Dewulf and Van Langenhove, 1995), whereas McDonald et al. (1988) measured concentrations up to 233ng.L^{-1} for benzene in the Brazos river mouth.

Table I.2.3. MAHs concentrations in estuaries (ng.L^{-1}).[1]

Estuary	Date	BENZ	TOL	ET-B	m/p-Xyl	o-Xyl	Reference
Humber (UK)	1992	<10	<10	<10		<10	Dawes & Waldock, 1994
Tees (UK)	1992	<10	<10-60.7	<10-46.3		<10-1340	Dawes & Waldock, 1994
Tyne (UK)	1992	<10	<10	<10		<10	Dawes & Waldock, 1994
Wear (UK)	1992	<10-29.6	<10	<10		<10	Dawes & Waldock, 1994
Tweed (UK)	1992	<10	<10	<10		<10	Dawes & Waldock, 1994
Brazos (US)	1981/82	10-233	20-110	30-50	1-56 [2]		McDonald et al., 1988
Scheldt (Neth/BE)	1993	21.0	46.4	36.9	23.0	21.0	Dewulf & Van Langenhove, 1995

[1] BENZ = benzene; TOL = toluene; ET-B = ethylbenzene; m/p-Xyl = m- and p-xylene; o-Xyl = o-xylene.

[2] Including o-xylene.

I.2.2.1.2. Factors affecting the concentration levels in estuaries

It is clear that the main factor determining the estuarine VOC concentration is the proximity of industrial sites as illustrated for some British estuaries. But within one estuary the concentration fluctuates considerably. The first factor affecting this fluctuation is the degree of dilution with sea water. This is shown by plotting the concentrations versus the salinity or conductivity (Helz and Hsu, 1978; Dyrssen et al., 1990; van Zoest and van Eck, 1991; Krysell and Nightingale, 1994). However this relationship is not linear. All researchers explained this nonlinearity by transfer to the atmosphere because of the high volatility of the compounds. Dyrssen et al. (1990) found that the concentrations measured in the Elbe estuary were 200 to 1000 times the air-water equilibrium concentration. Using a two film approach of the air/water exchange they calculated the yearly flux from water into air for the Elbe estuary as 350000kg chloroform, 3000kg 1,1,1-trichloroethane, 49000kg tetrachloromethane, 120000kg trichloroethylene and 39000kg tetrachloroethylene. The maximum flux rates corresponded to 2450, 34.2, 342, 876 and 50kg.km^{-2}.yr^{-1} respectively. The air/water exchange thesis is supported by the measurements of Helz and Hsu (1978). They found decreasing concentrations towards the bay for the Back River as well in February as in May. But the decrease in May was more pronounced. The authors explained this fact being the result of more volatilization since the Back River was almost completely ice-covered in February. A second explanation for the lower May concentration was possible biodegradation.

I.2.2.2. BEACH, BAY, FJORD, COASTAL AND SHELF SEA WATER

Reported concentrations in beach, bay, fjord, coastal and shelf sea waters for CHCs and MAHs are summarized in Table I.2.4 and I.2.5, respectively.

I.2.2.2.1. CHCs

Chloroform

A wide range of chloroform concentrations is found in bay, fjord, shelf sea and coastal waters. Levels below 20ng.L^{-1} are reported for the Swansea Bay (Dawes and Waldock, 1994), the Byfjorden (Fogelqvist et al., 1986), the Stenungsundfjorden (Abrahamsson et al., 1989) with extreme low levels for the Byfjorden, i.e. below 0.5ng.L^{-1}. Comparable concentrations were measured in shelf sea waters, like in the British shelf sea waters at Firth of Forth, Moray Forth, North Minch and the Bristol Channel (Dawes and Waldock, 1994) and in the Belgian shelf sea (Dewulf and Van Langenhove, 1995).

On the contrary μg.L^{-1} levels were measured in the Liverpool Bay in 1972-73 (Pearson and McConnell, 1975), the Idefjorden (Fogelqvist and Krysell, 1986) and for the Swedish West coast (Fogelqvist et al., 1982). All these regions are near industrial areas. The Liverpool Bay is situated near to organochlorine plants and near to the highly industrialized area of south Lancashire and north Cheshire. The Idefjorden, a fjord on the border between Norway and Sweden, is polluted by the discharges of a pulp and paper bleachery via the river Tista. Finally, the Swedish West coast investigated by Fogelqvist et al. (1982) was near a pulp mill. At 4.2km from the bleaching effluent of the pulp mill, concentrations up to 9000ng.L^{-1} were detected.

In the Stenungsundfjorden Abrahamsson et al. (1989) found different chloroform concentrations at depths between 1m and 5-10m. The same observation was made for 1,1,1-trichloroethane and tetrachloroethane. They concluded that the Stenungsundfjorden can not be considered as a well mixed system. These results were confirmed by Fogelqvist and Krysell (1986) for the Idefjorden. They found maximum concentrations for chloroform (and tetrachloroethylene) at about 5m depth in the inner part of the fjord. They proposed different explanations. The inflow of river water with lower density and the evaporation of volatile hydrocarbons were suggested.

Table I.2.4. CHCs concentrations in beach, bay, fjorden, coastal and shelf sea water (ng.L^{-1}).[1]

Location[2]	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Vineyard Sound, USA (BE)	1977-78						0.3-5.7	Gschwend et al., 1982
Liverpool Bay, UK (BA)	1972-73	<1000	<2400		<3300	<3600	<2600	Pearson & McConnell, 1975
Bay at Särö, Swed. (BA)	1990-91		0.25-1.65					Klick, 1992
Swansea Bay, UK (BA)	1992	<10	<25	<25	<10	<10	<25	Dawes & Waldock, 1994
Byfjorden, Swed. (FJ)	1985	<0.48	2.9		11	0.28	45	Fogelqvist et al., 1986
Stenungsundfjorden, Swed. (FJ)	1988	5.4-14.8	0.89		2.7		2.5	Abrahamsson et al., 1989
Idefjorden, Swed. (FJ)[3]	1985	<10^3-5.10^3					<10-50	Fogelqvist & Krysell, 1986
Baltic Sea (SH)	1992		0.08-1.80					Krysell et al., 1994
Skagerrak (SH)	1985						6	Fogelqvist & Krysell, 1986
Skagerrak (SH)[4]	9/1990		<2.6			<2.6	<2.6	Abrahamsson & Ekdahl, 1993
Skagerrak (SH)[4]	11/1990		<4.8			<4.8	<4.8	Abrahamsson & Ekdahl, 1993
Skagerrak (SH)[4]	4/1991		<5.8			<5.8	<5.8	Abrahamsson & Ekdahl, 1993
Firth of Forth, UK (SH)	1992	<10	<25	<25	<10	<10	<25	Dawes & Waldock, 1994
Moray Forth, UK (SH)	1992	<10	<25	<25	<10	<10	<25	Dawes & Waldock, 1994
North Minch, UK (SH)	1992	<10	<25	<25	<10	<10	<25	Dawes & Waldock, 1994
Bristol Channel, UK (SH)	1992	<10	<25	<25	<10	<10	<25	Dawes & Waldock, 1994
Belgian Cont. Shelf (SH)	1993	11.3-17.4	0.6-2.4	4.9-9.8	2.1-3.6	4.9-7.3	1.0-1.4	Dewulf & Van Langenhove, 1995
Swed. W. Coast (CO)[5]	1979	<9000						Fogelqvist et al., 1982
Central North Sea (SH)	4/1986						<2-2	Hurford et al., 1989

[1] 1,2-DCE = 1,2-dichloroethane; TRI = 1,1,1-trichloroethane; TCE = trichloroethylene; TTCE = tetrachloroethylene. [2] BE: beach; BA: bay; FJ: fjord; SH: shelf sea; CO: coastal water. [3] The upper limit indicated for all compounds corresponds to the highest iso-concentration profile line. [4] The values mentioned are the sum of CCl_4, TCE and TTCE. [5] 4.2km from the effluent of a pulp mill.

Tetrachloromethane

Tetrachloromethane concentrations of 0.1-5ng.L^{-1} are reported for the Bay at Särö (Klick, 1992), the Byfjorden (Fogelqvist et al., 1986), the Stenungsundfjorden (Abrahamsson et al., 1989), the Baltic Sea (Krysell et al., 1994), the Skagerrak (Abrahamsson and Ekdahl, 1993) and the Belgian continental shelf (Dewulf and Van Langenhove, 1995). Dawes and Waldock did not observe tetrachloromethane above their 25ng.L^{-1} LOD in British shelf sea waters.
Because the Bay at Särö is an isolated region, Klick (1992) concluded that the concentrations were determined by atmospheric inputs. This statement was confirmed by the higher winter and lower summer concentrations, reflecting the dependance of the air/water equilibrium partitioning on temperature, provided that the air concentration can be considered as a constant.
The measurements in the Baltic Sea (Krysell et al., 1994) showed for all sampling stations decreasing concentrations with increasing depth. Since the half life time of tetrachloromethane due to hydrolysis is of the order of 1000 years (Jeffers et al., 1989; Jeffers and Wolfe, 1989) and since the Baltic Sea is not well mixed and since the mean age of the anoxic bottom water is assumed to be 15-25 years, it seemed plausible to the authors that the increase of the CFC-11 to tetrachloromethane ratio was due to the removal of tetrachloromethane from anoxic sea water by some other process, possibly intermediated bacterially.
In contrast with the other data Pearson and McConnell (1975) found levels up to 2400ng.L^{-1} in 1972-73 in the Liverpool Bay near a heavily industrialized region.

1,2-Dichloroethane

Dawes and Waldock (1994) did not detect 1,2-dichloroethane in British Shelf water above their 25ng.L^{-1} LOD. Dewulf and Van Langenhove (1995) found 4.9-9.8ng.L^{-1} in Belgian continental shelf waters.

1,1,1-trichloroethane

1,1,1-trichloroethane was not detectable above 10ng.L^{-1} in British shelf sea waters (Dawes and Waldock, 1994), whereas Dewulf and Van Langenhove (1995) detected 1,1,1-trichloroethane at 2.1-3.6ng.L^{-1} in the Belgian shelf waters. Comparable to this values are the 2.7 and 11ng.L^{-1}

concentrations in Swedish fjorden (Fogelqvist et al., 1986; Abrahamsson et al., 1989). Similar to tetrachloromethane high levels of 1,1,1-trichloroethane (up to 3300ng.L^{-1}) were found in the Liverpool Bay by Pearson and McConnell (1975), explained by the neighbourhood of an industrial site.

Trichloroethylene

Except levels up to 3600ng.L^{-1} in the Liverpool Bay (Pearson and McConnell, 1975) the measured levels are below 10ng.L^{-1} such as those reported for British shelf waters (LOD) (Dawes and Waldock, 1994), for the Belgian continental shelf (Dewulf and Van Langenhove, 1995), for the Skagerrak (Abrahamsson and Ekdahl, 1993) and the Byfjorden (Fogelqvist et al., 1986).

Tetrachloroethylene

The lowest reported levels, i.e. below 6ng.L^{-1}, are reported for the Vineyard Sound beach (Gschwend et al., 1982), the Stenungsundfjorden (Abrahamsson et al., 1989), the Skagerrak (Fogelqvist and Krysell, 1986; Abrahamsson and Ekdahl, 1993), the Central North Sea (Hurford et al., 1989), and the Belgian continental shelf (Dewulf and Van Langenhove, 1995). Dawes and Waldock (1994) did not observe tetrachloroethylene above the 25ng.L^{-1} LOD for British shelf sea waters.

Concentrations up to 50ng.L^{-1} are reported for the Byfjorden and the Idefjorden (Fogelqvist et al., 1986; Fogelqvist and Krysell, 1986). Comparable to tetrachloromethane, 1,1,1-trichloroethane and trichloroethylene, µg.L^{-1} concentrations for tetrachloroethylene were found in the Liverpool Bay by Pearson and McConnell (1975).

Fogelqvist and Krysell (1986) explained the higher concentrations in the Idefjorden by the input of runoff water from the city Halden. The maximum concentrations were found at 5m depth and were explained similarly to chloroform profiles.

I.2.2.2.2. MAHs

The lowest polluted beach, bay, shelf sea and coastal waters (see Table I.2.5) with levels for the individual MAHs below 10ng.L^{-1} are the Coast of Peru (Gschwend et al., 1980), the deep waters in the Gulf of Mexico (Sauer et al., 1980) and most of the locations on the Continental shelf around Britain (Dawes and Waldock, 1994). The low concentrations at the Coast of Peru (±5 - ±70km offshore) are explained by the authors by the isolated character of the region. Terrestrial and anthropogenic inputs from the sparsely populated arid Peruvian coast should be minimal. Since MAHs in surface samples were a factor two or three higher than at 1000m depth, it seemed to the authors that the origine of the MAHs is from marine traffic. The water samples in the Gulf of Mexico at 1000m depth (Sauer et al., 1980) indicate extreme low concentrations though in this region higher concentrations are reported for surface waters and the sampling region is not isolated from potential sources.

A non isolated region is the North Sea. Hurford et al. (1989) reported that the quantities of benzene, toluene and xylenes imported to North Sea ports are 812000, 239000 and 922000 ton $year^{-1}$ respectively. Despite these potential sources, Dawes and Waldock (1994) did not measure concentrations above 10ng.L^{-1} at several sampling sites in British Continental Shelf Seas in most cases. Only for benzene at Firth of Forth a concentration of 32.9ng.L^{-1} was measured.

Higher MAHs concentrations are measured in beach waters at Vineyard Sound (US) (Gschwend et al., 1982; Mantoura et al., 1982) and at La Pineda (Spain) (Gomez-Belinchon et al., 1991). From their observations at the Vineyard Sound beach Gschwend et al. (1982) drew a few conclusions. First, no obvious seasonality for the concentration was found. Secondly, great biweekly variability was observed. Thirdly, the strong covariancy between the MAHs indicates common sources and environmental fate. Vehicular fuel uses are thought to be important sources of alkylbenzenes. Summer concentrations on Monday and Tuesday were much higher while the Wednesday and Thursday summer levels decayed to levels similar to those observed in winter time. The authors suggest that the summer weekend inputs are removed predominantly by air/sea exchange. The covariability of MAHs and the weekend effect with depletion in two or three days caused by air/water exchange was confirmed by Mantoura et al. (1982).

Table I.2.5. MAHs concentrations in beach, bay, shelf sea and coastal waters (ng.L^{-1}).[1]

Location[2]	Date	BENZ	TOL	ET-B	m/p-Xyl	o-Xyl	BTEX	Reference
Vineyard Sound, US (BE)	1977-78		10-54	1.8-22	4.5-66	1.8-25		Gschwend et al., 1982
Vineyard Sound, US (BE)	1978-79		4.6-44	3-52	2.5-30			Mantoura et al., 1982
Vineyard Sound, US (BE)[3]	1978					12-42		Mantoura et al., 1982
La Pineda, SP (BE)	1986		100	26	34	210		Gomez-Belinchon et al., 1991
Gulf of Mexico (CO+SH)	1977						10.0-98.9	Sauer, 1980
Gulf of Mexico (CO+SH)[4]	1977						246.0-332.8	Sauer, 1980
Gulf of Mexico (CO+SH)[5]	1977	1.6	1.5					Sauer, 1980
Gulf of Mexico (CO)	1977	9.3-101.0	4.5-376.0	0.4-4.5	2.7-24.4	0.3-10.1		Sauer et al., 1978
Coast of Peru (CO)	1978						<10	Gschwend et al., 1980
Vilanova/Sitges, SP (CO)	1986		200	22	72	4.0		Gomez-Belinchon et al., 1991
Barcelona, SP (CO)	1986		27	5.5	15	6.1		Gomez-Belinchon et al., 1991
Campeche shelf (SH)	1979	12-66	19-42	4.3-11	22-59	<1-13		Brooks et al., 1981
Campeche shelf (SH) [6]	1979	1800	1100	120	730	330		Brooks et al., 1981
Campeche shelf (SH) [7]	1979	13900	6000	380	1580	13700		Brooks et al., 1981
Firth of Forth, UK (SH)	1992	32.9	<10	<10		<10		Dawes & Waldock, 1994
Moray Forth, UK (SH)	1992	<10	<25	<10		<10		Dawes & Waldock, 1994
North Minch, UK (SH)	1992	<10	<10	<10		<10		Dawes & Waldock, 1994
Bristol Channel (SH)	1992	<10	<10	<10		<10		Dawes & Waldock, 1994
North Sea (SH)	1990		<10-25	<10-37	<10-50	<10-35		Kristiansen et al., 1992
Belgian Cont. Shelf (SH)	1993	26.5-34.7	35.2-52.0	9.4-18.7	11.0-15.1	9.8-11.9		Dewulf & Van Langenhove, 1995
Swansea Bay (BA)	1992	<10	<10	<10		<10		Dawes & Waldock, 1994

[1] BENZ = benzene; TOL = toluene; ET-B = ethylbenzene; m/p-Xyl = m- and p-xylene; o-Xyl = o-xylene; BTEX = sum of benzene, toluene, ethylbenzene and the xylenes. [2] BE: beach; BA: bay; CO: coastal water, SH: shelf sea.[3] Samples taken during one week: difference by weekend effect. [4] Samples taken near known sources. [5] Depth 1000m. [6] 33.3 km near a well head. [7] 1.4 km near a well head.

Similar high MAHs concentration data are those for the coastal and shelf sea waters in the Gulf of Mexico (Sauer et al., 1978; Sauer, 1980), the Norwegian sector of the North Sea (Kristiansen et al., 1992), the Belgian shelf sea water (Dewulf and Van Langenhove, 1995), the Mediterranian Coast at Vilanova, Sitges and Barcelona (Gomez-Belinchon et al., 1991) and the Campeche Shelf (Brooks et al., 1981). For these coastal and shelf sea water concentrations several sources are suggested. The sampling stations in the Gulf of Mexico for the measured sum of BTEX (benzene, toluene, ethylbenzene and the xylenes) were locations near known sources (Sauer, 1980). Other sampling sites were close to shipping lanes and/or oil platforms (Sauer et al., 1978). The sources suggested for the Spanish coastal waters were high marine traffic for the Vilanova and Sitges region (5-6km offshore) and high marine traffic and river input for the Barcelona coast (500-2000m offshore) (Gomez-Belinchon et al., 1991).

Finally, the highest levels reported, above $10\mu g.L^{-1}$, were found in the Campeche Shelf near an oil-well (Brooks et al., 1981).

I.2.2.3. RIVERS AND LAKES

I.2.2.3.1. CHCs

Reported CHCs concentrations measured in lakes and rivers are given in Table I.2.6. Two locations with isolated lakes are reported: Antartica lakes (Zoccolillo and Rellori, 1994) and Crawford Lake in Canada (Comba and Kaiser, 1983). This latter site is an isolated, meromictic water body, i.e. a lake which does not undergo complete circulation and where the primary water mass does not mix with the lower portion, located in an agricultural setting not exposed to any known source of industrial or municipal runoff. When compared to the concentrations of the Antartica lakes, the concentration levels are of the same order of magnitude for tetrachloromethane, trichloroethylene and tetrachloroethylene. According to the authors, sources for the Crawford lake are supposed to be atmospheric.

The Lake St. Clair and the Lake Zurich, both with known direct sources of CHCs, generally show higher CHCs concentrations (Kaiser and Comba, 1986; Schwarzenbach et al., 1979).

CHCs concentrations measured in the Mersey River, the Manchester Ship Canal, Weaver River, Ditton Brook and the Gowy River, all fresh water inputs for the Mersey estuary, indicate levels from about $1ng.L^{-1}$ (trichloroethylene and tetrachloroethylene in the Mersey

Table I.2.6. CHCs in lakes and rivers ($ng.L^{-1}$).[1]

Location	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Antartica lakes[2]	1988-90		0.6-22			1.2-20	0.2-4.3	Zoccolillo & Rellori, 1994
Crawford lake (Can)	10/1981	58	3.8		5.9	32	9	Comba & Kaiser, 1983
Lake St. Clair (Can)	1984	0-278	0-904		0-112	0-36	0-473	Kaiser & Comba, 1986
Lake Zurich (Switz)	1977-78						25-75	Schwarzenbach et al., 1979
Inland Sea (Jpn)	2-7/1991	36	<1		30	10	10	Yamasaki et al., 1992
Kako R. (Jpn)	2-7/1991	35	1		40	50	13	Yamasaki et al., 1992
Mersey R. (UK)	1987-89	600	<100		400	1.1	0.6	Rogers et al., 1992
Weaver R./Manch. Ship Canal	1987-89	2200-70000	300-110000		2700	3300-0.97.10^6	95300	Rogers et al., 1992
Ditton Brook (UK)	1987-89	500	900		700	600	400	Rogers et al., 1992
River Gowy (UK)	1987-89	1800	900		8300	2800	200	Rogers et al., 1992
Thames (UK)	4/1986						<2-160	Hurford et al., 1989
Humber (UK)	4/1986						<2-19	Hurford et al., 1989
Tees (UK)	4/1986						<2-5	Hurford et al., 1989
Forth (UK)	4/1986						<2-3	Hurford et al., 1989

[1] 1,2-DCE = 1,2-dichloroethane; TRI = 1,1,1-trichloroethane; TCE = trichloroethylene; TTCE = tetrachloroethylene.[2] Between 73°43'-74°59'S and 162°33'-165°07'E

River) over 1μg.L^{-1} (e.g. Ditton Brook, River Gowy) to almost 1mg.L^{-1} (trichloroethylene in the Manchester Ship Canal/ River Weaver) (Rogers et al., 1992). It was concluded that the Weaver and the Manchester Ship Canal were the main contributors to the pollution of CHCs in the Mersey estuary. The data on tetrachloroethylene of Hurford et al. (1989) for the rivers the Thames, the Humber, the Tees and the Forth are rather similar to those of the Mersey river, though for the Thames also levels up to 160ng.L^{-1} are measured.

I.2.2.3.2. MAHs

Measured MAHs concentrations are given in Table I.2.7. Concentrations of individual MAHs in the Besos and Llobregat rivers in Spain were in the range of 1 to 25μg.L^{-1} (Gomez-Belinchon et al., 1991). Both rivers are situated in heavily polluted areas where the Llobregat river is reported to receive domestic, industrial and agricultural waters. Xylene concentrations in the Adige river in northern Italy were lower (5ng.L^{-1} to 5μg.L^{-1}) (Benfenati et al., 1992). Also here industrial sites are suggested as a source for these concentrations.

Table I.2.7. MAHs in rivers (ng.L^{-1}).[1]

Location	Date	BENZ	TOL	ET-B	m/p-Xyl	o-Xyl	Reference
Besos River (Sp.)	1985-86		22000	15000	24000	8100	Gomez-Belinchon et al., 1991
Llobregat River (Sp.)	1985-86		4100	1900	4700	830	Gomez-Belinchon et al., 1991
Adige River (It.)[2]	1989				<5-11940	<5-4790	Benfenati et al., 1992

[1] BENZ = benzene; TOL = toluene; ET-B = ethylbenzene; m/p-Xyl = m- and p-xylene; o-Xyl = o-xylene.

[2] Minimum and maximum values of m/p-xylene are for m-xylene and p-xylene individually.

I.2.2.4. OPEN SEA CHCS CONCENTRATIONS

Open sea concentrations for CHCs are given in Table I.2.8. Tetrachloromethane, 1,1,1-trichloroethane or tetrachloroethylene concentrations in the north east Atlantic Ocean, in the Arctic Ocean, in the Weddell Sea, at the Antarctic coast and in the Sea of Japan are of a low level, i.e. about $1ng.L^{-1}$ (Murray and Riley, 1973; Singh et al., 1983; Krysell and Wallace, 1988; Fogelqvist, 1985; Krysell, 1992; Yamasaki et al., 1992; Zoccolillo and Rellori, 1994). Concentration levels for chloroform are higher, like those for the north east Atlantic Ocean (Murray and Riley, 1973) and for the Sea of Japan (Yamasaki et al., 1992). Similar levels are found for trichloroethylene in the north east Atlantic Ocean (Murray and Riley, 1973), at the Antarctic coast (Zoccolillo and Rellori, 1994) and for the Sea of Japan (Yamasaki et al., 1992).

For the Arctic Sea in the Svalbard area depth profiles suggest that the halocarbons are brought into the Arctic Ocean with the inflowing Atlantic water (Fogelqvist, 1985).

Finally, extreme low tetrachloromethane and 1,1,1-trichloroethane concentrations are reported by Krysell (1992) in the deep waters of the Weddell Sea, even below the LOD of 0.023 and $0.053ng.L^{-1}$ respectively.

Table I.2.8. CHCs concentrations in open Seas ($ng.L^{-1}$). [1]

Location	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
NE-Atl. Ocean[2]	8/1972	4-13	0.12-0.26			5-11	0.2-0.8	Murray & Riley, 1973
Arctic Ocean[3]	7-8/1987		0.73-1.55		0.66-4.22			Krysell & Wallace, 1988
Arctic Ocean[4]	7-8/1987		0.015-0.58		<0.053-0.29			Krysell & Wallace, 1988
Arctic Sea [5]	8-9/1980		0.83		2.5		0.68	Fogelqvist, 1985
Weddell Sea [6]	12/88-2/89		<0.023-1.22		<0.053-1.98			Krysell, 1992
Antarctica [7]	1990		1.8			3.8	0.7	Zoccolillo & Rellori, 1994
Sea of Japan	2-7/1991	<10	<1		<10	<10	<1	Yamasaki et al., 1992
E. Pacific Ocean	12/1981		0.25-1.23			0.1-0.7	0.1-2.1	Singh et al., 1983

[1] 1,2-DCE = 1,2-dichloroethane; TRI = 1,1,1-trichloroethane; TCE = trichloroethylene; TTCE = tetrachloroethylene.[2] Stations between 26° 07' - 26° 21' N and 14° 38' - 14° 56' N. [3] depth 0-1000m at 84° 01' N and 30° 33' E. [4] depth 1000-4000m at 84° 01' N and 30° 33' E. [5] depth 0-10m. [6] The upper limit indicated for all compounds corresponds to the highest iso-concentration profile line. [7] At the Antarctic coast (74° 42' S and 164 06' E).

I.2.3. SOURCES AND FATE OF CHCS AND MAHS IN THE MARINE ENVIRONMENT

I.2.3.1. SOURCES

Both CHCs and MAHs are principally emitted in the environment by anthropogenic sources, as summarized by Howard (1990).

I.2.3.1.1. CHCs

I.2.3.1.1.1. Anthropogenic sources

Chloroform is produced by chlorination of drinking or waste water where it results from the breakdown of organic substances in the presence of chlorine (Fogelqvist, 1982; Christman et al., 1983; Dyrssen et al., 1990; Abrahamsson and Ekdahl, 1993). It is used in the production of fluorocarbons, as industrial solvent, in pulp and paper bleacheries and in the prevention of bioactivity in power-plant cooling systems (Fogelqvist et al., 1982; Fogelqvist and Krysell, 1986; Dawes and Waldock, 1994). Tetrachloromethane is applied in the manufacture of fluorocarbons (CFC12 and CFC11), as metal degreaser, as solvent and in paint and ink formulations (Dawes and Waldock, 1994; Howard, 1990). 1,2-Dichloroethane applications are found in the production of vinylchloride and polyvinylchloride and in extraction and cleaning techniques. 1,1,1-trichloroethane is used as metal degreaser and as industrial solvent, trichloroethylene as metal degreasing solvent and tetrachloroethylene as dry cleaning solvent and in industrial metal cleaning (Dawes and Waldock, 1994; Howard, 1990).
Anthropogenic CHCs are brought into the marine environment in two ways. First, direct input from fresh waters via rivers is reported. Rogers et al. (1992) reported the CHCs inputs in the Mersey estuary from the fresh waters Manchester Ship Canal and the River Weaver as 15.7, 11.7 53.7 and 45.6 ton.year^{-1} for chloroform, tetrachloromethane, trichloroethylene and tetrachloroethylene respectively. It has to be said that the Mersey estuary is considered as one of the heaviest polluted estuaries in Europe. Similar direct input for chloroform and tetrachloroethylene into a Swedish fjord was found where the sources were a pulp and paper bleachery and a city, respectively (Fogelqvist and Krysell, 1986). The direct riverine discharges seemed to be the main sources of chlorinated VOCs in the coastal area of

Barcelona (Gomez-Belinchon et al., 1991). Tetrachloromethane and tetrachloroethylene could be used to trace the plume of riverine water as it mixes into the outer estuary (Krysell and Nightingale, 1994). Finally, Fogelqvist (1985) estimated the oceanic transport of some CHCs across the Fram strait. The inflow in the Svalbard area in the Arctic region is estimated as 50, 46 and 114 ton.year^{-1} of tetrachloromethane, tetrachloroethylene and 1,1,1-trichloroethane respectively, due to contamination of the Atlantic water in the industrial latitudes. On the contrary the outflows through the same transection were estimated as 50, 60 and 129 ton.year^{-1} respectively, with an uncertainty of 50%. All estimations were based on measured concentrations and on conductivity/temperature/depth data.

Secondly, atmospheric deposition has to be considered, as well in coastal regions as in more isolated areas. According to Dyrssen et al. (1990) the Elbe estuary predominantly acts as an atmospheric source since evaporation is a favoured process in the strongly supersaturated water. Through the atmosphere the CHCs can be distributed to areas like the Arctic surface waters where they can be transported from air into water due to low temperatures and concentrations. Fogelqvist (1985) stated that the atmospheric transport to the Arctic region is much more rapid than the transport by sea currents. The atmospheric deposition is suggested too by Comba and Kaiser (1983). The CHCs concentrations found in the isolated Crawford Lake were thought to be originating from atmospheric deposition.

I.2.3.1.1.2. Biogenic sources

Chloroform is reported to be produced by the tropical red algae *Asparagopsis armata* (McConnell and Fenical, 1976). Also the red seaweed *Asparagopsis taxiformis* produces chloroform but tetrachloromethane too, both as minor components besides major products like bromoform, dibromoiodomethane or chlorodibromomethane (Fenical, 1982). For the other CHCs considered no biogenic sources are reported.

I.2.3.1.2. MAHs

The main sources of MAHs are the exploitation of oil-wells, the transport of oil and oil products and the further industrial and private use of oil and oil products. Oil-wells can be considered as natural sources. Other natural sources are not reported for MAHs except the biogenic formation of toluene in eutrophic lakes, reported by Juttner and Henatsch (1986).

All MAHs are used as solvent. They are intermediates in the chemical industry, e.g. p-xylene in an intermediate in the dimethyl terephthalate and terephthalic acid production for polyester (Howard, 1990).

The input into the marine environment can be due to atmospheric tranport. Desideri et al. (1994) suggested that MAHs found in Arctic snow are probably due to long range atmospheric transports from industrial regions, similar to the transport of polychlorobiphenyls (Risebrough et al., 1976). In contrast with CHCs, MAHs are less photochemically stable due to atmospheric reactions with OH-radicals, which can limit the atmospheric MAHs transport. Direct inputs could happen similarly to CHCs and via the marine traffic of oil products. Gomez-Belinchon et al. (1991) suggested that the MAHs in coastal waters off Barcelona were due to contributions from the Besos and the Llobregat river and/or to in situ inputs related to marine traffic activities. According to the same authors the MAHs on the La Pineda beach might result from marine traffic or from contributions from the nearly petrochemical complex.

I.2.3.2. FATE

I.2.3.2.1. Air/water exchange

When the air and water concentration of CHCs or MAHs are not in equilibrium, air/water exchange occurs. The equilibrium partitioning according to Henry's law, is dependant on the compound itself but also on the temperature and salinity (Hunter-Smith et al., 1983; Gossett, 1987; Moore et al., 1995; Dewulf et al., 1995). For the velocity of the exchange all models used are essentially based on the two film approach (Whitman, 1923; Liss and Slater, 1974). It is clear from the model that the exchange of VOCs is determined by the liquid boundary layer. The importance of the air/water exchange for the deposition of VOCs into isolated areas is already discussed (Comba and Kaiser, 1983; Fogelqvist, 1985; Dyrssen et al., 1990; Desideri et al., 1994).

In rivers the exchange is enhanced by the turbulence induced by the stream current. Trichloroethylene and tetrachloroethylene showed half lives due to air/water exchange of four to six days in the river Main in Germany (Brüggemann and Trapp, 1988). The estimation of the total yearly flux of halocarbons from water to air for the Elbe estuary confirms this exchange (Dyrssen et al., 1990). Using the two film model and a transfer rate coefficient of 15cm.h^{-1} the maximum fluxes were calculated as 350, 49, 3, 120 and 39 ton.year^{-1} for

chloroform, tetrachloromethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene respectively.

The high Monday and Tuesday concentrations of MAHs in the coastal water of Vineyard Sound beach (US) were explained by a pulse input during the weekend (Gschwend et al., 1982). The depletion of the enhanced concentrations within two or three days were considered to be due to air/sea exchange. This was illustrated by the application of the two film model to calculate the residence time where a period of approximately two days was calculated. Similar results were obtained by mesocosm experiments for VOCs in coastal sea water (Wakeham et al., 1983). For all CHCs it was found that the time after which the concentration in water was halved, was the same as for freon F12. This proved that biodegradation nor sorption was causing the depletion, but the air/water exchange. Moreover, the depletion in winter was faster than in summer time. This was explained by higher wind speeds creating a thinner stagnant water film layer.

I.2.3.2.2. Chemical degradation

No chemical degradation for VOCs (aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated C_2-hydrocarbons and chlorinated aromatic hydrocarbons) in marine waters is mentioned in an intensive fate and persistence study in coastal sea water (Wakeham et al., 1983). The study was on a time scale of about two months. This conclusion was confirmed by Chodola et al. (1989) for benzene, toluene, trichloroethylene and tetrachloroethylene.

Studies on the long term stability of CHCs were carried out in the fifties and eighties. Half life times for hydrolysis were found to be of the order of thousands of years in the fifties (Hine, 1950; Hine et al., 1956). More recently hydrolysis rate constants were determined by Jeffers et al. (1989) and by Jeffers and Wolfe (1989). For hydrolysis at 25°C and at pH 7, half life times of 1850, 40.5, 61.3, 72.0, 1.1, 1.3 10^6 and 9.9 10^8 years were calculated for chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene respectively. The rate of hydrolysis is very dependant on temperature. For tetrachloromethane and 1,1,1-trichloroethane the half life times of 40.5 and 1.1 years at 25°C increase to 468 and 12.2 years at 10°C and to 2790 and 74.2 years at 0°C, respectively.

In general it is clear that half life times for chemical degradation kinetics are far much higher than those for air/water exchange.

I.2.3.2.3. Biodegradation

No marine biodegradation of CHCs is reported. Only Krysell et al. (1994) suggested that tetrachloromethane could be removed by biological activity from the water mass under hypoxic and or anoxic conditions. Biodegradation for CHCs and MAHs in coastal waters was investigated by Wakeham et al. (1983). CHCs biodegradation was excluded since half life times were similar to the freon F12 half life time which was thought to be completely dependant on volatilization. In experiments with and without addition of mercury dichloride, which inhibits microbial activity, CHCs exhibited the same behaviour.
On the contrary, in the spring and summer biodegradation of MAHs in the same microcosm experiments was observed with concentration breaks after a lag period. These concentration breaks were interpreted as evidence of rapid biodegradation under the relatively warm spring and summer water temperatures. The lag period after the spiking was explained as the time for the microbial population to become acclimated. The biodegradation supposition was supported by mercury dichloride poisoned experiments. In conclusion, obvious microbial degradation was observed for MAHs but at concentrations of $3\mu g.L^{-1}$, much higher than mean environmental concentration levels.

I.2.3.2.4. Sorption and bioaccumulation

Since the CHCs and MAHs show low octanol/water partitioning coefficients ($\log K_{ow}<3.20$) (Verschueren, 1983; Schwarzenbach et al., 1993) sorption onto suspended solids or onto aquatic sediments is expected to be low, especially because the organic content of sea and lake sediments is low, with levels below 0.15% (Brusseau and Rao, 1991; Gamerdinger et al., 1994; Dewulf et al., 1995a). Wakeham et al. (1983) concluded that the sorption of CHCs and MAHs onto suspended particles is neglegible. Based on data of the octanol/water partitioning coefficicient and of the organic fraction of the suspended solid fraction, they calculated for tetrachloroethylene and toluene the fraction on suspended solids in the Narragansett Bay as 0.013 and 0.008% respectively. Dewulf et al. (1995) concluded similarly that the sorption of CHCs and MAHs on dissolved organic matter in sea water is neglegible. They found that the CHCs and MAHs air/water partitioning for an air/artificial sea water system (artificial sea water consisting of water and dissolved salts) was not significantly different from the partitioning in an air/natural sea water system.

I.2.4. CONCLUSIONS

The available sampling and analysis techniques enabled measurements of CHCs and MAHs in marine water samples during the last 20 years. In general, purge and trap is the most currently used preconcentration technique both for CHCs and MAHs. For the analysis of CHCs only, liquid/liquid extraction is the preferred technique because it can be combined with electron capture detection.

CHCs concentration data for estuaries, lakes and rivers are within a wide range, from as low as 1ng.L^{-1} concentration like in the Rhine estuary (Krysell and Nightingale, 1994) over a 10µg.L^{-1} level as in the Mersey estuary (Rogers et al., 1992) up to 1mg.L^{-1} concentrations in the Manchester Ship Canal (Rogers et al., 1992). All these data are depending on direct inputs of industrial sites and on volatilization. Less data are available on MAHs concentrations. Dewulf and Van Langenhove (1995) found 20-50ng.L^{-1} concentrations for individual MAHs in the Scheldt estuary, whereas Gomez-Belinchon et al. (1991) measured 4000-24000ng.L^{-1} concentrations in the Besos and Llobregat rivers.

CHCs concentrations in beach, fjorden, coastal and shelf sea waters are generally of a level from below 10 to 50ng.L^{-1}, except when known direct sources are present, e.g. for chloroform in the Idefjorden (Fogelqvist and Krysell, 1986). MAHs concentrations in these areas vary from below 10 to 14000ng.L^{-1}. Oil sources (Brooks et al., 1981; Sauer, 1980), vehicular transport (Gschwend et al., 1982) and shipping lanes and/or oil platforms (Sauer et al., 1978; Gomez-Belinchon, 1991) are cited as local inputs.

The lowest CHCs concentration data, with levels below 0.050ng.L^{-1}, are found in open oceans, especially in isolated areas like the Arctic ocean (Fogelqvist, 1985; Krysell and Wallace, 1988) and the Weddell Sea (Krysell, 1992).

The nature of these mainly anthropogenic compounds implies good stability with negligible chemical degradation. Data on the biodegradibility *in situ* at environmental concentration levels are not available. The physicochemical characteristics do not suggest important accumulation in biota or sediment. From this consideration and from their high air/water partitioning coefficient, air/water exchange is expected to be the main process in the fate of these VOCs in marine and riverine waters.

I.2.5. REFERENCES

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I.3. SEDIMENT

I.3.1. SAMPLING, STORAGE AND ANALYSIS

In this overview methods which have been developed to analyse CHCs and MAHs in real environmental aquatic sediments are discussed. In addition some analytical techniques in order to measure CHCs and MAHs in soil matrices are included since the soil and sediment matrices are similar.

I.3.1.1. SAMPLING AND STORAGE

Bianchi and Varney (1989a) used 850mL glass sampling vessels for the analysis of MAHs in estuarine sediment. Subsequent analysis by means of purge and trap was executed in the same vessel. After cleaning with detergent, acid and water and storing overnight at 150°C, the vessels were filled with approximately 100g sediment sample, taken with Van-Veen sediment grabs from the shipboard. The vessels were capped and stored on a dry-ice bed inside a collection box. Sodium azide was added to prevent any biological process and to minimise the degradation of organic compounds by bacteria. A similar technique is described for the analysis of 1,2-dihaloethanes (Bianchi and Varney, 1989b) and for the analysis of a wide range of compounds including alkanes, MAHs, CHCs, volatile sulfur compounds, alcohols, aldehydes, ketones, polycyclic aromatic hydrocarbons and furans (Bianchi et al., 1991).

Whelan et al. (1980) used a 1m long sphincter corer and a Casten corer to sample surface sediments from Walvis Bay in order to measure volatile C_1- to C_7-compounds, including benzene and toluene. They sectioned the cores on shipboard and placed them in Kopak Bags (Kopak Corp., Minnesota) which were heat-sealed and then frozen until the time of analysis. Another core sample was frozen in the core barrel and shipped to the laboratory before sectioning.

Ferrario et al. (1985) took samples from the sediment of Lake Pontchartrain (U.S.). Samples were immediately packed in ice, then frozen and kept at -5°C until analysis.

Marchand et al. (1994) sampled sediment in the Guaymas Basin (gulf of California) using a deep-sea submersible Nautile. The samples were stored frozen until analysis.

I.3.1.2. ANALYSIS

I.3.1.2.1. Preconcentration techniques

Prior to the analysis on a gas chromatograph (GC)-detector system for separation, identification and quantification, the VOCs have to be extracted and preconcentrated out of the sediment (or soil) matrix. Methods cited in literature are based on dynamic or static headspace techniques, on solvent extraction or on solid phase extraction.

I.3.1.2.1.1. Headspace techniques

I.3.1.2.1.1.1. Dynamic headspace analysis: the purge and trap technique

In the purge and trap method an aliquot of organic free water is added to a sample in a purge device (Ferrario et al., 1985; Charles and Simmons, 1987; Bianchi et al., 1991; Yan et al., 1992; Voice and Kolb, 1993; Al-Rekabi et al., 1995) whereas Bianchi and Varney (1989b) did not add any water to the sediment sample.
During purging samples were heated by immersion in a heated water bath (Bianchi and Varney, 1989b; Bianchi et al., 1991) or stirred (Charles and Simmons, 1987) to enhance the extraction efficiency. Bianchi and Varney (1989b) added a mass of purified salt to increase the ionic strength of the sample and to facilitate the "salting-out" effect. After temperature equilibration, clean gas (helium) is purged through the sample. The gas leaving the purge vessel is led through a sorbent trap, e.g. Tenax (Ferrario et al., 1985; Charles and Simmons, 1987; Bianchi and Varney, 1989b; Bianchi et al., 1991; Yokouchi and Sano, 1991; Yan et al., 1992; Voice and Kolb, 1993), Chromosorb-106 (Bianchi and Varney, 1989b; Bianchi et al., 1991), Sphericarb (Bianchi et al., 1991; Yan et al., 1992) or silicagel (Ferrario et al., 1985). After the purge and trap step, the sorbent is thermally desorbed with a pure gas which transfers the VOCs to a cold trap. The cold trap can be packed with a sorbent like Tenax TA (Bianchi and Varney, 1989b). The VOCs are injected into a GC by rapid heating of the cold trap. Ferrario et al. (1985) trapped the VOCs at the head of the analytical column at -50°C. The experimental setup of a purge and trap system used by Charles and Simmons (1987) is presented in Figure I.3.1.

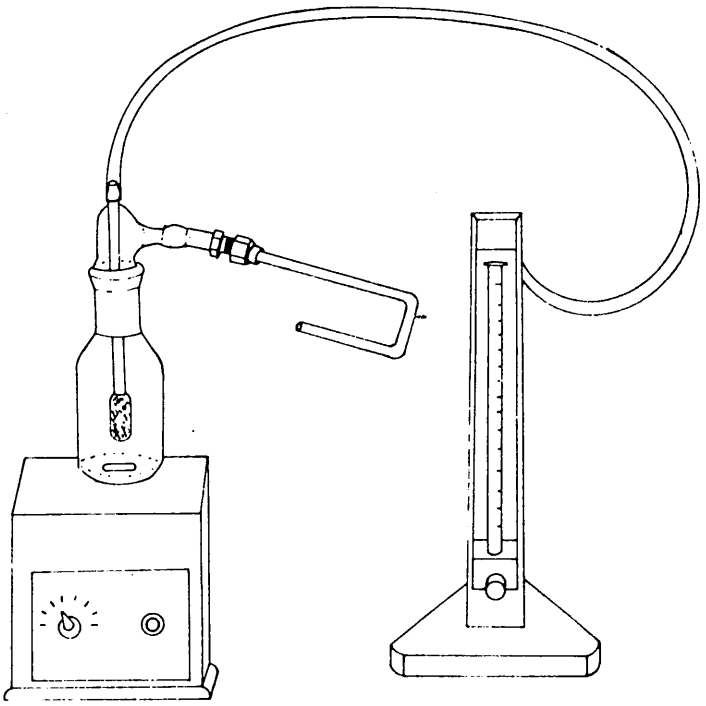


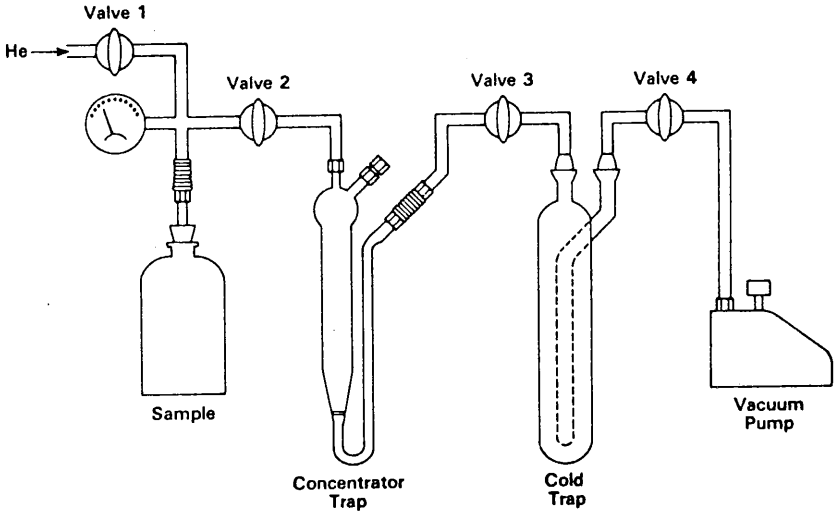
Figure I.3.1. Purge and trap analytical setup of Charles and Simmons (1987). The purge and trap vessel is placed on a magnetic stirrer. The flow of the input purge gas is checked with a flow meter and the output gas is led through a U-shaped adsorbent tube.

The EPA methods 5030 (general method), 8010 (specific for halogenated VOCs) and 8240 (combined with GC-MS analysis) are worked out for the measurement of VOCs in solids including sediments (US-EPA, 1989). For samples with concentrations below 1mg.kg^{-1} it is advised to add water and purge the samples at elevated temperatures, e.g. 40°C. Proposed sorbents are 1/3 Tenax, 1/3 silica gel and 1/3 coconut charcoal.

Murray and Riley (1973) placed their sample tubes (without any addition of water) in a tube furnace and the samples were heated up to 200°C during purging. The purge gas was led over a cryogenic trap (-78°C) after it had passed through a drying tube containing anhydrous magnesium perchlorate. Similarly Yokouchi and Sano (1991) purged nitrogen through soil samples at 150°C for 7 minutes in order to sweep the VOCs from the soil sample onto a Tenax GC trap, which was kept at 10°C.

I.3.1.2.1.1.2. The vacuum extraction technique

The vacuum extraction instrumentation, presented in Figure I.3.2a (Hiatt, 1981), consists of a helium inlet, a sample vessel, a concentrator trap, a cold trap and a vacuum pump. All parts can be isolated by valves. To start an extraction, the system is evacuated while an empty



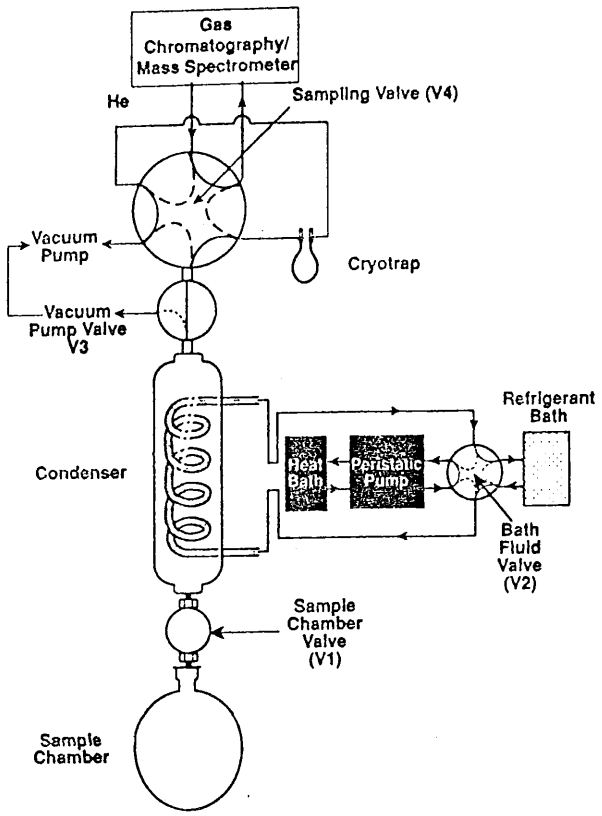


Figure I.3.2. Experimental setup of the vacuum extraction technique of Hiatt (1981) (a) and of Hiatt et al., (1994) (b).

vial is connected. Subsequently the sample to be analysed is connected while valve 2 remains closed and the concentration trap is cooled with a liquid nitrogen bath. Then valve 2 is opened to permit the vapors to reach the concentrator. The sample is heated to 50°C by means of an ultrasonic bath. After 5 minutes valve 3 is opened to create a lower pressure to hasten the transfer of VOCs from the sample to the concentrator. Finally, valve 3 is closed, the sample and the preconcentration trap are pressurized (1atm.) with helium, and valve 1 and valve 2 are closed in order to isolate the concentrate. After this vacuum extraction (15min) the concentrate is held at liquid nitrogen temperature until it is analysed with a conventional purge and trap procedure.

Another vacuum distillation apparatus is presented in Figure I.3.2b (Hiatt et al., 1994; Hiatt and Farr, 1995). In this experimental setup a condensor in inserted between the sample and the cryotrap in order to condense water vapours at -5°C. In addition, the cryotrap can be placed on-line with a GC-MS system by means of a sampling valve.

I.3.1.2.1.1.3. Closed-loop stripping/ steam distillation combination

The closed-loop stripping/steam distillation (Amin and Narang, 1985), as presented in Figure I.3.4, is basically a stripping technique. VOCs are purged out of the sediment sample and they are trapped on a sorbent (Porapak N) which is afterwards analysed by thermal desorption combined with cryotrapping. During the preconcentration, air leaving the sorbent trap is pumped into the closed vessel and so a closed loop is created. In addition, the sample is heated to 120°C by which the purging is combined with a steam distillation.

I.3.1.2.1.1.4. Static headspace technique

Bianchi and Varney (1989a) analysed MAHs in estuarine sediment samples with a static headspace technique (Figure I.3.3). To approximately 100g frozen sediment, 500mL de-ionised water was added in an 850mL vessel. Ultrapure helium was purged into the headspace above the water level for 1 minute. Then, the frozen sediment was allowed to thaw at room temperature for 1h. The vessel was agitated for 5min. to achieve dispersion of the solid phase into the water phase and the vessel was subsequently placed in a hot water-bath of 80°C. After a 45 min. equilibration time, 2mL headspace was analysed by GC-FID.

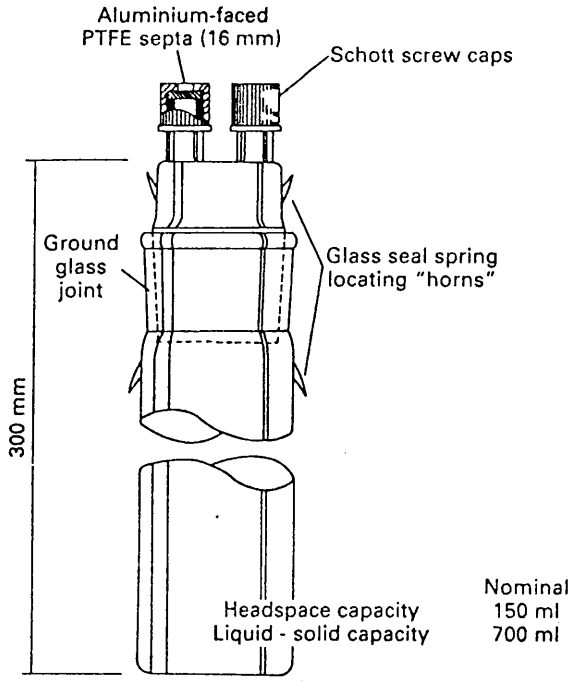


Figure I.3.3. Experimental setup for the static headspace technique of Bianchi and Varney (1989a).

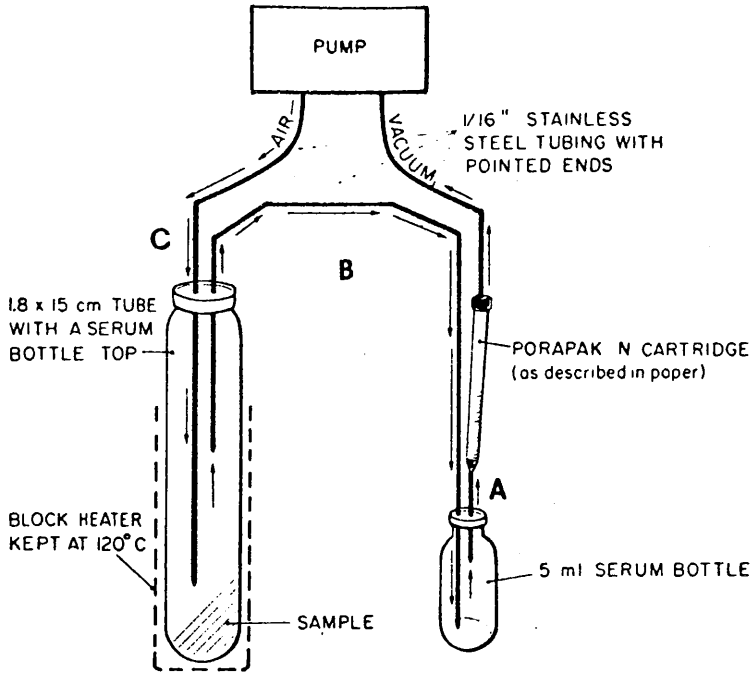


Figure I.3.4. Closed-loop stripping/steam distillation technique of Amin and Narang (1985).

Kawata et al. (1988) developed a similar technique for CHCs. To the sediment 5M NaCl, containing $^2H_4$-1,2-dichloroethane as internal standard, was added and the sample vial was ultrasonicated. After equilibration at 40°C, 0.2mL headspace was analysed by GC-MS.
Voice and Kolb (1993) also applied sonication in the headspace analysis. After adding 3mL of water to a 1g sample, the sample was sonicated for 15 minutes at 80°C and analysed by an automated headspace analyzer after equilibration at 95°C.
Whelan et al. (1980) filled a can, equipped with silicone rubber septums, with water and frozen sediment. A helium headspace was made by injecting 150mL helium and withdrawing 150mL of water. After thawing the sediment, the can was shaken and heated for 30 minutes at 95°C. 5 to 30mL headspace was analyzed after a preconcentration in a stainless steel loop at liquid nitrogen temperature.

I.3.1.2.1.2. Solvent extraction techniques

I.3.1.2.1.2.1. Solvent extraction

Siegrist and Jenssen (1990) extracted 10g soil samples with a 10mL of 2-propanol and 4mL of pentane. The solvent mixture was transferred to a small seperatory funnel and the extraction was repeated with 5mL of 2-propanol and 4mL of pentane. The extracts were combined, and the pentane phase was isolated by extraction with deionized water. The pentane extract was washed with 2mL of water and dried with sodium sulphate prior to gas chromatographic analysis.

I.3.1.2.1.2.2. Solvent extraction followed by headspace analysis after dilution in water

In a number of reports a method is reported in which methanol extraction of the sample is followed by dynamic or static headspace analysis of the methanol extract after dilution in pure water (Voice and Kolb, 1993; Amaral et al., 1994; Marchand et al., 1994).
Amaral et al. (1994) extracted 1-3g sediment with 5mL of methanol. Subsequently 200µL was diluted in 100mL in Milli-Q-purified water and 5mL of this water was analyzed by purge and trap (dynamic headspace).
Marchand et al. (1994) analysed aliphatic and aromatic hydrocarbons and volatile sulfur compounds by extracting the sediment with methanol under ultrasonication. After extraction

and centrifugation, an aliquot of the methanol solution was added to laboratory water which was submitted to purge and trap analysis.
Voice and Kolb (1993) added 3mL of cold methanol (-32°C) to 1g of sample. After sonication for 15 minutes at 30°C and chilling again for 1h at -32°C, one mL of methanol extract was removed and quickly transferred to a headspace vial containing 9mL of water, saturated with sodium chloride. Subsequently static headspace analysis at 95°C was done by means of an automated headspace analyser.

A second solvent applied in order to extract VOCs out of the solid matrix with this approach is methyl glycol. Preuss and Attig (1986) added 25mL of methyl glycol to 25g of sample. 0.5mL of the extract was added to 5mL of water. After equilibrium during 30 minutes at 60°C, static headspace analysis was done.

A related technique is the technique of Siegrist and Jenssen (1990). After methanol extraction, water and pentane are added to the extract. Pentane is removed and a second pentane extraction is done. The pentane extracts are combined and after washing with deionized water and drying with sodium sulfate the pentane extracts were analyzed.

I.3.1.2.1.2.3. Steam distillation with concentration into hexane

Kawata et al. (1986) extracted the CHCs 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene from soils into hexane by steam distillation.

I.3.1.2.1.3. Supercritical fluid extraction

Levy and Rosselli (1989) developed a preconcentration technique based on supercritical fluid extraction (SFE), on-line with a gas chromatograph. This technique allowed the analysis of a wide range of compounds including CHCs and MAHs. The SFE extractor consisted of a 250mL syringe pump with pressure limits up to 500atm and an extraction cell with 2 micron frits at each end. The extractor permitted an automatic operation of a four-port selection valve and automatically initiated the run on the GC after the transfer of the extraction effluent.

I.3.1.2.2. Separation and detection

In all studies on the analysis of CHCs and MAHs in aquatic sediments, the VOCs are separated by gas chromatography with commercially available capillary or packed columns. Capillary columns with stationary phases like poly (100%-dimethylsiloxane) (Kawata et al., 1988; Bianchi and Varney; 1989a; Bianchi and Varney, 1989b; Hewitt et al., 1992; Al-Rekabi et al., 1995), poly (5%-diphenyl-95%-dimethylsiloxane) (Amin and Narang, 1985; Yan et al., 1992), poly (20%-diphenyl-80%-dimethylsiloxane) (Amaral et al., 1994; Hiatt et al., 1994) and poly (14%-cyanopropylphenyl-86%-dimethylsiloxane) (Bianchi et al., 1991; Yan et al., 1992) are reported.

VOCs were separated on packed columns with stationary phases consisting of poly (dimethylsiloxane), poly (35%-diphenyl-65%-dimethylsiloxane) and poly (50%-cyanopropylmethyl-50%-phenylmethylsiloxane) by Amin and Narang (1985) and with poly (3-nitro-p-phtalic (poly ethylene glycol)) by Hewitt et al. (1992). Also Preuss and Attig (1986) used this type next to poly ethylene glycol type stationary phases. Finally, styrene-divinylbenzene polymers as stationary phase were used by Yokouchi and Sano (1991) in order to separate a wide range of compounds (ketones, aldehydes, alkanes, MAHs, terpenes...).

After gas chromatographic separation, detection is carried out by means of common used detectors like flame ionization detectors (FID) (Bianchi and Varney, 1989a; Preuss and Attig, 1986), electron capture detectors (ECD) (Murray and Riley, 1973; Preuss and Attig, 1986; Amin and Narang, 1986; Kawata et al., 1986; Siegrist and Jenssen, 1990; Amaral et al., 1994), photoionization detectors (PID) (Amin and Narang, 1985; Hewitt et al., 1992), miniaturized thermal conductivity detectors (TCD) (Yan et al., 1992) and mass spectrometers (MS), either in full scan mode (Whelan et al., 1980; Ferrario et al., 1985; Yokouchi and Sano 1991; Hewitt et al., 1992; Hiatt et al., 1994; Marchand et al., 1994) or in selective ion monitoring mode (Kawata et al., 1988; Siegrist and Jenssen, 1990). A combination of FID/MS (50:50) was applied by Bianchi and Varney (1989b) and by Bianchi et al. (1991), whereas Al-Rekabi et al. (1995) used a FID/ECD (50:50) combination. Voice and Kolb (1993) used a Hall detector in series with a PID-detector.

I.3.1.2.3. Limits of detection and precision

Data on limits of detection and on precision are presented in Table I.3.1. The lowest limits

of detection reported (LODs, usually defined as a signal to noise ratio equal to three) are in the ng.kg^{-1} concentration range. Bianchi et al. (1991) found LODs from 10 (benzene, toluene) to 20 (ethylbenzene, o- and m-xylene) ng.kg^{-1} for MAHs and from 10 (chloroform and 1,1,1-trichloroethane) to 15 ng.kg^{-1} (trichloroethylene) for CHCs with purge and trap preconcentration and MS/FID detection. With the same preconcentration and detection system Bianchi and Varney (1989b) reported 5ng.L^{-1} as LOD for 1,2-dichloroethane. Al-Rekabi et al. (1995) reported 40-50ng.kg^{-1} detection limits for the use of purge and trap preconcentration combined with FID/ECD detection.

With static headspace and MS-detection in selective ion mode Kawata et al. (1988) measured LODs of 20ng.kg^{-1} for 1,1-dichloroethane and 400ng.kg^{-1} for tetrachloroethylene. The same preconcentration technique, showed detection limits (defined as a signal to noise ratio of 2) of 9, 10, 70, 80 and 80ng.kg^{-1} for benzene, toluene, ethylbenzene, o-xylene and m-xylene respectively (Bianchi and Varney; 1989a).

Higher LODs reported are in the µg.kg^{-1} range. Amin and Narang (1985) measured a LOD (signal to noise ratio 5:1) of 7µg.kg^{-1} for PID-active VOCs (MAHs) and 1µg.kg^{-1} for ECD-active compounds (CHCs) with closed loop stripping/vacuum distillation preconcentration. They analysed smaller sample volumes (5g dry matter) than other researchers: e.g. Bianchi et al. (1991) analysed 300-400g wet sediment. LODs for trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane with steam distillation preconcentration and ECD-detection were 10, 3 and 3ppb, respectively (Kawata et al., 1986). For the vacuum distillation technique, Hiatt et al. (1994) found LODs in the range from 1.7 to 4.4ppb for 1,1-dichloroethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethylene, benzene, tetrachloroethylene, toluene, ethylbenzene, p-xylene and o-xylene. Concentration of 10ppb tetrachloroethylene can be detected by means of methylglycol extraction followed by headspace analysis after dilution in water (Preuss and Attig, 1986).

Higher LODs for CHCs are reported for methanol extraction followed by purge and trap analysis after dilution in water (20-200µg.kg^{-1}) (Amaral et al., 1994), for solvent extraction (4-100µg.kg^{-1}) (Siegrist and Jenssen, 1990), for methanol extraction followed by pentane/water extraction (2-50µg.kg^{-1}) and for purge and trap analysis in combination with TCD detection (5-25µg.kg^{-1}) (Yan et al., 1992). For MAHs LODs of 5-25µg.kg^{-1} are reported for purge and trap analysis in combination with TCD detection (Yan et al., 1992), of 40µg.kg^{-1} for methanol extraction followed by pentane/water extraction (Siegrist and Jenssen, 1990), of 50µg.kg^{-1} for pentane/propanol extraction (Siegrist and Jenssen, 1990) and of 500µg.kg^{-1} for methyl glycol

extraction followed by headspace analysis after dilution in water (Preuss and Attig, 1986).
Less data are available on reproducibility. Reproducibility data for the purge and trap preconcentration were investigated by Bianchi et al. (1991) at 100ng.kg^{-1}, 1000ng.kg^{-1} and 100µg.kg^{-1}. For MAHs (benzene, toluene, ethylbenzene, o- and m-xylene) relative standard deviations varied between 1.1 and 3.5% whereas for CHCs (chloroform, 1,1,1-trichloroethane and trichloroethylene) reproducibilities of 2.1 to 3.7% are reported. For 1,2-dichloroethane a reproducibility with less than 3% standard deviation was obtained with the same preconcentration technique (Bianchi and Varney, 1989b).
Replicate analyses of samples from the middle of the Southampton estuary with concentrations from 2.2 to 49.3 µg.kg^{-1} for MAHs showed reproducibilities with standard deviations from 1.1 to 2.0% with static headspace preconcentration (Bianchi and Varney, 1989a). Similarly Whelan et al. (1980) reported 5% relative standard deviations for the headspace technique.
For on-line SFE/GC analysis of CHCs in sediment, relative standard deviation from 4.2 to 5.8% are reported by Levy and Rosselli (1989).
Finally, higher relative standard deviations are given by Preuss and Attig (1986) (10-20%) for methyl glycol extraction followed by headspace analysis after dilution in water, and by Hewitt et al. (1992) for the headspace technique (1.3-23%) and for the purge and trap technique (0.8-38%).
A summary on detection limits and reproducibility is presented in Table I.3.1.

I.3.1.2.4. Calibration

The optimum sediment matrix in order to make calibration standards is the matrix from the sample itself (Bianchi and Varney, 1989a; Bianchi et al., 1991). Sediment particle size distribution and organic matter content vary between samples and may affect the sorption and subsequent desorption of VOCs. Bianchi and Varney (1989a) took sediment from a relatively unpolluted estuarine site. The sediment was subjected to solvent extraction methods in addition to boiling, stripping with nitrogen and washing with water prior to drying in an oven at 105°C for 72h. It was recognised by the authors that these procedures could destroy or modify the adsorptive sites within the grain-particle matrix.

Table I.3.1. Limits of detection (LODs) and reproducibilities (in % relative standard deviation, %SD) of techniques analysing CHCs and MAHs in sediment with respect to preconcentration technique (Prec. techn.) and detection system (Det. syst.).[1]

VOCs	Prec. techn.	Det. syst.	LOD ($\mu g.kg^{-1}$)	%SD	Reference
$CHCl_3$, TRI, TCE	P&T	MS/FID	0.010 - 0.015	2.1 - 3.7	Bianchi et al., 1991
1,2-DCE	P&T	MS/FID	0.005 [2]	3	Bianchi and Varney, 1989b
1,1-DCE	HS	MS	0.020	-	Kawata et al., 1988
TTCE	HS	MS	0.400	-	Kawata et al., 1988
$CHCl_3$, CCl_4, TRI, TCE, TTCE	CLS/SD	ECD	1	-	Amin and Narang, 1985
TRI, TCE, TTCE	SD	ECD	3-10	-	Kawata et al., 1986
$CHCl_3$, CCl_4, 1,1-DCE, 1,2-DCE, TRI, TCE	VD	MS	1.7 - 2.6	-	Hiatt et al., 1994
CCl_4, 1,1-DCE, TRI, TCE	SFE	ECD	-	4.2 - 5.8	Levy and Rosselli, 1989
$CHCl_3$, CCl_4, 1,1-DCE, 1,2-DCE, TRI, TCE, TTCE	MeOH/PT	ECD	20 - 200	-	Amaral et al., 1994
TTCE	MeGl/HS	ECD	10	10 - 20	Preuss and Attig, 1986
1,2-DCE, TRI, TCE	Extr.	ECD	4 - 100	-	Siegrist and Jenssen, 1990
1,2-DCE, TRI, TCE	MeOH/Ex	ECD	2 - 50	-	Siegrist and Jenssen, 1990
$CHCl_3$, 1,1-DCE, TTCE	P&T	TCD	5 - 25	-	Yan et al., 1992
TCE	HS	PID	-	1.3 - 23	Hewitt et al., 1992
TCE	P&T	MS	-	0.8 - 38	Hewitt et al., 1992
BENZ, TOL, ET-B, m-Xyl, o-Xyl	P&T	MS/FID	0.010 - 0.020	1.1 - 3.5	Bianchi et al., 1991
BENZ, TOL, o-Xyl, m-Xyl, p-Xyl	P&T	FID	0.040 - 0.050	-	Al-Rekabi et al., 1995
BENZ, TOL, ET-B, o-Xyl, m-Xyl	HS	FID	0.009 - 0.080	1.1 - 2	Bianchi and Varney, 1989a
BENZ, TOL, ET-B, o-Xyl, p-Xyl	VD	MS	2.9 - 4.4	-	Hiatt et al., 1994
BENZ, TOL, o-Xyl, p-Xyl	CLS/SD	PID	7	-	Amin and Narang, 1985
BENZ	MeGl/HS	FID	500	10 - 20	Preuss and Attig, 1986
TOL	Extr.	MS	50	-	Siegrist and Jenssen, 1990
TOL	MeOH/Ex	MS	40	-	Siegrist and Jenssen, 1990
BENZ, TOL	HS	MS	-	5	Whelan et al., 1980
BENZ, TOL	P&T	TCD	5 - 25	-	Yan et al., 1992
BENZ, TOL	HS	PID	-	1.3 - 23	Hewitt et al., 1992
BENZ, TOL	P&T	MS	-	0.8 - 38	Hewitt et al., 1992

[1] Abbreviations: 1,1-DCE: 1,1-dichloroethane, 1,2-DCE: 1,2-dichloroethane, TRI: 1,1,1-trichloroethane, TCE: trichloroethylene, TTCE: tetrachloroethylene, BENZ: benzene, TOL: toluene, ET-B: ethylbenzene, m-Xyl: m-xylene, o-Xyl: o-xylene, p-Xyl: p-xylene, P&T: purge and trap, VD: vacuum distillation, HS: static headspace, CLS/SD: closed loop stripping/steam distillation, SD: steam distillation, SFE: supercritical fluid extraction, MeOH/PT: methanol extraction followed by purge and trap analysis after dilution in water, MeGl/HS: methyl glycol extraction, followed by static headspace analysis, Extr.: solvent extraction, MeOH/Ex: methanol extraction followed by pentane/water extraction, MS: mass spectrometer, FID: flame ionization detector, ECD: electron capture detector, PID: photoionization detector, TCD: miniaturized thermal conductivity detector. [2] in $\mu g.L^{-1}$

However, a suitable compromise was sought between the necessity for a representative 'blank' sediment and the physico-chemical integrity of the original sediment itself. The calibration was done by adding spiked water to these blanks. In a same way Yan et al. (1992) calibrated purge and trap analysis of soils by adding a water solution containing the standards to a soil matrix.

In the methanol extraction technique followed by dilution in water, standards were prepared in methanol (Amaral et al., 1994). In a same way Preuss and Attig (1986) prepared standards in methyl glycol before dilution in water. Whelan et al. (1980) injected the VOCs for calibration in a blank can in order to calibrate headspace analyses. Blank water, purged with helium, was spiked with purchased standards in order to calibrate methanol extracts in the report of Marchand et al. (1994). In this applications the effects of the matrix is not considered with respect to the calibration.

I.3.1.2.5. Recovery

Charles and Simmons (1987) measured overall recoveries, i.e. the percentages of measured VOCs of the total mass spiked, for the purge and trap method as 38% for chloroform and 48% for trichloroethylene. Recoveries for the same preconcentration technique were 50-62% for MAHs and 69% for chloroform in the study of Al-Rekabi et al. (1995). With the same method Voice and Kolb (1993) found for several types of soils recoveries below 50% for 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, benzene, toluene, ethylbenzene and the xylenes in most cases. They observed an increasing recovery with decreasing volatility, suggesting that volatilization losses can be substantial. It was hypothesized that these losses occur as a result of the need to transfer the soil to the purging vessel. Also Yan et al. (1992) found recoveries for purge and trap analysis of soils below 50% for chloroform (43.6%), 1,1-dichloroethane (32.8%), benzene (39.2%) and toluene (34.5%).

The purge and trap technique of Murray and Riley (1973) applying heating of the sample up to 200°C during purging showed better recoveries. For the CHCs chloroform, tetrachloromethane, trichloroethylene and tetrachloroethylene, they found recoveries of 57, 83, 94 and 83% respectively.

Hiatt (1981) compared the recoveries in the vacuum extraction technique with those of the purge and trap technique. Vacuum extraction showed recoveries from 96 to 106% for CHCs (1,1-dichloroethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloromethane,

trichloroethylene and tetrachloroethylene) whereas for MAHs (benzene, toluene and ethylbenzene) recoveries of 94 to 102% were measured. Purge and trap showed lower recoveries: for CHCs from 57% (tetrachloroethylene) to 94% (tetrachloromethane), for toluene 34% and for benzene 59%. Recoveries from a soil matrix with this vacuum distillation technique were 67±19, 114±28, 99±14, 137±23, 82±59, 52±16, 54±12, 56±16, 50±13, 70±23, 60±19 and 66±20% for 1,1-dichloroethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethylene, benzene, tetrachloroethylene, toluene, ethylbenzene, p-xylene and o-xylene respectively (Hiatt et al., 1994).

Voice and Kolb (1993) found higher recoveries for the direct headspace analysis. The recoveries were from 68 to 88% for 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, benzene, toluene, ethylbenzene and the xylenes. Kawata et al. (1988) measured recoveries of 85.9 to 99.9% for CHCs with the static headspace technique.

Amin and Narang (1985) spiked sediments with CHCs (chloroform, tetrachloromethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene), directly or by adding spiked water. They found no significant differences in recoveries, varying between 70 and 102%, using the closed loop stripping/steam distillation.

For on-line SFE/GC recoveries from 84 to 94% are reported for CHCs (Levy and Rosselli, 1989).

Recoveries for steam distillation into hexane were 86-90, 92-98 and 84-88% for trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane, respectively (Kawata et al., 1986).

The methanol extraction technique followed by purge and trap analysis after dilution in water showed recoveries from 68 to 81% for the chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene (Amaral et al., 1994). The methyl glycol extraction followed by headspace analysis after dilution in water (Preuss and Attig, 1986) showed recoveries from 91 to 105% for compounds including CHCs and MAHs. Finally the pentane/propanol extraction technique of Siegrist and Jenssen (1990) had recoveries for 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and toluene of 73, 100, 112 and 115% respectively.

I.3.2. MEASUREMENTS

Bianchi et al. (1991) analysed the sediment in the Solent estuary, a water body separating the Isle of Wight from the channel of Southampton Water on the coastline of central southern England, for more than 100 organic compounds. The investigated site is a semi-industrial estuary accommodating a broad range of activities including oil-refining, petrochemical processing, electricity generation and intense recreational and merchant-marine activities. Measurement results are presented in Table I.3.2 for CHCs and Table 3 for MAHs. Other CHCs measurements were carried out by Ferrario et al. (1985) in Lake Pontchartrain, an estuary located in the deltaic plain of the Mississippi River, where concentrations from below 0.01 (1,2-dichloroethane) to 18$\mu g.kg^{-1}$ were observed (Table I.3.2). Inputs could arise from anthropogenic sources.

Table I.3.2. Concentrations of CHCs ($\mu g.kg^{-1}$) in the Solent estuary over a 18-months period (from Bianchi et al., 1991) and in Lake Pontchartrain, an estuary in the deltaic plain of the Mississippi River (Ferrario et al., 1985)

CHC	Solent Estuary	Lake Pontchartrain
Chloroform		1.7 - 18
Tetrachloromethane	0.075 - 1.856	0.3
1,2-Dichloroethane	0.070 - 11.045	<0.01 - 0.1
1,1,1-Trichloroethane	0.070 - 31.031	0.01
Trichloroethylene	0.070 - 4.005	0.1 - 0.2
Tetrachloroethylene	0.085 - 20.177	0.3

In the study of Bianchi et al. (1991), the most significant variations in VOCs concentrations occurred as a result of seasonal changes, apart from random pollution related events. VOCs in sediments reached minimum concentrations during July-August and their maximum from October to January. The higher summer temperatures were suggested to accelerate evaporation from surface water relative to sorption and deposition processes. Other factors explaining the seasonality were cooler sea-surface temperatures, significant increases in organic load to the estuary from its source rivers (e.g. autumn leaf-fall), and increased anthropogenic inputs to the estuary during autumn (i.e. increased rainfall run-off, increased use of fossil fuels and

Table I.3.3. MAHs concentration measurements in aquatic sediments (μg.kg^{-1})

Location	BENZ	TOL	ET-B	o-Xyl	m-Xyl	Reference
Solent estuary (UK)	0.30 - 96.74	0.55 - 120.20	0.51 - 201.10	0.87 - 480.56	0.88 - 480.20	Bianchi et al., 1991
Southampton estuary (UK)	8.4	49.3	7.1	2.2	4.7	Bianchi and Varney, 1989a
Moravia & Danube Rivers (Slovakia)	<0.04 - 1.67	<0.04 - 290		<0.04 - 0.29	<0.04 - 1.53 [2]	Al-Rekabi et al., 1995
Guaymas Basin (US)	1574	663				Marchand et al., 1994
Lake Ponchartrain (US)	8 - 21	0.7				Ferrario et al., 1985
Walvis Bay	0 - 20.4	0 - 197				Whelan et al., 1980

[1] Abbreviations: BENZ: benzene, TOL: toluene, ET-B: Ethylbenzene, o-Xyl: o-xylene, m-Xyl: m-xylene.

[2] Sum of m-xylene and p-xylene.

urban pollution). The MAHs were considered as fully anthropogenic, except toluene which has also several biological formation pathways (Jüttner and Henatsch, 1986). The authorssuggested that toluene was generated by identical processes *in situ* within surface sediments in the Southampton Water, especially in the weeks following the autumn leaf fall. Bianchi and Varney (1989a) measured MAHs in the Southampton estuary (Table I.3.3). In a mid-estuarine sediment sample they found 8.4, 49.3, 7.1, 4.7 and 2.2$\mu g.kg^{-1}$ benzene, toluene, ethylbenzene, m-xylene and o-xylene respectively. These data are comparable with those of the Solent estuary (Bianchi et al., 1991).

Al-Rekabi et al. (1995) measured MAHs in the Morava and Danube Rivers in Slovakia in spring and summer 1992 (Table I.3.3). Sampling sites included sites exposed to pollutants for an industrial zone, municipal discharges from the Bratislava city and oil refineries. Concentrations for benzene, toluene, m/p-xylene and o-xylene were <0.04 - 1.67, <0.04 - 290, <0.04 - 1.53 and <0.04 - 0.29 $\mu g.kg^{-1}$.

Similar concentration levels are observed for the Lake Pontchartrain by Ferrario et al. (1985) (Table I.3.3). They found concentrations for benzene and toluene of 8-21 and 0.7$\mu g.kg^{-1}$ respectively. Also in this case anthropogenic sources were suggested.

Marchand et al. (1994) measured MAHs in the southern depression of the Guaymas Basin (gulf of California) in November 1991. The thermal alteration of recent sedimentary organic matter was found to generate hydrothermal hydrocarbons. At depths from 0-15cm, concentrations up to 1574 and 663ppb were found for benzene and toluene respectively, whereas ethylbenzene and xylenes were not detected. The benzene and toluene concentrations were explained by their production from thermal degradation of many organic materials such as phenylalanine and β-carotene.

Whelan et al. (1980) measured at three sites in the Walvis Bay benzene and toluene among other VOCs (Table I.3.3). At two out of three sites they found higher levels of toluene (10.6-197$\mu g.kg^{-1}$). These two sites are more anoxic than the third site where concentrations from 0 to 10$\mu g.kg^{-1}$ were detected. The authors suggested microbial breakdown of terpenes. Also biological reactions were suggested. If, for example, methylcyclohexene is a breakdown product of terpenes, toluene could result from a series of allylic hydroxylations and dehydrations. A similar path from cyclohexene could lead to the small but significant amounts of benzene detected.

I.3.3. SOURCES

The main input of CHCs and MAHs in aquatic sediments is considered to originate from the water layer. CHCs and MAHs can enter the aquatic sediment via diffusion, percolation or deposition of suspended solids. For the sources of the VOCs in the water column, it is referred to the literature study on CHCs and MAHs in the water column.

For benzene and especially for toluene *in situ* sediment sources are suggested. Marchand et al. (1994) explained benzene and toluene concentrations in the Guaymas Basin in the Gulf of Mexico by thermal degradation processes of organic materials. Whelan et al. (1980) suggested microbial and biological processes to explain benzene and toluene concentrations in the Walvis Bay. In this case the authors could exclude thermal processes. In a first explanation terpenes (e.g. β-carotene) are supposed to undergo microbial breakdown. Alternatively, biological reactions could give rise to precursors which could react at low temperatures with sediment to give toluene. For example, terpenes are potential sources of furans and cycloalkenes. If methylcyclohexene is produced, toluene could result from a series of allylic hydroxilations and dehydrations (Figure I.3.5). Similar paths for cyclohexene could lead to small amounts of benzene.

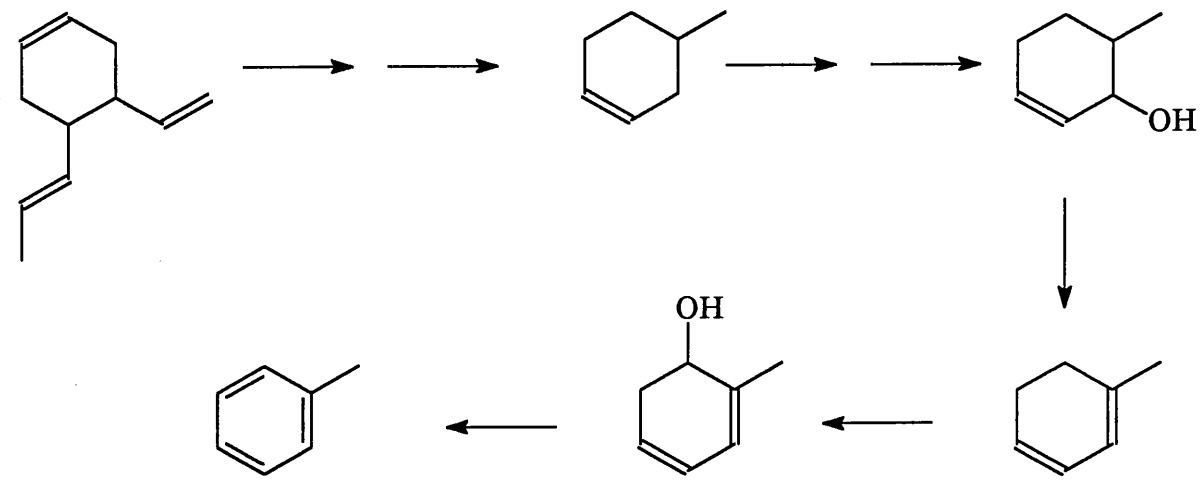


Figure I.3.5. Suggested natural pathway for the formation of toluene in sediments (Whelan et al., 1980).

I.3.4. FATE

I.3.4.1. DISTRIBUTION WITHIN THE SEDIMENT

A VOC in the aquatic sediment is distributed over the different fractions. It is solved in the pore water, sorbed on organic matter and on inorganic matter:

$$C_s = C_w \cdot f_w + C_{org} \cdot f_{org} + C_{inorg} \cdot f_{inorg}$$

whereas C_s, C_w, C_{org} and C_{inorg} are the concentrations (mole.L^{-1}) of the VOC in the sediment and in the sediment fractions water, organic matter and inorganic matter, respectively. f_w, f_{org} and f_{inorg} represent the volume fractions of water, organic matter and inorganic matter respectively.

Since the apolar nature of both the VOCs and the organic matter fraction, the partitioning in the sediment in mainly ruled by sorption on the organic matter fraction. Then, the relationship can be written as (Means et al., 1980; Schwarzenbach et al., 1993):

$$C_s = C_{org} \cdot f_{org}$$

In the seventies the partitioning to the organic matter was considered to be an adsorption process (Haque; 1975; Brown and Chesters, 1977), but later on (Chiou, 1979) absorption is considered to rule the partitioning. Because of the "porous" nature of the natural organic macromolecules which are coiled into globular units, the VOCs can physically penetrate between the chains and are "dissolved" in the nonaqueous medium (Schwarzenbach et al., 1993). The discrepancy of the determined surface area of organic matter by N_2-adsorption and ethylene glycol confirmed that the inner surface of the organic matter is much larger than the outer surface (Chiou et al., 1990).

Sorption on sediment-associated organic matter can be lower than on free organic matter (Isaacsson and Frink, 1984). According to these authors, the difference may lie in the overall structure of sediment-associated organic matter, in different particle size fractions and in the case of penetration of organic molecules into the bulk of the organic matter.

In order to describe the equilibrium distribution of apolar organic compounds, the Freundlich

model is proposed (Means et al., 1980; Garbarini and Lion, 1985; Zytner et al., 1989):

$$C_s = K \cdot C_w^n$$

where K is the Freundlich constant and n the non-linearity exponent. The model can be simplified into a linear sorption model if n=1. Another model is the biphasic model of Pavlostathis and Mathavan (1992). This model states that one fraction of the sorbed organic compounds can be desorbed whereas a second fraction resists desorption:

$$C_s = C_{s1} + K' \cdot C_w$$

C_{s1} is the desorption resistant concentration in the sediment (mole.L^{-1}) and K' the equilibrium constant for the fraction undergoing desorption.
Usually the linear model is applied in order to describe the sorption. If the partitioning is determined by the organic matter fraction, then

$$K = K_{org} \cdot f_{org}$$

with K_{org} the organic matter/ water equilibrium partitioning coefficient. In this way K_{org} has to be estimated. Relationships between K_{org} and the aqueous solubility but mainly between K_{org} and the octanol/water equilibrium coefficient are established (Means et al., 1980; Karickhoff, 1981; Schellenberg et al., 1984):

$$\log K_{org} = a \cdot \log K_{ow} + b$$

However, because of the heterogenity of the organic matter, variations on K_{org} for toluene were a factor of 2.5 (Garbarini and Lion, 1985). Log K_{org}-log K_{ow} relationships involving CHCs and MAHs are presented in Table I.3.4. Log K_{ow} of CHCs and MAHs are presented in Table I.3.5.

Table I.3.4. Log K_{om}-log K_{ow} relationships for organic compounds: log K_{om} = a.log K_{ow} + b

a	b	n	r^2	compounds*	Reference
0.989	-0.048	5	0.997	benzene and PAHs	Karickhoff, 1981**
0.72	0.707	13	0.95	PCE, n-Bu-benz., Cl- and Me-benzenes	Schwarzenbach & Westall,1981**
0.904	-0.779	12	0.989	MAHs, PCBs, Cl-benzenes, anisole	Chiou *et al.*, 1983
0.69	0.428	5	0.99	TCE, PCE, benzene, DCB	Piwoni & Banerjee, 1989**
0.82	0.14	34	0.93	Arom. HCs, Cl-HCs, Cl-S-triazines, PUs	Schwarzenbach *et al.*, 1993

*Abbreviations: PAHs: polycyclic aromatic hydrocarbons, PCE: perchloroethylene, n-Bu-benz.: n-butyl-benzene, MAHs: monocyclic aromatic hydrocarbons, PCBs: polychlorobiphenyls, TCE: trichloroethylene, DCB: dichlorobenzene, arom.: aromatic, HCs: hydrocarbons, PUs: phenyl ureas

** The coefficients a and b are calculated from the original relationship log K_{oc}= a'.log K_{ow}+b', assuming K_{om} = $K_{oc/2}$ with K_{oc} the organic carbon-water partitioning coefficient.

Table I.3.5. Log K_{ow} values (from Schwarzenbach *et al.* (1993) and Verschueren (1983)).

VOC	log K_{ow}
Chloroform	1.93
Tetrachloromethane	2.73
1,1-Dichloroethane	1.79
1,1,1-Trichloroethane	2.48
Trichloroethylene	2.42
Tetrachloroethylene	2.88
Toluene	2.69
Et-benzene	3.15
o-Xylene	3.12
m-Xylene	3.20
p-Xylene	3.18

I.3.4.2. DEGRADATION

I.3.4.2.1. CHCs

Van Beelen et al. (1991) and van Beelen and van Vlaardingen (1993) investigated the mineralization of chloroform in Dutch river sediments. River sediments were collected from the Rhine estuary, the river Meuse and from an unpolluted ditch (Oostvaardersplassen). Mud samples showed mineralization half-life times ranging from 0.9 to 37 days in microcosms. But most sand samples were not able to perform mineralization of chloroform under anaerobic conditions. Relatively unpolluted samples showed a similar mineralization rate compared with the heavily polluted sediments from the rivers Rhine and Meuse. The persistence of chloroform in sandy sediments was explained by the inactivity of chloroform mineralizing bacteria under the conditions present in the sandy sediments.
For the biodegradation of chloroform in sediment from the river Rhine chloroform followed first order kinetics with a half life time of 12 days at 10°C and 2.6 days at 20°C at concentrations of 4μg.L^{-1} (van Beelen and van Keulen, 1990). Chloroform was considered to be mineralized to carbon dioxide in methanogenic sediments according to the following stoichiometry:

$$CHCl_3 + 1.5\ H_2O \rightarrow 0.75\ CO_2 + 0.25\ CH_4 + 3\ HCl$$

Jafvert and Wolfe (1987) found no loss (biotic or abiotic) for 1,2-dichloroethane after 35 days incubation in an aqueous suspension containing sediment from a pond in Georgia, U.S.A..

I.3.4.2.2. MAHs

Edwards et al. (1992) showed that sediment from a gasoline-contaminated sandy silt from Seal Beach (California) was capable to degrade toluene and xylenes in sulfate reducing conditions in microcosms. The Seal beach aquifer material used had been exposed to gasoline and contained relatively high concentrations of sulfate because of its proximity to an intertidal marsh. So, the authors stated that it was highly likely that the degradation process was occuring naturally at the contaminated Seal Beach site, since toluene degradation in microcosms began with virtually no adaptation lag period. On the other hand it was concluded

that the degradation of MAHs in the field may be prevented not because of the lack of appropiate organisms or enzymes, but because of the presence of other more readily degraded substrates since the cultures showed definite substrate preferences (lactose, glucose or yeast extract over toluene, toluene over xylenes). In addition, Lovley et al. (1995) proved that an aquatic sediment, collected from the San Diego Bay (California) which was assumed to be contaminated with organic compounds, was capable to oxidize benzene when coupled with sulfate reduction. This investigation too illustrated the possibility of MAHs degradation by aquatic sediments.

The breakdown pathway of MAHs to carbon dioxide was not fully clear in both investigations. Potential pathways for the anaerobic metabolism of benzene like hydroxylation to produce phenol, carboxylation to produce benzoate or initial reduction of the ring to form cyclohexane, were believed to be unimportant to Lovley et al. (1995) since none of the potential intermediates cited were detected as extracellular intermediates. Furthermore, acetate, an expected key intermediate if benzene were first fermented to organic acids, was not produced. In conclusion, the authors suggested that benzene may be directly oxidized to carbon dioxide within single cells of sulfate-reducing microorganisms.

Van Beelen and van Keulen (1990) found 5% degradation of benzene to carbon dioxide in Rhine sediments after one day, but then the mineralization ceased while the disappearance of benzene proceeded. A half life time of 60 days was measured. According to these authors benzene was thought to be mineralized with phenol and propionic acid as intermediates:

$$C_6H_6 + 4.5\ H_2O \rightarrow C_6H_5OH + H_2 + 3.5\ H_2O \rightarrow 2\ C_3H_6O_2 + H_2 + 0.5\ H_2O$$

The formed propionic acid and hydrogen gas can be converted to methane and carbon dioxide by methanogenic bacteria with the following overall stoichiometry:

$$C_6H_6 + 4.5\ H_2O \rightarrow 2.25\ CO_2 + 3.75\ CH_4$$

I.3.5. CONCLUSIONS

Several preconcentration techniques are developed in order to analyse CHCs and MAHs in aquatic sediments. Mostly applied are purge and trap, vacuum extraction and static headspace. Further on, closed loop stripping in combination with steam distillation, methanol or methyl glycol extraction followed by headspace techniques after dilution in water and supercritical fluid extraction are reported.

In order to separate and detect the VOCs after preconcentration, gas chromatography combined with common detectors (FID, PID, ECD and MS) is applied. Limits of detection are in the $ng.kg^{-1}$ range for purge and trap and static headspace preconcentration. Closed loop stripping/steam distillation, vacuum distillation, steam distillation and solvent extraction followed by headspace techniques after dilution in water, showed to be able to detect at $\mu g.kg^{-1}$ concentrations.

Few data on environmental concentrations of CHCs and MAHs in aquatic sediments are available. CHCs measurements in the Solent Estuary (UK) were carried out by Bianchi et al. (1991) where 0.070-31$\mu g.kg^{-1}$ concentrations were found for the individual compounds. In Lake Pontchartrain in the deltaic plain of the Mississippi River, Ferrario et al. (1985) measured concentrations from below 0.01 to 18$\mu g.kg^{-1}$ for six individual CHCs.

MAHs in the solent estuary were in the 0.30-480$\mu g.kg^{-1}$ range (Bianchi et al., 1991). Other MAHs measurements were carried out in the Southampton estuary (UK) (2.2-49.3$\mu g.kg^{-1}$) (Bianchi and Varney, 1989a), in Lake Pontchartrain (0.7-21$\mu g.kg^{-1}$) (Ferrario et al., 1985), in the Moravia and Danube rivers (Slovakia) (<0.04-290$\mu g.kg^{-1}$) (Al-Rekabi et al., 1995), while Marchand et al. (1994) measured 663$\mu g.kg^{-1}$ toluene and 1574$\mu g.kg^{-1}$ benzene in the Guaymas Basin in the Gulf of California. Finally, benzene and toluene concentrations in the Walvis Bay were in the 0-20.4 and 0-197$\mu g.kg^{-1}$ range, respectively (Whelan et al., 1980).

Sources of the CHCs and MAHs in aquatic sediments are in general considered to be anthropogenic. However, *in situ* natural processes such as thermal degradation of organic matter (Marchand et al., 1994) and microbial and biological pathways (Whelan et al., 1980) are suggested as sources for toluene.

The VOCs are considered to be mainly sorbed on the organic matter fraction within the sediment. Biotic degradation in river sediments was found for chloroform with half-life times of 0.9-37 days (van Beelen et al., 1991; van Beelen and van Vlaardingen, 1993). The same authors found benzene half lifes of 60 days. Edwards et al. (1992) observed degradation of

toluene and xylenes in a gasoline-contaminated sandy silt sediment. However, according to the authors *in situ* degradation could be prevented because of the preference of other substrates.

I.3.6. REFERENCES

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I.4. BIOTA

I.4.1. SAMPLING AND ANALYSIS OF CHCs AND MAHs IN MARINE BIOTA

I.4.1.1. SAMPLING, PRE-TREATMENT AND STORAGE

I.4.1.1.1. Sampling equipment and contamination originating from the sampling equipment

No special methods have been found in the literature regarding the sampling of biota for the determination of volatile organic compounds (VOCs). It can be assumed that the sampling methods are largely based on traditional fishing techniques such as beam trawling. Similarly, no evidence of contamination originating from sampling equipment and during sampling is recorded in the literature. Whether such contamination occurs is unlikely, since it would have to either originate from the sampling equipment (nets) or the ambient air and be the result of partitioning of the volatiles through the outer epidermis of the fish.

I.4.1.1.2. Sample storage and pre-treatment

Sample storage

As a general rule, care should be taken in all forms of sample storage and pre-treatment to avoid losses due to volatilisation and contamination of the samples from ambient air or the materials which are used for storage. Dickson and Riley (1973) minimised losses and contamination by cooling the samples to -78°C and storing them at the same in temperature in a Dewar vessel filled with solid carbon dioxide. Analysis was carried out within three days after collection. Similarly, Hiatt (1983) used fish samples stored under dry ice. Easley *et al.* (1981) wrapped freshly obtained fish in aluminium foil and stored the latter in the freezer until analysis. Once dissected, the fish tissue was stored in a container protected from laboratory solvent fumes by activated charcoal. Pearson and McConnel (1975) stored all field samples in sealed containers prior to manipulation in the laboratory. All manipulations in the laboratory were performed in a glove box under a nitrogen atmosphere. Ferrario *et al.* (1985) immediately packed the samples in ice and stored them at -5°C. Similar practices are used for the analysis of volatiles in the food sector. Page and Lacroix (1995) advised the storage

of packed foods in plastic or paper film unopened at -20°C. Once opened, a suitable storage container was advised with PTFE or aluminium lining. Samples packaged in glass or thick walled plastic could be stored at 4°C.

Pre-treatment

Pre-treatment of the samples mainly consists of dissection of the fishes to obtain edible (muscle) tissue or organs (Dickson and Riley (1973), Easley *et al.* (1981), Reinert *et al.* (1983) and homogenisation of the tissue (Gotoh *et al.* (1992), Hiatt (1981), Pearson and McConnel (1975), Reinert *et al.* (1983), Yashura and Morita (1987)). Again, due to the volatility of the compounds, samples are preferably cooled to at least 4 °C during the treatment. Gotoh *et al.* (1992) homogenised frozen shellfish tissue with a mortar and pestle. Hiatt (1983) used a food cutter for homogenisation of fish tissue and added liquid nitrogen during chopping. Easley *et al.* (1981) used ultrasonification for tissue disruption and cooled the sample in an ice bath during the process. Ferrario *et al.* (1985) spiked the tissue with a three component recovery standard (bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane) and homogenised the samples with a Brinkman Polytron tissue homogeniser. All manipulations were performed in a desk-top cold room at 4°C. Reinert *et al.* (1983) developed a homogeniser that served at the same time as the purging vessel (see later). The tissue sample was placed in a glass tube, mixed with anhydrous sodium sulphate and ground with a glass rod (figure I.4.1.). Cooling is not necessary as this procedure involves no further sample handling.

Finally, Yashura and Morita (1987) added distilled water to the sample and homogenised the tissue with a non defined tissue homogeniser at 10 000 prm. The sample is not cooled during this step, but was rapidly cooled afterwards to -80 °C and immediately transferred to the extraction vessel.

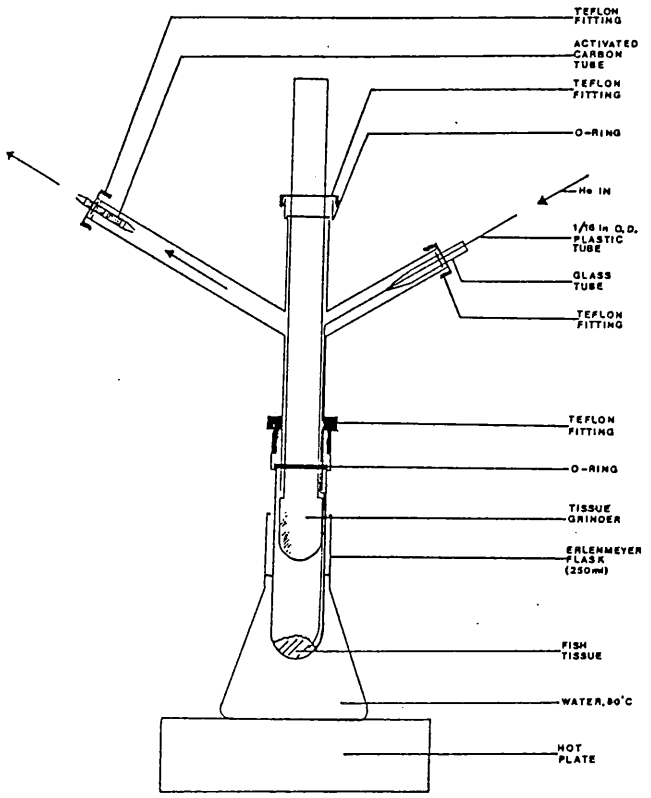

Figure I.4.1.: Self contained grinding purge and trap vessel developed by Thomas Sabatino, Rutgers University (Ace Scientific) after Reinert et al. (1983)).

Finally, sample handling should in any case be kept to a minimum to prevent both losses and contamination.

I.4.1.2. EXTRACTION AND PRE-CONCENTRATION TECHNIQUES

Well known organic contaminants such as polychlorinated biphenyls (CBs) are traditionally extracted from biological material with liquid extraction techniques, such as soxhlet extraction. have been used for the isolation of contaminants from biological tissue. Further processing of the extract involves, generally, a concentration step in which the volume of the extract is reduced by evaporation (e.g. under a nitrogen stream or by using a rotary evaporator). However, in the case of volatile contaminants the latter is impossible due to the fact that the

boiling points of the analytes equal or approach that of the solvents currently used. Direct injection of the extract is possible but the detection limit will become largely dependent on the sensitivity of the detection system. Most extraction or mobilisation techniques for the determination of VOCs therefore rely on volatilisation of the contaminants from the matrix, although liquid extraction techniques have been used.

I.4.1.2.1. Liquid extraction

Pearson and McConnel (1975) used a Dean and Stark distillation apparatus and n-pentane for the extraction of volatile chlorinated compounds from biological tissues. Analysis was then carried out using a gas chromatograph (GC) equipped with a ^{63}Ni electron capture detector (ECD). Gotoh *et al.* (1992) crushed the frozen biological material with a mortar and pestle and extracted the volatiles with a mixture of water-n-hexane (50/50). The extract was further cleaned up on a micro-Florisil columns and analysed by means of GC-ECD. In both cases, the authors reported detection limits in the lower ng/g range which were solely due to the high selectivity of the electron capture detector for halogenated compounds. It would be impossible to reach similar detection limits using the same techniques for volatile aromatic compounds such as benzene and toluene. Although, the recent introduction of large-volume injectors, which enable the injection of volumes up to 100 µl, in combination with the enhanced sensitivity of modern GC-MS systems may again open new possibilities.

I.4.1.2.2. Static headspace techniques

In this technique the sample is generally heated at a closely controlled temperature in a closed container. The temperature results in the volatilisation of the contaminants from the matrix to the headspace above the matrix. The headspace is then sampled with a heated gas-tight syringe and injected into a gas chromatograph. Although, the technique had been used in the analysis of food (Page and Charbonneau, 1983), soil (Roe *et al.*, 1989) and biological tissue (Ogata *et al.*, (1984) it is not often used for the analysis of solid environmental samples. As with the previous technique, detection limits are often insufficient. The difficulty in applying this technique is also that it relies on the equilibrium partitioning of the analytes between the matrix of interest and the headspace and thus relies on the gas/sample partition coefficient. The method should therefore be calibrated for each matrix which of course is

impractical for environmental analysis with its wide variety of samples. A way to overcome this problem was shown by Maggio *et al.* (1991). They used Multiple Headspace Extraction-Capillary Gas Chromatography (MHE-GC) in which the headspace is not sampled once but several times (9) allowing extrapolation of the "real" analyte concentration in the sample.

Voice and Kolb (1993) reported superior recoveries and precision when comparing static headspace with dynamic headspace (Purge and Trap (P&T)) analysis of soil samples. However, the concentration levels used in the experiment (1 μg/g) are much higher then the detection limits reported for P&T techniques. This remains a weak point for the analysis of environmental samples.

I.4.1.2.3. Dynamic headspace techniques

Murray and Riley (1973) were among the first to report the determination of VOCs in biota with a dynamic headspace or P&T technique. Both sediment and biota samples were heated to 200°C in an oven under a stream of purified nitrogen (figure I.4.2.).

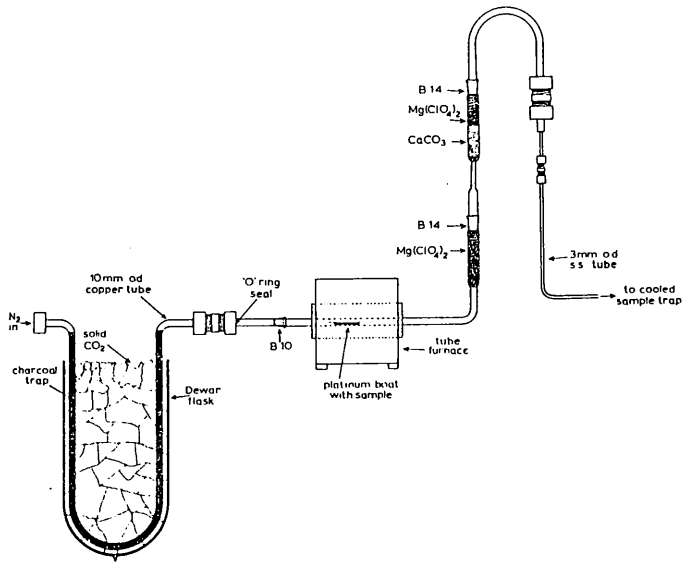

Figure I.4.2.: Purging device reprinted from Murray and Riley (1973).

VOCs were swept away by the nitrogen and trapped on a column packed with 3% silicone oil (SE 52) on Chromsorb W , and cooled to -78°C (figure I.4.3.). Next the trap was allowed to warm up to room temperature and the trapped VOCs were injected into the GC with a

stream of argon.

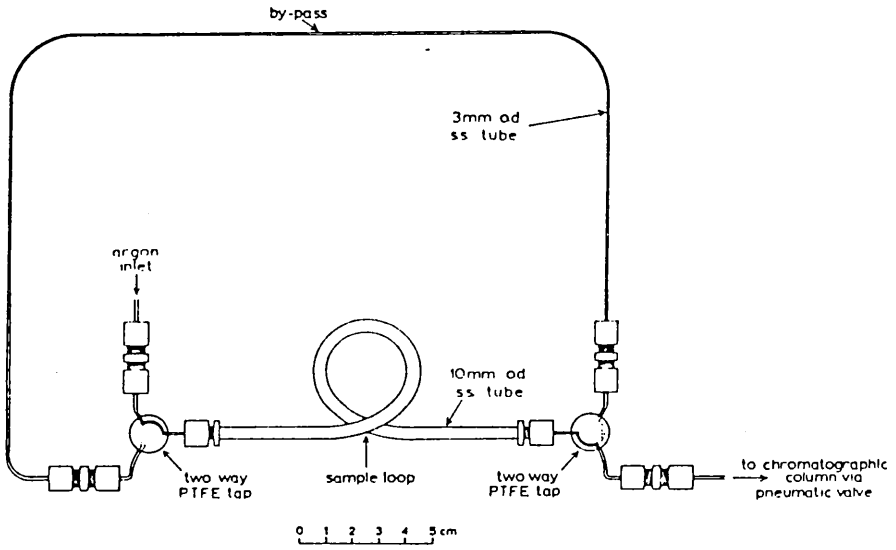

Figure I.4.3.: Sampling trap and associated pipework reprinted from Murray and Riley (1973).

Hiatt (1981) developed a method based on Method 624 of the Environmental Protection Agency (EPA) (1979). The analytes were vaporised from the sample in an ultrasonic bath at 50°C under vacuum and trapped in a super-cooled trap (-196°C) which was essentially a 25 ml purge tube that is used for the determination of volatiles in water samples(figure I.4.4.).

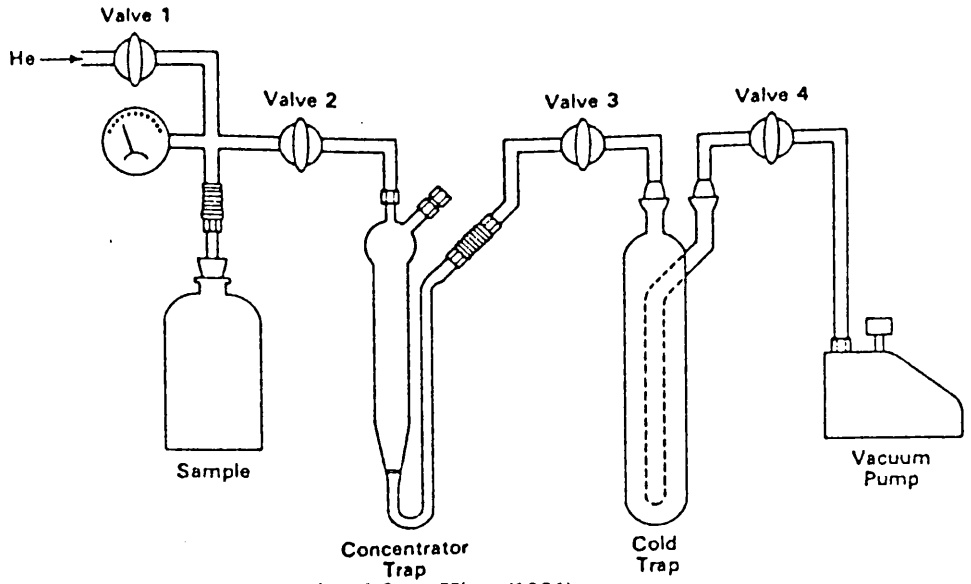

Figure I.4.4.: Vacuum extractor reprinted from Hiatt (1981).

Treating fish samples in an ultrasonic bath at 50°C generates a lot of water vapour which will interfere with the final analysis, so an additional trap cooled to -20°C with ethanol was inserted just before the cryogenic trap (figure I.4.4.). The concentrator trap was then transferred to a P&T apparatus and treated as a water sample in accordance with EPA Method

624. A major drawback of this system is that it requires the transfer of the purging tube to the P&T apparatus (off-line system).

Newman and Gschwend (1987) used a vacuum distillation apparatus for the determination of VOCs in marine microalgae similar to that of Hiatt (1981). The cryogenic trap was however replaced by a volatiles trap consisting of quartzite sand, pre-ignited at 550°C. After the trap is placed in a water bath at 30 °C and stripped with clean air onto a Tenax-GC trap (figure I.4.5.).

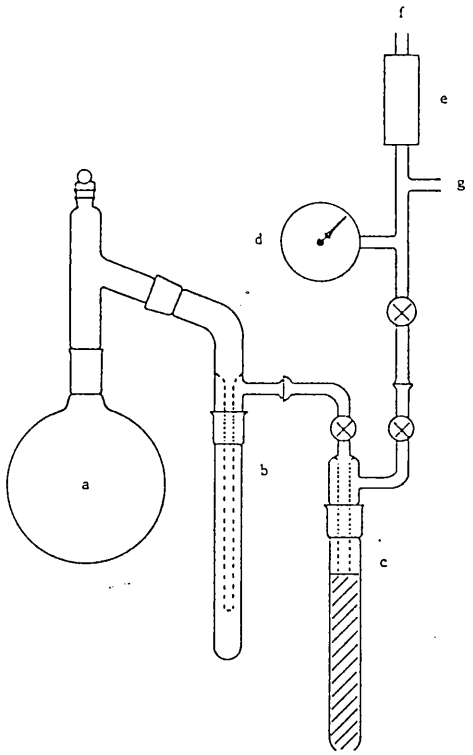

Figure I.4.5.: Distillation apparatus reprinted from Newman and Gschwend (1987), with a = 500 ml 24/40 round bottom flask, b = vacuum trap chilled in ice bath to collect water, c = vacuum trap with glass stopcocks, filled with coarse pre-ignited quartz sand and chilled in liquid nitrogen to collect organic volatiles, d = vacuum gauge, e = $CaCl_2$ dessicant trap, f = vacuum line to regultion valve and vacuum pump, g = vacuum line to parallel apparatus.

The latter is than desorbed in the injection port of the chromatograph. The water trap was similar to that of Hiatt (1981) but it was cooled to about 0°C in an ice bath. Hiatt (1983) further developed the above technique and designed an on-line distillation apparatus. The sample was treated as described above but the cryogenic trap was directly connected to a GC-MS system through a double 6-port valve. After purging the cryogenic trap is allowed to warm up to room temperature and the analytes are transferred with the carrier gas to a sample

loop held at -196°C. The latter is then rapidly heated to 150 °C and the analytes are transported to the column by the carrier gas (figure I.4.6.).

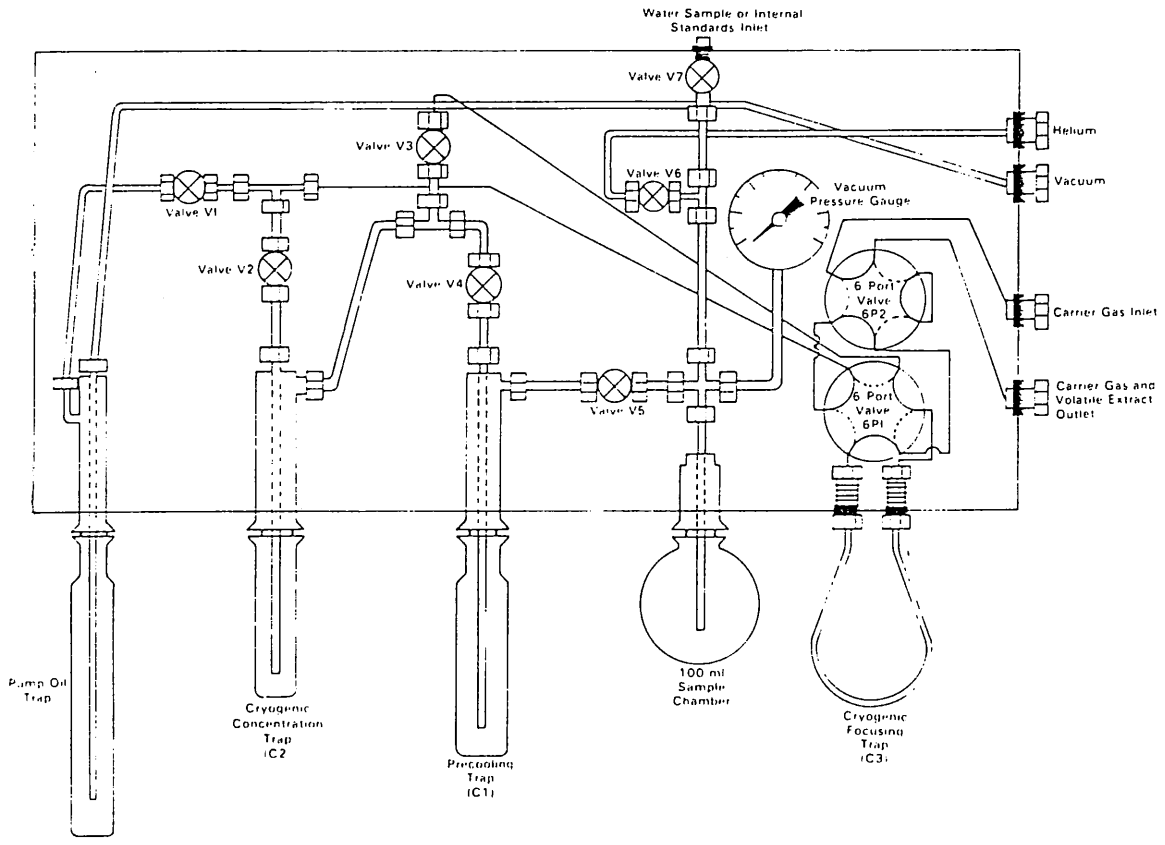

Figure I.4.6.: On line vacuum extractor reprinted from Hiatt (1983).

This technique was again modified by Hiatt *et al.* (1994) with the introduction of a condenser coil placed after the sample chamber (figure I.4.7.). This set-up eliminated the need to use a series of temperature baths and facilitated temperature control. Yashura and Morita (1987) also used steam distillation in a similar way to Hiatt (1983) for the determinations of VOCs in mussel.

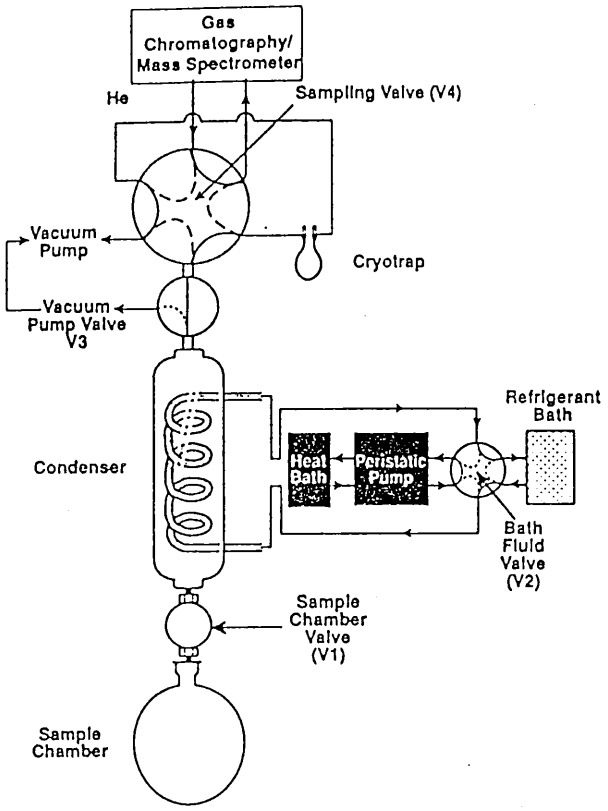

Figure I.4.7.: Vacuum distillation apparatus reprinted from Hiatt *et al.* (1994).

Easley *et al.* (1981) also developed a method based on procedures used for water analysis. They developed a purge vessel consisting of a 25 ml glass sample vial and a glass impinger connected to each other by a Wheaton connector (figure I.4.8.).

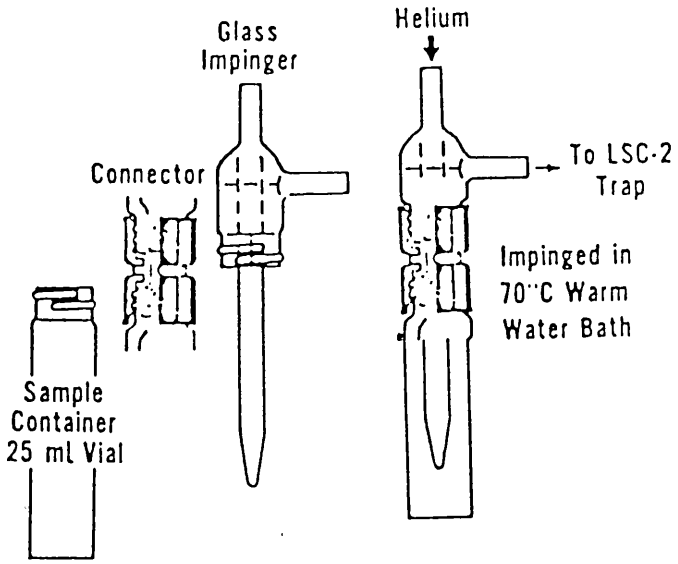

Figure I.4.8.: Purging device reprinted from Easley *et al.* (1981)

The volatiles were forced out of the tissue by heating the sample to 70°C and purging with a constant flow of helium. The analytes are trapped on a sorbent consisting of equal volumes

of Tenax, silica and activated charcoal. After purging the trap is backflushed with helium and simultaneously heated and the analytes are transferred to a GC-MS system. No special considerations were taken to avoid the presence of water vapour and the authors reported no problems of foaming at this elevated temperature. Foaming had been observed with this method (Roose et al., unpublished results) in lean fish tissues.

Michael *et al.* (1980) compared to gass stripping devices for the analysis of human blood, urine and adipose tissue samples. With the original set-up the sample is stripped with a flow of He gas passing through the sample by means of a glass dispersion tube (figure 1.4.9a.).

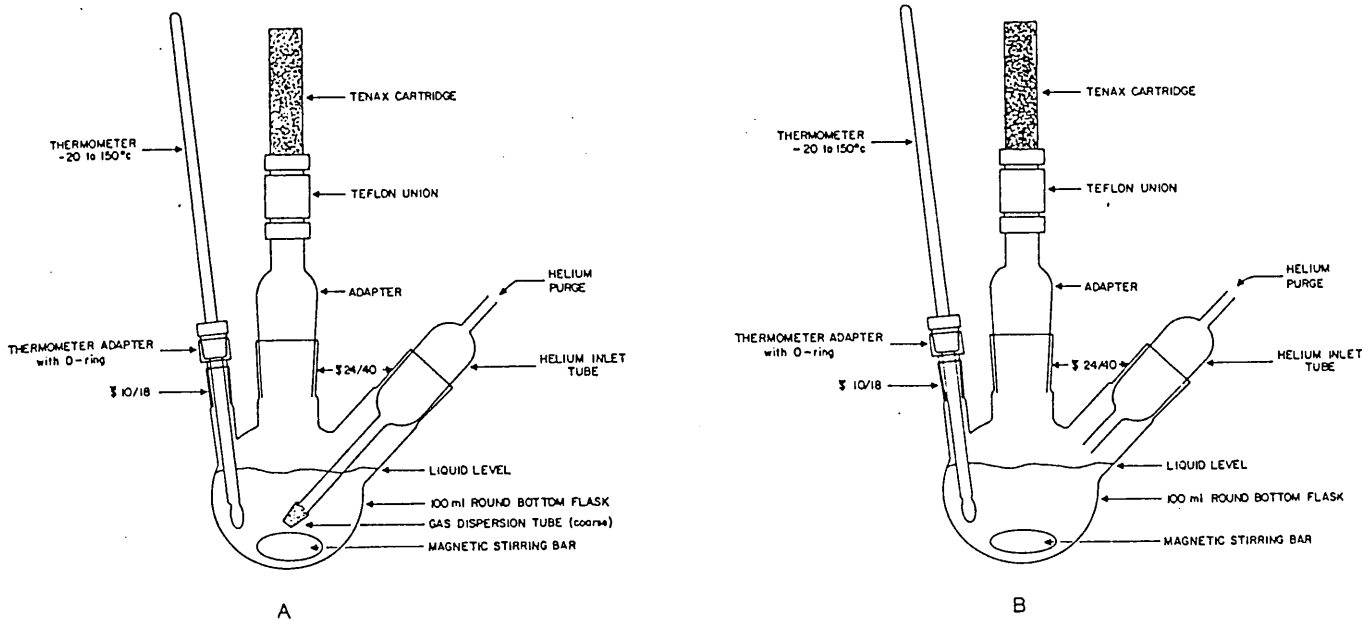

Figure I.4.9.: Flow through gas stripping apparatus (A) and dynamic headspace gas stripping apparatus (B) reprinted from Michael *et al.* (1980).

The volatiles are trapped onto a Tenax trap situated on top of the apparatus. With this method, the authors experienced substantial foaming that was not reduced by decreasing the purge temperature or flow. If the foam is allowed to pass through the transfer lines and enter the sorbent trap, several negative effects, such as deactivation of the trap and introduction of thermal degradation product of non volatile materials, are likely to interfere with the analysis (Rose and Colby, 1979). Michael *et al.* (1980) therefore stripped the headspace in stead of the sample with a modified version of their apparatus (figure I.4.9b.). Ferrario *et al.* (1985) used a system with nitrogen as the purge gas and a Tenax/silicagel sorbent trap (80/20).

Reinert *et al.* (1983) described the use of a P&T apparatus designed by Sabatino (Rutgers

University, Wheaton Scientific). The samples were heated to 50°C with a water mantle, purged with a stream of He gas and trapped on an activated carbon trap (figure I.4.10.).

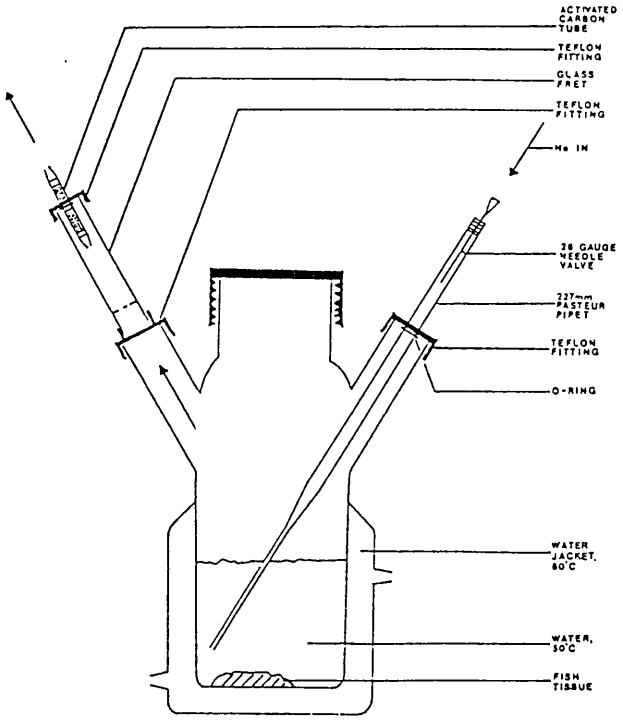

Figure I.4.10.: 100 ml purge and trap vessel developed by Thomas Sabatino, Rutgers University (Ace Scientific) after Reinert et al. (1983))

The volatiles adsorbed on the carbon trap are then desorbed in a vial containing a volume of carbon disulfide and injected into a GC equipped with an FID (Flame Ionisation Detector). The same authors compared this method to the grinder/purging apparatus described earlier (figure I.4.1.). This vessel allowed the grinding of biological tissue and served as the purge vessel at the same time. The tissue was first ground in the presence of sodium sulfate to fine particles. The grinding rod was then lifted to the upper portion of the apparatus and sealed in place with a Teflon O ring. The volatiles are subsequently purged out of the tissue by purging with He at a flow of 100 ml/min for 1 h and trapped onto an activated carbon trap. The latter is then treated in the same way as above.

Another method which could allow the analysis of fish samples is described by Page and Lacroix (1995). The authors use a on-line steam distillation/P&T system for the determination of volatile halogented compounds in food. Volatiles are extracted with a modified Garman steam distillation apparatus directly coupled to the purging vessel of a Tekmar LSC2000 P&T

apparatus (figure I.4.11.).

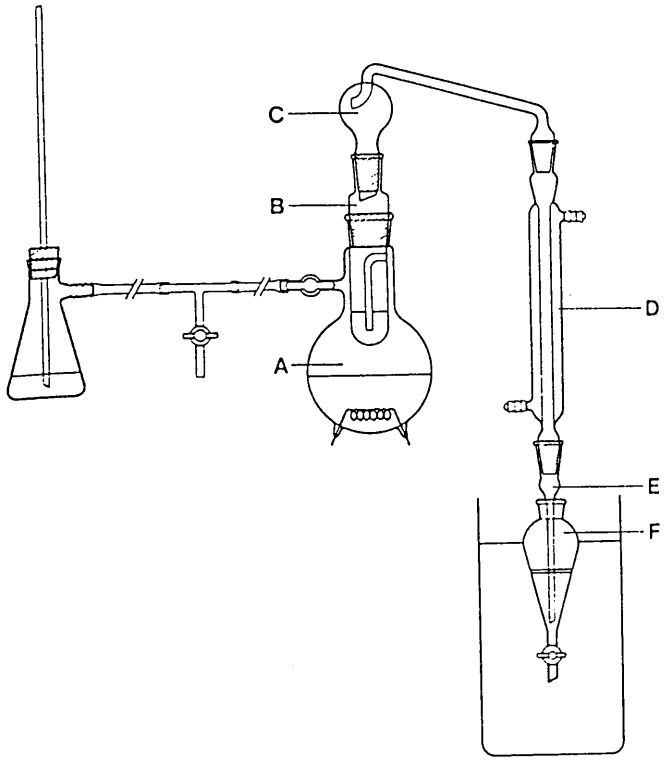

Figure I.4.11.: Garman steam distillation apparatus and accessories reprinted from Page and Lacroix (1995) with A = boiler, B = sample chamber, C = pressure indicator, D = head for solid sample injector, E = alternative head for syringe injection, F = alignment connector and G = modified 25 ml sparger for on-line P&T concentration and GC.

I.4.1.2.4. Other techniques

Page *et al.* (1987) used a method for the determination of volatile compounds in cereal products that could be applicable for biological samples. The procedure is based on a modified Garman steam distillation apparatus. The volatiles were extracted from the sample with the water vapour and the latter was condensed and collected in a separatory funnel (figure I.4.12.).

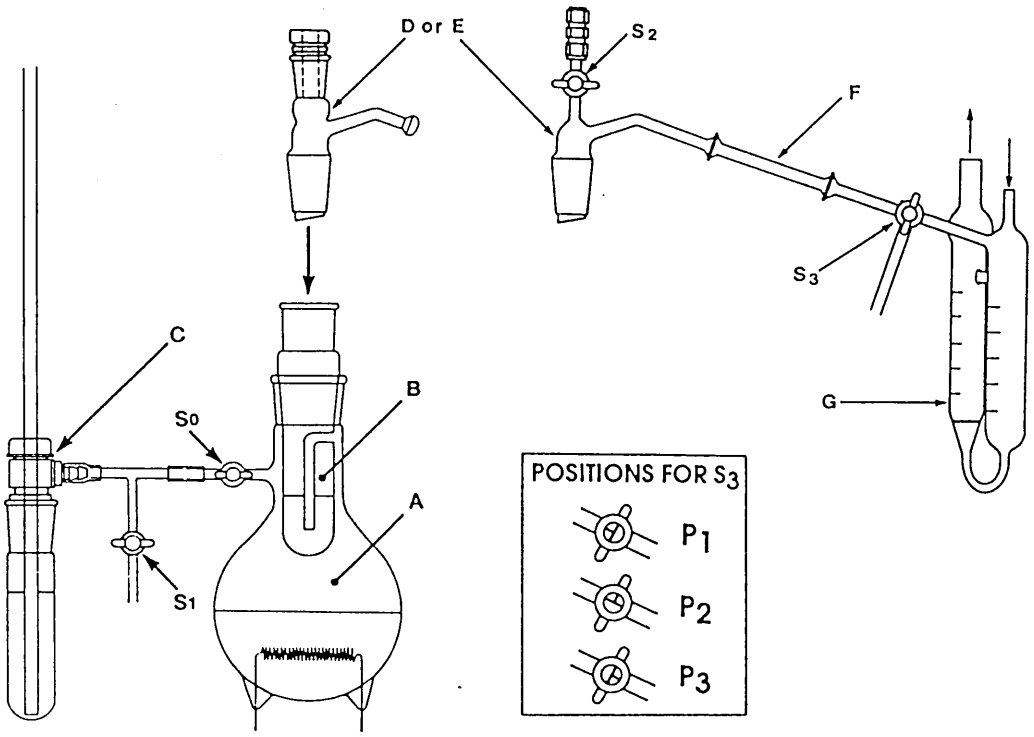

Figure I.4.12.: Garman steam distillation apparatus and accessories reprinted from Page *et al.* (1987) with A = 1 l steam generator, B = sample chamber, C = splash head, D = Leibig condensor, E = delivery tip and F = separatory funnel.

Non-polar compounds were subsequently partitioned into hexane and the mixture was injected into a GC-ECD system. As mentioned earlier, detection limits will be largely dependent on the sensitivity of the detector and the method will therefore only work for the determination of low levels of halogenated volatiles.

I.4.1.3. ANALYSIS: SEPARATION AND DETECTION, LIMITS OF DETECTION

Early authors used packed columns, and GCs equipped with ECDs, due to the excellent sensitivity of these detectors for halogenated hydrocarbons (Murray and Riley (1973), Pearson and McConnel (1975)). Later on, capillary fused silica columns and GC-MS systems (Hiatt 1983) were used which allowed a much broader range of components to be determined, although sensitivity did suffer somewhat. An overview of the different columns and analytical techniques can be found in Table I.4.1. Data on reproducibility and detection limits are rather

Table I.4.1: Overview of the analytical techniques used for the determination of CHCs and MAHs in marine biota.

Analytical column	Detector	Extraction technique	Trap	LOD	Recovery	RSD %	Reference
Glass 150cm*0.4cm i.d. packed with 15% Dexsil 300 on 72/85 mesh Diatomite	ECD	Distillation with n-pentane	None				Pearson and McConnel (1975).
Glass 4m*0.4cm with 3% SE 52 on Chromosorb W.	ECD	Heating in an oven under a stream of nitrogen	Stainless steel with 3% SE 52 on 80-100 mesh Chromosorb W at -78°C		57-94 %		Murray and Riley (1973).
		Vacuum distillation	Glass vessel -196°C		80-108%	± 10 %	Hiatt (1981).
Glass column 6ft*.25 packed with 0.2% Carbowax on 60-80 mesh Carbopack C with a precolumn of 3% Carbowax 1500 on 60-80 mesh Chromosorb W.	MS	Purging with helium at 70°C.	Tenax/Silicagel/Activated charcoal (1/1/1)	10 ppb	± 60-90%	± 10-20%	Easley et al. (1981).
DB 5 fused silica capillary 30m, 0.32 mm i.d., 1.0 µm film	MS	Vacuum distillation	Glass vessel -196°C	± 1 ppb			Hiatt (1983).
SE-54 WCOT glass capillary 60 m x 0.25 mm i.d.	FID	Purging with He at 50°C	Activated carbon		39 - 81 %	5 - 10 %	Reinert et al. (1983)
Glass column with 5 % Benton 34 + 5 % DIDP on celite 60-80 mesh, 0.3 cm x 5 m.	FID	Static headspace technique at 80°C.					Ogata et al. (1984).
WCOT 50m * 0.4mm SF-96 column	MS	Purging with nitrogen at 70°C	Tenax/Silicagel (80/20)				Ferrario et al. (1985).
SE-54 cross linked capillary column 12 m.	MS	Vacuum distillation	Quartzite sand (pre-ignited at 550° C) as trap 1 an Tenax as trap 2.	± 1 ppb	57 - 60 %	± 5 %	Newman and Gshwend (1987).
20 % Chromosorb W AW DCMS 60-80 mesh 3m x 3 mm.	ECD	Liquid extraction water/n-hexane (50/50) and florisil clean-up.	None	0.01 - 0.5 ppb	91.5 - 100.0 %		Gotoh et al. (1992).
DB - 624 30 m fused silica capillary , 0.53 mm i.d., 3 µm film.	MS	Vacuum distillation	8*1/8 inch stainless steel tubing at -196°C.	1.1 - 4.3 ppb	46 - 129 %	± 30 %	Hiatt et al. (1994).
DB 624 fused silica capillary 30m, 0.32 mm i.d., 1.8 µm film.	ECD	Steam distillation (modified Garman apparatus)	VOCARB 4000	2-40 ppt	± 80-100%	± 2-12%	Page and Lacroix (1995)[1].

ECD = electron capture detector, MS = mass spectrometer, ppb = parts pro billion or ng/g wet weight, ppt = parts pro trillion or pg/g wet weight, RSD = Relative Standard Deviation, LOD = Limit of Detection, [1] Method reported by Page and Lacroix (1995) was developed for food analysis but is probably applicable for biota analysis.

sparse in the earlier papers. With ECDs detection limits are generally good for chlorinated compounds ranging from 10 ng/g to as low as 2 pg/g (Hiatt, 1981, Page and Lacroix, 1995). Easley *et al.* (1981) reported detection limits of about 10 ng/g with a GC-MS system, although better detection limits are certainly possible with modern systems. Bianchi *et al.* (1991) reported detection limits of 10 pg/g using similar techniques for the analysis of volatile compounds in sediments. The advantage of the latter technique is clearly the larger number of compounds that can be determined simultaneously. The recoveries that are reported by the various authors were generally good, ranging form about 60-100 % (Murray and Riley (1973), Hiatt (1981), Reproducibilities vary between 2 and 20 % (Murray and Riley (1973), Easley *et al.* (1981), Page and Lacorix (1995)).

I.4.2. DETERMINATIONS OF CHCS AND/OR MAHS IN MARINE BIOTA

I.4.2.1. CONCENTRATIONS

An overview of concentration levels that have thus far been reported is given in Table I.4.2 for chlorinated hydrocarbons (CHCs) and Table I.4.3 for monocyclic aromatic hydrocarbons (MAHs). The number of data for these compounds in biota is sparse compared to data for water and sediment samples. Although the compounds are mentioned as priority pollutants by various authorities (GESAMP, 1990, Declarations of the Third Ministerial Conference on the North Sea, 1990, Norwegian Pollution Control Authority, 1994) there appear to be no on-going monitoring programmes, as is the case for other organic pollutants such as polychlorinated biphenyls (OSPARCOM, 1990). The data presented in Tables I.4.2 and I.4.3 are therefore mostly the results of once-only surveys.

I.4.2.1.1. Chlorinated Hydrocarbons

Pearson and Mc Connel (1975) were among the first to report concentrations of trichloroethylene, tetrachloroethylene, trichloroethane, tetrachloromethane and chloroform in various marine organisms from sampling locations along the British coast. The results showed that CHCs were present at all trophic levels. The detectable concentrations ranged from 0.02 to 180 ng/g wet weight for invertebrates, from 9 to 35 ng/g wet weight for marine algae, from

0.02 to 50 ng/g wet weight for fish, from 0.7 to 58 ng/g wet weight for sea and freshwater birds and from 0.02 to 66 ng/g wet weight for mammals (Table I.4.2). The levels of chloroform generally were higher than those of the other CHCs with the exception of the concentrations in eggs of marine birds from the Irish Sea, where the concentrations of the other CHCs were equal to or even higher than those of chloroform. The highest concentrations in invertebrates were found in crab (*Cancer pagurus*) (180 ng/g of chloroform) form the Firth of Forth, the highest concentrations in fish were found in the liver of ray (*Raja clavata*) (56 ng/g of trichloroethylene) from Liverpool bay and the highest concentrations in birds were found in kittiwake (*Rissa tridactyla*) (58 ng/g of chloroform) and guillemot (*Uria aalge*) (65 ng/g of chloroform) from the Irish Sea. The CHC concentrations in fish and invertebrates were similar, which suggests that no biomagnification from invertebrates to fish occurred. However, the concentrations in eggs of the above mentioned CHCs were about 10-fold higher than those in fish. This could indicate that some sort of biomagnification occurred. The highest concentrations were, in any case, found in marine birds.

For marine mammals only the concentrations in the grey seal (*Halichromis grypus*) were reported. Strikingly, the concentrations were not higher than those in fish. The concentration differences between marine birds and the grey seal can be attributed to different metabolisation capacities. The course should not be sought in the diet since they are all fish eaters.

Dickson and Riley (1976) determined the same compounds in three species of molluscs and five species of fish mainly from Liverpool Bay (UK) and found similar results. The results were similar to the those from the study of Pearson and Mc Connel (1975). The levels were approximately the same if allowance is made for the fact that the data are expressed on a dry weight basis. The detectable concentrations ranged from 0.1 to 1040 ng/g dry weight in invertebrates and from 0.1 to 851 ng/g dry weight in fish (Table I.4.2). The highest concentration of a CHC for invertebrates was 1040 ng/g dry weight for chloroform in the gill of *Pecten maximus* and for fish 851 ng/g dry weight in the liver of coalfish (*Pollachius birens*) (Table 2). The concentrations of chloroform were again higher compared to the other CHCs with the exception of trichloroethylene. The lowest concentrations are found for tetrachloromethane in invertebrates and for trichloroethane in fish. On average, the order of potential concentration for the various organs appeared to be: brain > gill > liver > muscle

Table I.4.2: Concentrations of CHCs in marine biota in ng/g wet weight.

Species	Tissue	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Invertebrates									
Plankton		1975	0.02-5	0.04-0.9		0.03-0.7	0.05-0.4	0.05-0.5	Pearson and McConnel (1975)
Nereis diversicolor (ragworm)		1975						2.9	Pearson and McConnel (1975)
Mytilus edulis (mussel)		1975	9-10	0.7-2		5-10	4-11.9	1-9	Pearson and McConnel (1975)
		1987			4080				Yasuhara and Morita (1987)
Cerastoderma edule (cockle)		1975	4-150	0.4-1		0-2	6-11	2-3	Pearson and McConnel (1975)
Ostrea edulis (oyster)		1975	3	0.1		0.9	2	0.5	Pearson and McConnel (1975)
Crassostrea virginica (oyster)		1980		1.3	95	310	2.2	10	Ferrario et al. (1985)
Crassostrea gigas (oyster)		1992	6.5	0.28		0.8		0.6	Gotoh, et al. (1992)
Rangia cuneata (clam)		1980		3.9	1-1.5	39-160	0.8-5.7	3.3	Ferrario et al. (1985)
Tapes japonica (clam)		1992	6.7	0.54		0.4			Gotoh, et al. (1992)
Paleomonetes pugio (grass shrimp)		1983			590				Reinert et al. (1983)
Buccinum undatum	Muscle	1975	10	0.9		6	ND	1	Pearson and McConnel (1975)
(whelk)	Muscle	1976	129	5			2	39	Dickson and Riley (1976) [1]
	Digestive gland	1976	117	8				33	
Crepidula fornicata (slipper limpet)		1975	6	0.3		4	9	2	Pearson and McConnel (1975)
Cancer pagarus (crab)		1975	3-180	0.3-5		1-34	2.6-15	2-9	Pearson and McConnel (1975)
Carcinus maenas (shore crab)		1975	15	3		14	12	6	Pearson and McConnel (1975)
Eupagurus bernhardus (hermit crab)		1975	20-73	0.2-1		0.7-2	5-15	2-15	Pearson and McConnel (1975)
Cragnon cragnon (shrimp)		1975	45	6		2	16	3	Pearson and McConnel (1975)

$CHCl_3$ = chloroform, CCl_4 = tetrachloromethane, 1,1-DCE = 1,1-dichloroethane, 1,2-DCE = 1,2-dichloroethane, TRI = trichloroethane, TCE = trichloroethylene, TTCE = tetrachloroethylene, [1] concentrations reported on a dry weight basis.

Table I.4.2: Concentrations of CHCs in marine biota in ng/g (cont.).

Species	Tissue	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Asterias rubens (starfish)		1975	13	0.8		5	5	1	Pearson and McConnel (1975)
Solastersp. (sunstar)		1975	3	0.2		3	2	2	Pearson and McConnel (1975)
Echinus esculentus (sea urchin)		1975	2	0.1		3	1	1	Pearson and McConnel (1975)
Modiolus modiolus	Digestive tissue	1976	56	20		4	56		Dickson and Riley (1976) [1]
	Mantle		438	114			250	63	
	Muscle		200	28			33	16	
Pecten maximus	Gill	1976	1040	14				88	Dickson and Riley (1976) [1]
	Mantle		224	2				40	
	Muscle		440	6				24	
	Ovary		720	16					
	Testis		448	3				176	
Marine algae									
Entheromorpha compressa		1975					19-20	14-14.5	Pearson and McConnel (1975)
Ulva lactuca		1975					236	22	Pearson and McConnel (1975)
Fucus vesiculosus		1975					17-18	13-20	Pearson and McConnel (1975)
Fucus serratus		1975					22	15	Pearson and McConnel (1975)
Fucus spiralis		1975					16	13	Pearson and McConnel (1975)
Fish									
Conger conger	Brain	1976		15		9	62	6	Dickson and Riley (1976) [1]
(eel)	Gill		50	3		2	29	2	
	Gut		43	9			29	3	
	Liver		474	51			43	43	
	Muscle		219	8			70	1	
Raja clavata	flesh	1975					0.8-5	0.3-8	Pearson and McConnel (1975)
(ray)	liver						5-56	14-41	
Pleurnonectes platessa	flesh	1975	17	3		9	0.8-8	4-8	Pearson and McConnel (1975)
(plaice)	liver						16-20	11-28	
Platychtys flesus	flesh	1975	21	2		4	3	2	Pearson and McConnel (1975)
(flounder)	liver		6	0.3		3	2	1	

$CHCl_3$ = chloroform, CCl_4 = tetrachloromethane, 1,1-DCE = 1,1-dichloroethane, 1,2-DCE = 1,2-dichloroethane, TRI = trichloroethane, TCE = trichloroethylene, TTCE = tetrachloroethylene, [1] concentrations reported on a dry weight basis.

Table I.4.2: Concentrations of CHCs in marine biota in ng/g (cont.).

Species	Tissue	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Limanda limanda	flesh	1975	23				3-5	1.5-11	Pearson and McConnel (1975)
(dab)	liver						12-21	15-30	
Scomber scombrus	flesh	1975	50	2		5	5	1	Pearson and McConnel (1975)
(mackerel)	liver		18	ND		3	8	ND	
Solea solea	flesh	1975	26	6		2	2	4	Pearson and McConnel (1975)
(sole)	liver		9	1		26	11	1	
Aspitrigla cuculus	flesh	1975	21	0.6		4	11	1	Pearson and McConnel (1975)
(red gurnard)	guts		2	0.3		10	6	2	
Trachus trachurus	flesh	1975	48	2		1	2	4	Pearson and McConnel (1975)
(scad)									
Trisopterus luscus	flesh	1975	15	0.3		2	2	2	Pearson and McConnel (1975)
(pout)									
Squalus acanthias	flesh	1975	110	1		ND	3	1	Pearson and McConnel (1975)
(spurdog)									
Clupea sprattus	flesh	1975	5				3.6	1.6	Pearson and McConnel (1975)
Gadus morhua	flesh	1975					0.8	<0.1	Pearson and McConnel (1975)
(cod)		1976	168	7		5	8	2	Dickson and Riley (1976) [1]
	airbladder	1975					<0.1	3.6	Pearson and McConnel (1975)
	Brain	1976	167	29		16	56	3	Dickson and Riley (1976) [1]
	Gill		156	21		14	21		
	Heart		67	10		11	11	3	
	Liver		19	4		5	66	8	
	Skeletal tissue		29	7					
	Stomach		7	6		7	7	6	
Pollachius birens	Alimentary canal	1976	51	32			306		Dickson and Riley (1976) [1]
(coalfish)	Brain			21			71		
	Gill		294	35				4	
	Heart		112	23					
	Liver		851	10			70	6	
	Muscle		168	7		6	8	2	
Scylliorhinus canicula	Brain	1976	404	38			40	12	Dickson and Riley (1976) [1]
(dogfish)	Gill		755	55			176	13	
	Gut		544	44			41		
	Heart		210	40			274		

$CHCl_3$ = chloroform, CCl_4 = tetrachloromethane, 1,1-DCE = 1,1-dichloroethane, 1,2-DCE = 1,2-dichloroethane, TRI = trichloroethane, TCE = trichloroethylene, TTCE = tetrachloroethylene, [1] concentrations reported on a dry weight basis.

Table I.4.2: Concentrations of CHCs in marine biota in ng/g (cont.).

Species	Tissue	Date	$CHCl_3$	CCl_4	1,2-DCE	TRI	TCE	TTCE	Reference
Scylliorhinus canicula	LiverMuscle		76	7			479	9	Dickson and Riley (1976) [1]
(dogfish)	Spleen		649	19			41		
			80	3			309		
Trisopterus luscus	Brain	1976	98	191					Dickson and Riley (1976) [1]
(bib)	Gill		212	209			40	27	
	Gut		137	16				4	
	Liver		48	18			143	0.3	
	Muscle		72	83			187		
	Skeletal tissue		50	22			185		
Tylosurus marinus		1983			730				Reinert et al. (1983)
(garfish)									
Menidia menidia		1983			1090				Reinert et al. (1983)
(silverside)									
Fundulus sp.		1983			3200				Reinert et al. (1983)
(killifish)									
Seabirds									
Sula bassana	liver	1975	7.4				4.5-6	1.5-3.2	Pearson and McConnel (1975)
(gannet)			1.9-2.0				9-17	4.5-26	
Phalacrocerax aristotelis	eggs	1975	0.7				2.4	1.4	Pearson and McConnel (1975)
(shag)									
Alca torda	eggs	1975	6.6-19.7				28-29	32-39	Pearson and McConnel (1975)
(razorbill)									
Uria aalge	eggs	1975	8-65				23-26	19-29	Pearson and McConnel (1975)
(guillemot)									
Rissa tridactyla	eggs	1975	58				33	25	Pearson and McConnel (1975)
(kittiwake)									
Mammals									
Halichoerus grypus	blubber	1975	7.6-22				2.5-7.2	0.6-19	Pearson and McConnel (1975)
(grey seal)	liver		0-12				3-6.2	0-3.2	
Sorex araneus		1975	41-66				2.6-7.8	1	Pearson and McConnel (1975)
(common shrew)									

$CHCl_3$ = chloroform, CCl_4 = tetrachloromethane, 1,1-DCE = 1,1-dichloroethane, 1,2-DCE = 1,2-dichloroethane, TRI = trichloroethane, TCE = trichloroethylene, TTCE = tetrachloroethylene, [1] concentrations reported on a dry weight basis.

Table I.4.3: Concentrations of MAHs in marine biota (ng/g wet weight).

Species	Tissue	Date	Benzene	Toluene	Ethylbenzene	o-xylene	m-xylene	p-xylene	Reference
Invertebrates									
Crassostrea virginica (oyster)	Soft tissue	1980	220	3.4	0.8				Ferrario et al. (1985)
Rangia cuneata (clam)	Soft tissue	1980	260	18					Ferrario et al. (1985)
Mytilus edulis (blue mussel)	Soft tissue	1987	7340		250	540	360	520	Yasuhara and Morita (1987)
Modiolus demissus (rbbed mussel)	Soft tissue	1983	450 - 580				100 - 140		Reinert et al. (1983)
Fish									
Tylosurus marinus (garfish)	Muscle	1983	690						Reinert et al. (1983)
Menidia menidia (silverside)	Muscle	1983	690 - 990				100 - 180		Reinert et al. (1983)
Fundulus sp. (killifish)	Muscle	1983	1030						Reinert et al. (1983)

with some exceptions. There were no concentration differences between invertebrates and fish with the exception of the concentrations of tetrachloroethylene where the concentrations appeared to be higher in invertebrates. This is probably the result of differences in the metabolisation potential of fish compared to invertebrates.

Reinert *et al* (1983) reported only a limited number of data for 1,2-dichloroethane in fish and shellfish to illustrate the validity of their method (Table I.4.2). In contrast to the fish (*Tylosurus marinus* (garfish), *Menidia menidia* (silverside) and *Fundulus* species and shrimp (*Paleomonetes pugio*), the clam *Modiolus demissus* (ribbed mussel) did not accumulate the CHC to any detectable level at three different locations. These differences were explained by the low lipid content of the organisms. The concentrations in the other species were of the same order of magnitude.

Ferrario *et al* (1985) reported concentrations of CHCs in the clam (*Rangia cuneata*) and the oyster (*Crassostrea virginica*) from the estuary Lake Ponchartrain (USA) (Table I.4.2). The detectable concentrations ranged from 0.8 ng/g wet weight for trichloroethylene in clam and 310 ng/g wet weight for 1,1,1-trichloroethane in oyster. Finally, Gotoh *et al* (1992) reported concentrations of chloroform, tetrachloromethane, 1,1,1-trichloroethane trichloroethylene and tetrachloroethylene in oyster (*Crassostrea gigas*) and the clam (*Tapes japonica*) from the Ariho and the Yoshinaga River (Japan). The detectable concentrations ranged from 0.3 ng/g wet weight for tetrachloroethylene in clam to 6.7 ng/g wet weight for chloroform in clam (Table I.4.2). Again the concentrations of chloroform were higher than those of the other CHCs. The anthropogenic origin of the contamination is clearly illustrated by the fact that only traces are found in the Yoshinaga river as against much higher concentrations in the Ariho river which passes through an industrial area with dry cleaning product factories among others.

I.4.2.1.2. Concentrations of MAHs

Ferrario *et al.* (1985) reported concentrations of the MAHs benzene, toluene and ethylbenzene in the clam (*Rangia cuneata*) and the oyster (*Crassostrea virginica*) from the estuary Lake Ponchartrain (USA) (Table I.4.3). Benzene exhibited the highest concentrations in both clam (260 ng/g wet weight) and oyster (220 ng/g wet weight). The concentrations of

both toluene and ethylbenzene were significantly lower (maximum 18 ng/g wet weight). No explanation was given for these differences, but the authors assume that the contaminants are from anthropogenic origin. The concentrations in sediment are higher for benzene as well. The higher concentrations of benzene in these invertebrates could therefore be explained by a higher environmental load of this contaminant. Yashura and Morita (1987) reported concentrations of benzene, ethylbenzene, o-xylene, p-xylene and m-xylene in *Mytilus edulis* (blue mussel) from two coastal locations in Japan. The concentrations ranged from 7.34 µg/g wet weight for benzene to 0.25 µg/g wet weight for ethylbenzene. These concentrations are high compared to other reported values and especially compared to CHCs.

I.4.3. EFFECTS OF CHCs AND OR MAHs ON MARINE BIOTA

I.4.3.1. ACUTE TOXICITY

Lethal or acute concentrations of chemicals are hardly ever encountered in the marine environment. Acute toxicity levels are therefore of minor relevance when dealing with environmental concentrations. However, they are often used as a tool to set guidelines for human exposure or ecosystems at risk (Matthiessen *et al.*, 1993, Van Leeuwen *et al.*, 1992). For instance, Matthiessen *et al* (1993) apply a safety factor of x100 to acute data to determine "safe" levels. Relevant acute toxicity data are given for CHCs in Table I.4.4 and for MAHs in Table I.4.5. Both the CHCs and the MAHs can be considered as narcotic chemicals, i.e. non-electrolyte chemicals that in the absence of specific effects have only a minimum of toxicity (Van Leeuwen *et al.*, 1992).

I.4.3.1.1. CHCs

Tetrachloroethylene is clearly the most toxic CHC causing 50 % mortality in dab (Limanda limanda), a common North Sea species, at a concentration of only 5 mg/l in the water over a period of 96 hours (Pearson and McConnell, 1975). The toxicity generally decreases with a decreasing degree of chlorination and a decreasing number of C atoms on the sequence: tetrachloroethane > trichloroethylene >trichloroethane> dichloroethanes >chloroform> tetrachloromethane, with the exception of chloroform which is more toxic than tetrachloromethane. Further, chlorinated alkenes appear to be somewhat more toxic than

Table I.4.4: Acute toxicity data for CHCs.

Chemical	Species	Effect.	Concentration	Source
$CHCl_3$	*Poeclia reticulata* (guppy)	14 d LC_{50}	102 mg/l	Köneman (1979) in Verschueren (1983)
	Limanda limanda (dab)	96 hr LC_{50}	28 mg/l	Pearson and Mc Connell (1975)
	Man	Severe toxic effects	9960 mg/m^3	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	2490 mg/m^3	Strafford *et al.* in Verschueren (1983)
CCl_4	*Poeclia reticulata* (guppy)	14 d LC_{50}	67 mg/l	Köneman (1979) in Verschueren (1983)
	Lepomis macrochirus	96 hr LC_{50}	125 mg/l	Gaynor *et al.* (1975/77) in Verschueren (1983)
	Menidia berylla	96 hr LC_{50}	150 mg/l	Gaynor *et al.* (1975/77) in Verschueren (1983)
	Limanda limanda (dab)	96 hr LC_{50}	50 mg/l	Pearson and Mc Connell (1975)
	Rat	oral LD_{50}	2.92 g/kg	Patty (1967) in Verscheuren (1983)
	Man	Severe toxic effects	12800 mg/m^3	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	3200 mg/m^3	Strafford *et al.* in Verschueren (1983)
1,1-DCE	*Lepomis macrochirus* (Bluegill)	96 hr LC_{50}	550 mg/l	Gaynor *et al.* (1975/77) in Verschueren (1983)
	Menidia berylla (Tidewater silverside)	96 hr LC_{50}	480 mg/l	Gaynor *et al.* (1975/77) in Verschueren (1983)
1,2-DCE	*Crangon crangon* (brown shrimp)	96 hr LC_{50}	65 mg/l	Adema (1976) in Verschueren (1983)
	Gobius minus (Common sand goby)	96 hr LC_{50}	185 mg/l	Adema (1976) in Verschueren (1983)
	Poeclia reticulata (guppy)	7 d LC_{50}	106 mg/l	Köneman (1979) in Verschueren (1983)
	Limanda limanda (dab)	96 hr LC_{50}	115 mg/l	Pearson and Mc Connell (1975)
	Man	Severe toxic effects	2050 mg/m^3	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	410 mg/m^3	Strafford *et al.* in Verschueren (1983)
TRI	*Pimephales promelas* (fathead minnow)	96 hr LC_{50} (F)	52.8 mg/l	Alexander *et al.* in Verschueren (1983)
		96 hr LC_{50} (S)	105 mg/l	Alexander *et al.* in Verschueren (1983)
	Poeclia reticulata (guppy)	7 d LC_{50}	133 mg/l	Köneman (1979) in Verschueren (1983)
	Limanda limanda (dab)	96 hr LC_{50}	33 mg/l	Pearson and Mc Connell (1975)
	Rat	oral LD_{50}	10.3 - 12.3 mg/g	Patty (1967) in Verscheuren (1983)
TCE	*Pimephales promelas* (fathead minnow)	96 hr LC_{50} (F)	40.7 mg/l	Alexander *et al.* in Verschueren (1983)
		96 hr LC_{50} (S)	66.8 mg/l	Alexander *et al.* in Verschueren (1983)
	Poeclia reticulata (guppy)	7 d LC_{50}	55 mg/l	Köneman (1979) in Verschueren (1983)
	Limanda limanda (dab)	96 hr LC_{50}	16 mg/l	Pearson and Mc Connell (1975)
	Man	Severe toxic effects	10490 mg/m^3	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	4376 mg/m^3	Strafford *et al.* in Verschueren (1983)
TTCE	*Pimephales promelas* (fathead minnow)	96 hr LC_{50} (F)	18.4 mg/l	Alexander *et al.* in Verschueren (1983)
		96 hr LC_{50} (S)	21.4 mg/l	Alexander *et al.* in Verschueren (1983)
	Poeclia reticulata (guppy)	7 d LC_{50}	18 mg/l	Köneman (1979) in Verschueren (1983)
	Limanda limanda (dab)	96 hr LC_{50}	5 mg/l	Pearson and Mc Connell (1975)
	Rat	oral LD_{50}	>5000 mg/l	Patty (1967) in Verscheuren (1983)

$CHCl_3$ = trichoromethane, CCl_4 = tetrachloromethane, 1,1-DCE = 1,1-dichloroethane, 1,2-DCE = 1,2-dichloroethane, TRI = trichloroethane, TCE = trichloethylene, TTCE = tetrachloroethene, 14 d LC_{50} = lethal concentration administered over a period of 14 days killing 50% of the animals, 96 hr LC_{50} lethal concentration administered over a period of 96 hours killing 50% of the animals, oral LD_{50} oral administered dose killing 50 % of the animals, 7 d LC_{50} = lethal concentration administered over a period of 7days killing 50% of the animals.

Table I.4.5: Acute toxicity data for MAHs.

Chemical	Species	Effect.	Concentration	Source
Benzene	*Paelomonetes pugio* (Grass shrimp)	96 hr LC_{50}	27 mg/l	Neff *et al.* (1976)
	Cancer magister (crab) larvae - stage 1	96 hr LC_{50}	108 mg/l	Caldwell *et al.* (1977) in Verschueren (1983)
	Cragnon franciscorum (bay shrimp)	96 hr LC_{50}	20 mg/l	Benville and Korn (1977)
	Morone saxtilis (bass)	96 hr LC_{50}	5.8-10.9 mg/l	Benville and Korn (1977)
	Poecilia reticulata (guppy)	14 d LC_{50}	63 mg/l	Köneman (1979) in Verschueren (1983)
	Rat	LD_{50}	5600-5700 µg/g	Mckee *et al.* (1963) in Verschueren (1983)
	Man	Severe toxic effects	1500 ppm	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	500 ppm	Strafford *et al.* in Verschueren (1983)
Toluene	*Paelomonetes pugio* (Grass shrimp)	96 hr LC_{50}	9.5 mg/l	Neff *et al.* (1976)
	Cancer magister (crab) larvae - stage 1	96 hr LC_{50}	28 mg/l	Caldwell *et al.* (1977) in Verschueren (1983)
	Cragnon franciscorum (bay shrimp)	96 hr LC_{50}	4.3 mg/l	Benville and Korn (1977)
	Morone saxtilis (bass)	96 hr LC_{50}	7.3 mg/l	Benville and Korn (1977)
	Poecilia reticulata (guppy)	14 d LC_{50}	68 mg/l	Köneman (1979) in Verschueren (1983)
	Man	Severe toxic effects	3830 mg/m^3	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	1149 mg/m^3	Strafford *et al.* in Verschueren (1983)
Ethylbenzene	coho salmon	100 % mortality after 24 hrs	50 mg/l	Morrow (1974) in Verschueren (1983)
	Rat	LD_{50}	3500 mg/kg	Dow Chemical (1978) in Verschueren (1983)
o-Xylene	*Paelomonetes pugio* (Grass shrimp)	96 hr LC_{50}	7.4 mg/l	Neff *et al.* (1976)
	Cancer magister (crab) larvae - stage 1	96 hr LC_{50}	6 mg/l	Caldwell *et al.* (1977) in Verschueren (1983)
	Cragnon franciscorum (bay shrimp)	96 hr LC_{50}	1.3 mg/l	Benville and Korn (1977)
	Poecilia reticulata (guppy)	7 d LC_{50}	35 mg/l	Köneman (1979) in Verschueren (1983)
	Morone saxtilis (bass)	96 hr LC_{50}	11 mg/l	Benville and Korn (1977)
	Man	Severe toxic effects	4410 mg/m^3	Strafford *et al.* in Verschueren (1983)
		Symptoms of illness	1323 mg/m^3	Strafford *et al.* in Verschueren (1983)
m-Xylene	*Morone saxtilis* (bass)	96 hr LC_{50}	9.2 mg/l	Benville and Korn (1977)
	Poecilia reticulata (guppy)	14 d LC_{50}	38 mg/l	Köneman (1979) in Verschueren (1983)
	Cancer magister (crab) larvae - stage 1	96 hr LC_{50}	12 mg/l	Caldwell *et al.* (1977) in Verschueren (1983)
	Cragnon franciscorum (bay shrimp)	96 hr LC_{50}	3.7 mg/l	Benville and Korn (1977)
p-Xylene	*Morone saxtilis* (bass)	96 hr LC_{50}	2.0 mg/l	Benville and Korn (1977)
	Poecilia reticulata (guppy)	14 d LC_{50}	35 mg/l	Köneman (1979) in Verschueren (1983)
	Cragnon franciscorum (bay shrimp)	96 hr LC_{50}	2.0 mg/l	Benville and Korn (1977)

14 d LC_{50} = lethal concentration administered over a period of 14 days killing 50% of the animals, 96 hr LC_{50} lethal concentration administered over a period of 96 hours killing 50% of the animals, LD_{50} oral administered dose killing 50 % of the animals, 7 d LC_{50} = lethal concentration administered over a period of 7days killing 50% of the animals,

chlorinated alkanes.

The acute toxicity levels are, in general, several orders of magnitude higher than the concentrations reported in the marine environment (Murray and Riley, 1973; Pearson and McConnell, 1975; Bianchi *et al.*, 1989; Dawes and Waldock, 1994; Dewulf *et al.*, 1995). Relative "safe" levels are calculated according to Matthiessen *et al.* (1993) and were compared with data for the water phase (Table I.4.6). In none of the cases is the "safe" concentration exceeded. Only for chloroform levels are reported that approach this safety level. Environmental concentrations are therefore unlikely to cause an immediate threat to organisms. Finally, concentrations reported in edible animal tissue (Pearson and Mc Connell, 1975; Reinert *et al.*, 1983; Ferrario *et al.*, 1985; Gotoh *et al.*, 1992) are unlikely to cause acute toxic effects in humans.

Table I.4.6: Comparison between acute toxicity data for marine biota, calculated "safe" concentrations and environmental concentrations for CHCs and MAHs.

Chemical	Acute toxicity concentrations [1]	Calculated "safe" concentrations [2]	Concentrations in water [3]
Trichloromethane	28 mg/l	_ 280 µg/l	0.004 -200 µg/l
Tetrachloromethane	50 mg/l	_ 500 µg/l	0.0001-0.3 µg/l
1,1-Dichloroethane	550 mg/l	_ 5500 µg/l	
1,2-Dichloroethane	65 mg/l	_ 650 µg/l	0.04 - 4 µg/l
Trichloroethane	33 mg/l	_ 330 µg/l	0.002 - 3 µg/l
Trichloroethene	16 mg/l	_ 160 µg/l	1.3 - 3.6 µg/l
Tetrachloroethene	5 mg/l	_ 50 µg/l	0.0001 - 0.2 µg/l
Benzene	5.8 mg/l	_ 58 µg/l	0.005 - 55 µg/l
Toluene	4.3 mg/l	_ 43 µg/l	0.003 - 490 µg/l
Ethylbenzene	50 mg/l	_ 500 µg/l	0.01 - 312 µg/l
o-Xylene	1.3 mg/l	_ 13 µg/l	0.001 - 400 µg/l
m-Xylene	3.7 mg/l	_ 37 µg/l	0.015 - 1 µg/l
p-Xylene	2.0 mg/l	_ 20 µg/l	0.003 - 0.07 µg/l [4]

[1] Lowest acute concentration reported in table 4 for CHCs and table 5 for MAHs, [2] Calculated "safe" concentration applying a safety factor of x100 for the acute concentrations (Matthiessen *et al.*, 1993), [3] Concentrations in marine and estuarine waters reported in Roose (1995a) and Roose (1995b), [4] combined concentrations of m- and p-xylene.

I.4.3.1.2. MAHs

The acute toxicity of the various MAHs considered in this study is of the same order of magnitude. Benville and Korn (1977), for instance, reported 96-h LC_{50} toxicities ranging from 2 to 11 mg/l for striped bass (*Morone saxitilis*) and 0.49 to 20 mg/l for bay shrimp (*Cragnon franciscorum*) (Table I.4.5). Acute toxicity increases with increasing methylation in the sequence ethylbenzene < benzene < toluene < m-xylene < p-xylene o-xylene, with the clear

exception of ethylbenzene being the least toxic. Toluene also exhibits acute toxicity in the early development and juvenile stadia of fathead minnow (*Pimephales promelas*). The LD_{50} are forembryos 55-72 mg/l, for newly hatched protolarvae 25-36 mg/l and for 30 day old fish 18-30 mg/l (Devlin, 1983). As above, "safe" environmental concentrations were calculated according to Matthiessen *et al.* (1993) (Table I.4.6). In contrast to the CHCs, concentrations have been reported that exceeded (toluene and o-xylene, Table I.4.6) or approached (benzene and ethylbenzene, Table I.4.6) safety levels. On the other hand, concentrations reported in edible animal tissue (Ferrario *et al.*, 1985) are unlikely to cause acute toxic effects in humans.

I.4.3.2. SUBLETHAL EFFECTS

Sublethal effects of CHCs and MAHs on marine organisms are of primary concern, since concentration levels hardly ever reach acute toxic levels. The potential of a substance to cause sublethal effects can have a long term consequences on a given population, leading, for instance, to a decrease in reproductive success, increased overall stress, a decrease in resistance against diseases or modifications of the genetic material. These effects can eventually lead to a severe decrease in a population. In the prediction of toxicological effects, results are often extrapolated between species. However, this practice can produce erroneous results. Droy and Hinton (1988) discovered that tetrachloromethane did not produce a consistent pattern of toxicity similar to the centrilobular pattern seen in rodent liver. This only proves that great care should be taken when assessing possible effects of a given substance for a broader range of organisms and more importantly the absence of toxic effects of a given compound for a given organism does not necessarily prove the absence of danger for other organisms.

I.4.3.2.1. CHCs

In general, halogenated aliphatic compounds are considered to be potent immunotoxic agents. Suppression of humoral and cellular immunity as well as host resistance to infections has been established both in laboratory animals and humans (Wong *et al.*, 1992). The bulk of toxicological data is, unfortunately, related to mammalian exposure studies. Extrapolation to marine animals such as fish, is possible but should be treated with the necessary caution.

Chloroform has been shown to be toxic to aquatic organisms. Moreover, chloroform has been demonstrated to be carcinogenic in mammals and to exhibit both temporary and lasting toxic effects (Sittig, 1980). Chloroform generates adverse effects on growth, survival and liver morphology. NoTable is a significant decrease in weight and a severe fatty change of the liver (Loekle *et al.*, 1983). The growth reduction was also recorded by Loekle (1987) for *Carassius auratus* during a long-term exposure experiment with the same chemicals. Mice exposed to chloroform showed a reduced antibody response (Munson, 1987 in Wong *et al.*, 1992).

Tetrachloromethane is a hepatotoxin and most sublethal effects will therefore primarily become manifest in the liver. Hiraoka *et al.* (1979) demonstrated that tetrachloromethane causes liver injury in trout (*Salmo gairdneri*). Droy *et al.* (1988) demonstrated the induction of DNA-synthesis as a result of administering CCl_4 trout (*Salmo gairdneri*). Casillas *et al.* (1983) noted a series of histopathological changes after CCl_4 was injected intraperitoneally in English sole (*Parophrys vetulus*). Tetrachloromethane also induces peroxidation of hepatic microsomal lipids in mullet (*Mugil cephalus*) (Woffford and Thomas, 1988). Significant effects were demonstrated in the blood chemistry of pinfish (Lagodon rhomboides) by Folmar *et al.* (1993), after injections of about 3 mg/l of CCl_4. The authors noted significant elevations of alanine aminotransferase (ALT), aspartate aminotransferase (AST), creatine kinase (CK) and lactate dehydrogenase (LD-L). Tetrachloromethane causes a decrease in xenobiotic metabolisation (Kalf *et al.*, 1987). It acts as a suicide substrate for cytochrome P-450 (De Groot and Haas, 1981). The toxicity of CCl_4 is mainly due to metabolisation resulting in free radicals with the chloroform free radical being the most important (Kalf *et al.*, 1987).

Chlorinated ethanes have shown to be at least mildly toxic for mammals and aquatic organisms, with the toxicity increasing with the degree of chlorination (Sittig, 1980, see earlier). Chloroform, tetrachloroethylene and trichloroethylene have been reported to generate adverse effects on growth, survival and liver morphology with a decrease in weight and a severe fatty change of the liver (Loekle *et al.*, 1983). Loekle (1987) reported a growth reduction for *Carassius auratus* during a long term exposure experiment with the same chemicals. Trichloroethane has been reported to cause a decreased T-dependent antibody production in mice (Sanders *et al.* 1985 in Wong *et al.*, 1992). Trichloroethylene has shown to produce tumours in rodents and is a suspect human carcinogen and the possibility exists that it can induce an autoimmune disorder known as systematic sclerosis (Halmes *et al.*,

1996). Halmes *et al.* (1996) demonstrated the existence of protein adducts of trichloroethylene metabolites in mice. The authors suggest that cytochrome P-450 2E1 is the target protein.

I.4.3.2.2. MAHs

In general and as above, contamination levels in the marine environment hardly ever reach acute toxic levels. As before, most of the toxicity reported in literature is for mammalian systems. However, MAHs and their derivatives are potent immunotoxic substances that suppress the immune system in general (Wong *et al.*, 1992) and should therefore be regarded as a potential environmental problem.

Benzene is a known leukemic agent in humans (Sittig (1980); Kalf *et al.* (1987)) and a myelotoxin resulting in blood dyscrasias including lymphocytophenia, thrombocytophenia and pancythophenia or aplastic anemia (Laskin and Goldstein, (1977), Goldstein (1983)). Benzene has also been demonstrated to affect the aquatic wildlife adversely. Benzene is a erythropoietic toxin in the rainbow trout (*Salmo gairdneri*). The effect can be observed as a reduction in the number of erythrocytes and hystological lesions in the head kidney (Kindt, 1986). Benzene also induces congestion of the spleen and a diffuse vacuolisation of hepatic parenchymal cells. Benzene toxicity is the result of metabolisation in the liver followed by phenol activation and covalent binding to the head kidney (Kalf *et al.*, 1987). Sublethal concentrations of benzene caused significantly less embryonic tissue growth, a significantly different oxygen consumption and a significantly greater assimilation in feeding larvae of Pacific herring (*Clupea harengus pallasi*) (Eldridge et al., 1977). Benzene is also a well documented immunotoxic substance. Reported adverse effects on the immune system are decreases in lymphoid organ weights, antibody production, cell-mediated immunity, host resistance to infections and to tumours (Wong *et al.*, 1992). Finally, benzene and its metabolites inhibit both nuclear and mitochondrial replication and transcription in mice (Kalf *et al.*, 1987). Moreover, during metabolisation both benzene and its metabolites are converted to reactive species that covalently bind to macromolecules like DNA, RNA and proteins (Kalf *et al.*, 1987). The covalent binding index (CBI) equals that of genotoxic carcinogens classed as weak initiators of carcinogenesis.

Toluene is a toxic substance to aquatic organisms. Devlin *et al.* (1985) observed the following effect after exposure of embryos of to concentrations between 30 and 45 mg/l: distortion of the embryonic axis, abnormal heart and circulatory system development, hydration and swelling of the pericardial coelom, haemorrhaging, an overall stunted appearance, micropthalmia, and a unique migration of the ventrally located yolk syncytial layer and its associated nuclei. Toluene (10-40 mg/l) increased succinate dehydrogenase levels but decreased lactate dehydrogenase levels in *Tilapia mossambica* (Ravindran, 1988). On exposure to toluene the anaerobic oxidation decreases while the aerobic oxidation increases. Stoss *et al.* (1979) also observed teratogenic effects of toluene at exposure to concentrations of 41 mg/l for embryos of the Japanese medaka (*Oryzias lapites*).

Although ethylbenzene is present in all levels of the marine environment, very little is known about the long term biological effects. No data has thus far been found in literature that indicates possible consequences of prolonged exposure to low levels of ethylbenzene.

Very little is also known about the toxic effects of xylenes on aquatic wildlife. Effects thus far reported are mainly on the level of early development stages. Kjoersvik et al. (1982) observed significant decreases in the fertilisation rate of cod eggs when exposed to concentrations of m- and p- xylene above 10 ppm, while o-xylene had no effect. Effects upon the early cleavage pattern became significant from a concentration interval of 2-7 ppm.

I.4.3.3. BIOCONCENTRATION POTENTIAL

The bioconcentration potential of a chemical compound is defined as the potential of that compound to concentrate from the surrounding water phase into biological tissue. Chemicals exhibiting a strong tendency to bioconcentrate can lead to concentrations in organisms that will eventually cause chronic effects even if the initial toxicity of the chemical is low and if the initial concentration in the water phase in low. Korn and Rice (1981), for instance, suggested that eggs may accumulate lethal concentrations of hydrocarbons during long term exposure and would therefore be more sensitive to hydrocarbons than indicated by short term exposure experiments. Once a contaminant is present at significant concentrations in organisms at the basis of the food chain it can move through the food chain causing increasing concentrations in organisms at higher levels. The concentrations in animals at the

top of the food chain can accumulate in such a way that they become dangerous to the organisms. This process is generally referred to as biomagnification.

The bioconcentration potential is generally represented by the bioconcentration factor, BCF, being the ratio between the chemical 's concentration in the organism, C_{org}, and its concentration in the aquatic environment, C_w, at equilibrium (Eq. I.4.1, Freitag *et al.*, 1985, Isnard and Lambert, 1988, Van der Kooij *et al.*, 1991).

$$BCF = \frac{Corg}{Cw} \quad \text{(I.4.1)}$$

This coefficient is supposed to be constant, meaning independent of exposure time and concentration (provided that the exposure time is long enough), not highly dependent on the species and therefore an intrinsic property of the chemical (Isnard and Lambert, 1988). BCFs are generally calculated as a result of laboratory experiments in which animals are exposed to contaminated water or food. In the absence of these experiments, BCFs can be calculated on the basis of the octanol-water partition coefficient of a chemical, K_{ow}, according to a general expression of the linear free energy relationship given in Eq. I.4.2 (Neely *et al.*, 1974, Connell and Hawker, 1988; Isnard and Lambert, 1988; Banerjee and Baughman, 1991)

$$Log(BCF) = a + \log(Kow) \quad \text{(I.4.2)}$$

were a and b are constants.

Table I.4.7: Octanol-water partition coefficients and bioconcentration factors for CHCs and MAHs.

Chemical	K_{ow} [1]	BCF	Reference [2]
Trichloromethane	93.33	6.03	Isnard and Lambert, 1988.
		1.6 - 10.35	Anderson and Lusty, 1980 in Howard, 1991.
Tetrachloromethane	676.08	17.38	Neely *et al.*, 1974.
		17.38	Isnard and Lambert, 1988.
		<10	Freitag *et al.*, 1985.
1,1-Dichloroethane	61.66	1.2	Lyman, 1981 in Howard 1991.
1,2-Dichloroethane	30.20	2.00	Isnard and Lambert, 1988.
		1.20	Barrows, 1980 in Howard, 1991.
1,1,1-Trichloroethane	309.03	8.91	Isnard and Lambert, 1988.
		90	Freitag *et al.*, 1985.
Trichloroethene	263.03	17	Barrows, 1980 in Howard, 1991.
		39	Lyman, 1981 in Howard 1991.
Tetrachloroethene	2511.89	38.91	Neely *et al.*, 1974.
		48.98	Isnard and Lambert, 1988.
Benzene	154.88	12.59	Isnard and Lambert, 1988.
		4.27	Ogata *et al.*, 1984.
		3.5	Ogata and Miyake in Howard, 1991.
		4.4	Korn et al., 1977 in Howard, 1991.
		<10	Freitag *et al.*, 1985.
Toluene	616.60	8.32	Ogata *et al.*, 1984.
		13.2	Ogata and Miyake in Howard, 1991.
		1.67	Nunes and Benville, 1979 in Howard, 1991.
		4.2	Geyer et al., 1982 in Howard, 1991.
		90	Freitag *et al.*, 1985.
o-Xylene	506.76	21.38	Isnard and Lambert, 1988.
		14.13	Ogata *et al.*, 1984.
		6.17	Nunes and Benville, 1979 in Howard, 1991.
p-Xylene	1412.54	14.79	Ogata *et al.*, 1984.
		23.44	Ogata and Miyake in Howard, 1991.
m-Xylene	1584.89	23.44	Isnard and Lambert, 1988.
		14.79	Ogata *et al.*, 1984.
		6.03	Nunes and Benville, 1979 in Howard, 1991.
Ethylbenzene	1412.54 [3]	15.48	Ogata *et al.*, 1984.
		4.68	Nunes and Benville, 1979 in Howard, 1991.

K_{ow} = octanol-water partition coefficient, BCF = bioconcentration factor, [1] Values reported in Van Leeuwen and Van Der Zandt, 1992, [2] References refer to the BCF, [3] Hansch and Leo, 1985 in Howard *et al.*, 1991.

An overview of bioconcentration factors and the octanol-water partition coefficient is given in Table I.4.7. Both CHCs and MAHs have a low tendency to bioconcentrate. For CHCs the bioconcentration potential generally increases with increasing chlorination while for MAHs it increases with methylation. Of all the compounds listed in Table I.4.7 tetrachloroethylene has the highest bioconcentration potential, with a BCF ranging from 38.91 to 48.98 (Neely *et al.* (1974), Isnard and Lambert (1988)). However, the bioconcentration potential is low compared to those of widespread pollutants such as PCBs. The bioaccumulation of tetrachloroethylene was intensively studied by Pearson and Mc Connell (1975) for the marine species *Limanda limanda* (dab). They showed that bioaccumulation does occur, with an

accumulation factor between 5 and 9 for flesh and between 200 and 400 for liver, but that it was not accompanied by indications of illness. The concentrations in the tissues tended to an asymptotic level and were generally higher in fatty tissues such as the liver. Once the fish were returned to clean sea water, the concentrations in the tissues decreased. Freitag *et al.* (1985) reported BCFs between 2320 and 3850 for PCBs, between <10 and 910 for PAHs, between <10 and 90 for CHCs and between <10 and 90 for MAHs for golden ide (*Leuciscus idus melanotus*). The differences with PCBs are obvious, but are much less pronounced for PAHs. Two reasons can be forwarded for these differences. Firstly, high-molecular-weight-compounds will have more difficulties to move through the membranes than low molecular weight compounds. Secondly, bioconcentration is not solely the result of a passive chemical diffusion process. It should be regarded as the result of a combination of uptake and elimination processes. For PAHs, although the compounds are very hydrophobic, metabolisation and subsequent secretion is an important elimination process. This partly explains the differences with PCBs, since PCBs are generally not metabolised. However, it has already been discussed that, for instance, benzene toxicity is related with its metabolisation (see earlier). A low bioconcentration potential therefore only indicates that a given compound will generally not reach high levels in organisms, it does not imply that there is no potential threat to the environment.

I.4.3.4. METABOLISATION AND BIODEGRADATION

I.4.3.4.1. Introduction

Marine water and sediment contain vast numbers of micro-organisms that are capable of degrading complex organic molecules, generally originating from marine organisms and plants. This biodegradation capability is of the utmost importance since it also allows the degradation of the various organic chemicals, that were introduced into the marine environment by anthropogenic activities.

The ability of an organism to metabolise xenobioitic compounds plays an important role in the toxicity of that compound. Metabolisation decreases, in the first instance, the concentration of harmful substances and thus reduces the immediate toxicity. Metabolisation further enhances excretion and thus prevents accumulation of chemicals to dangerous concentrations

in the lipids of organisms. Unfortunately, metabolisation is often a prerequisite for toxicity (see earlier). Low concentrations in the organisms does therefore not imply the absence of a threat.

I.4.3.4.2. Biodegradation by bacteria and organisms of the lower trophic levels

CHCs

Howard (1991) reviewed the biodegradation of the CHCs discussed in this study. On the whole, biodegradation is slow or non-existent. The presence of an acclimation period generally enhances biodegradability. The number and position of the chlorine atoms will largely determine the biodegradability. As a rule, the higher the chlorination, the higher the resistance to biodegradation. The effect of the position of the chlorine atom is particularly evident for 1,1-dichloroethane which is more degradable than 1,2-dichloroethane. The chlorine atom on the second carbon of the ethane chain probably blocks an approach of the enzymes.

MAHs

The biodegradation of the MAHs has also been reviewed by Howard (1991). A brief overview of the results is given here.

Benzene is readily biodegradable in both marine and freshwater systems with half-lives in marine systems of 6 days. There is a clear seasonal effect with the highest biodegradation rates in summer and the lowest in winter. The most important metabolites are phenol and unidentified phenols, catechol, and cis 1,2-dihydroxy-1,2-dihydrobenzene.

As benzene, toluene is readily biodegraded in aquatic systems. Reported half-lives in marine systems vary from 4 to 90 days. Biodegradation is faster in oil polluted waters than in relatively clean waters thus illustrating the importance of acclimation of the micro-organisms. Microbial attack proceeds via immediate hydroxylation of the benzene ring followed by ring cleavage or oxidation of the side chain followed by hydroxylation and ring cleavage.

Xylenes are degraded in standard biodegradability tests using sea water. Degradation also occurs anaerobically, but required denitrifying conditions. A lag period of several months is

than required to establish the necessary enzymes for denitrification. After this the biodegradation proceeds rapidly.

Ethylbenzene is completely biodegraded in sea water. No degradation is observed under anaerobic conditions.

I.4.3.4.3. Metabolisation by fish and organisms of the higher trophic levels

Most of the literature deals with the metabolisation of CHCs and MAHs in mammalian systems. Although extrapolation to aquatic organisms is allowed, care should be taken when doing so. Metabolisation is usually cytochrome P-450 mediated and generally takes place in the liver of higher organisms.

Degradation of trichloroethylene and tetrachloroethylene has been reported in mammalian systems (Daniel (1963) in Pearson and Mc Connell (1975)). Degradation products included di- and trichloracetic acids. Rechnagel and Glende (1973) postulated that tetrachloromethane is metabolised through a homolytic cleavage of the carbon-chlorine bond. The reaction occurs anaerobically following the reaction of CCl_4 with cytochrome P-450 (in Kalf *et al.*, 1987).

Benzene is metabolised in the liver of higher organisms Sammett *et al.* (1979) in Kalf *et al.*, 1987. Benzene is converted via a cytochrome P-450 mediated pathway to benzene oxide in mouse liver (Gonasum *et al.*, 1973). The latter is than transformed to the 1,2-dihydrol by epoxide hydratase and eventually leads to the formation of catechol or phenol (Kalf *et al.*, 1987). Toluene and ethylbenzene are metabolised by the chinook salmon (*Oncorynchus tschawytscha*) to benzylalcohol and 1-phenylethanol (Kennish et al., 1988).

I.4.3.5. RISK/HAZARD ASSESMENT FOR HUMANS AND MARINE ORGANISMS

I.4.3.5.1. Introduction

Once the presence of a certain contaminant has been established in the marine environment, it remains to be determined whether this compound will pose a threat to both humans and aquatic organisms. Humans are mainly exposed through the consumption of sea food. This

results in the question if the average daily intake of contaminated animals will result in either short term (e.g. illness) or long term effects (e.g. cancer). Aquatic animals can be exposed both through the ingestion of contaminated food or through direct uptake from the water in the case of gill-breathing organisms. The interactions between the organisms and their environment are very complex and a proper evaluation of the hazard will therefore be more difficult than in the case of human consumption. This is especially the case for the prediction of long term effects of environmental pollution.

I.4.3.5.2. Determining the potential hazard of a chemical

In a first stage, criteria need to be established to determine if a chemical is potentially harmful to the marine environment. GESAMP (1990) based its selection of potentially harmful chlorinated substances on the following criteria: log K_{ow}, persistence, toxicity, production and use. Products were regarded as potentially dangerous when:

Log $K_{ow} > 3$
Persistence > 1 week
Toxicity (LC_{50}, EC_{50}) < 10 mg/l

The production and use of the chemical was used to influence the hazard assessment when in doubt. A product was considered to be potentially harmful when two or more of the criteria were met. When insufficient information is present concerning a given chemical quantitative structure activity relationships (QSARs) are used to estimate the potential hazard. The criteria mentioned above were used to evaluate the VOCs that are the subject of this study. An overview of the results is given in Table I.4.8.

Table I.4.8: Evaluation of the potential to cause harm for CHCs and MAHs.

Chemical	Log K_{ow} [1]	Persistence in weeks[2]	Toxicity in mg/l[3]	GESAMP[4]	New evaluation[5]
Trichloromethane	1.97	1 - 24	28	Yes	Yes
Tetrachloromethane	2.83	1 - 52	50	Yes	Yes
1,1-Dichloroethane	1.79	4 - 88	550	Not	?
1,2-Dichloroethane	1.48	14 - 96	65	Not	?
1,1,1-Trichloroethane	2.49	20 - 156	33	nd	?
Trichloroethene	2.42	14 - 234	8[6]	Yes	Yes
Tetrachloroethene	2.39	14 - 234	3.5[6]	Yes	Yes
Benzene	2.19	<1 - 96	5.8	nd	Yes
Toluene	2.79	<1 - 30	7.3	nd	Yes
o-Xylene	3.12	1 - 48	1.3	nd	Yes
p-Xylene	3.15	1 - 16	2	nd	Yes
m-Xylene	3.20	1 - 16	2	nd	Yes
Ethylbenzene	3.15 [3]	<1 - 33	50	nd	Yes

[1] Log(octanol - water partition coefficient, [2] Aquatic half-life, lowest and highest value in Howard *et al.* (1991), [3] Lowest toxicity in Pearson and Mc Connell (1975), [4] Evaluation by GESAMP (1990): Yes = potentially harmful, Not = no or insufficient data, nd = not determined, [5] New evaluation according to criteria of GESAMP (1990) and recent findings: Yes = potentially harmful, no = no potential danger,? = unknown.

Most of the VOCs in this study should be considered as a potential threat to the marine environment. The criteria are not exceeded for chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane and 1,1,1-trichloroethane with exception of the persistence. GESAMP (1990) concluded that for the dichloroethanes no or insufficient data were available to evaluate the potential harm, but considered chloroform and tetrachloromethane potentially harmful substances on the basis of the persistence, the production and widespread use of the chemicals. In view of the fact that the production and use of for instance 1,1-dichloroethane exceeds even that of tetrachloromethane (Pearson and Mc Connel, 1975), it is advisable to treat the substances that do not meet the criteria with the same caution as the others in the list. To conclude, most of the VOCs considered in this study should be regarded as potentially harmful substances.

I.4.3.5.3. Establishing safe levels for the marine environment

Once it has been established that a given chemical poses a threat, it remains to be determined what levels of contamination are accepTable in the marine environment. Van Leeuwen *et al.* (1992) used QSARs, extrapolation of toxicity data and equilibrium partitioning for the assessment of the effects of narcotic industrial pollutants. The extrapolation of toxicity data generated by QSARs was used to derive safe levels for water. The QSARs in the study were

expressed as:

$$Log(NOEC) = a \log K_{ow} + b \quad (I.4.3)$$

with NOEC the no-observed-effect concentration. These concentrations were derived from literature data or, in case were no chronic data were available, estimated from acute toxicity data using acute/chronic ratios (ACR). The safety level was arbitrarily set at 95%. This implies that a concentration is calculated which is unlikely to cause harm for 95 % of the aquatic community, in the sense that the NOEC is not exceeded. This value was defined as the HC5 or the hazardous concentration that will affect 5 % of the species. The safe levels for aquatic sediments and biota were derived using the equilibrium partitioning theory. Using the equilibrium theory the following relationships could be established:

$$C_{tot} = C_w \times (1+1.85 \times 10^{-6} K_{ow}) \quad (I.4.4)$$

were C_{tot} is the total concentration in the water phase and C_w is the concentration in solution, to describe the relationship between the concentration in water and the total concentration in the water fase (including suspended matter).

$$C_{sed} = 0.031 \times C_w \times K_{ow} \quad (I.4.5)$$

were C_{sed} is the concentration in sediment, to describe the relation between the concentration in sediment and water and finally

$$C_{org} = 0.05 \times C_w \times K_{ow} \quad (I.4.6)$$

were C_{org} is the concentration in the organisms, to describe the relation between the concentration in water and the concentration in the organism. The HC5 for total water, sediment and biota could then be calculated by substituting the HC5 for water in equations I.4.4, I.4.5 and I.4.6. The results of these calculations are summarised in Table I.4.9.

Table I.4.9: Environmental safety levels for CHCs and MAHs.

Chemical	HC5 [1] in mg/l	$HC5_{tot}$ [2] in mg/l	$HC5_{sed}$ [3] in mg/kg	$HC5_{org}$ [4] in mg/kg	Safe level for water in µg/l
Trichloromethane	1.67	1.67	5.00	8.07	0.280
Tetrachloromethane	0.321	0.321	6.07	9.79	0.500
1,1-Dichloroethane	2.19	2.19	4.15	6.69	5.500
1,2-Dichloroethane	4.34	4.34	4.12	6.65	0.650
1,1,1-Trichloroethane	0.573	0.573	5.43	8.76	0.330
Trichloroethene	0.716	0.716	5.39	8.69	0.160
Tetrachloroethene	0.0796	0.0796	6.00	9.68	0.050
Benzene	0.683	0.683	3.25	5.29	0.058
Toluene	0.192	0.192	3.64	5.92	0.043
o-Xylene	0.107	0.107	4.03	2.72	0.013
p-Xylene	0.0835	0.0837	3.97	5.90	0.020
m-Xylene	0.0835	0.0837	3.97	6.62	0.037
Ethylbenzene					0.050

[1] Hazardous concentration in water that will affect 5 % of the species (Van Leeuwen *et al.*, 1992), [2] hazardous concentration in water including suspended matter that will affect 5 % of the species (Van Leeuwen *et al.*, 1992), [3] hazardous concentration in sediment that will affect 5 % of the species (Van Leeuwen *et al.*, 1992), [4] hazardous concentration in biota that will affect 5 % of the species (Van Leeuwen *et al.*, 1992). [5] Calculated safe concentration in water calculated according to Matthiessen *et al.* (1993).

The HC5 varies between 0.08 mg/l for tetrachloroethylene and 4.34 mg/l for 1,2-dichloroethane in water (with or without suspended matter), between 3.25 µg/g for benzene and 6.07 µg/g for tetrachloromethane in sediment and finally, between 2.72 µg/g for o-xylene and 9.79 µg/g for tetrachloromethane in organisms. Concentrations thus far reported in literature for water and sediment are, generally, at least an order of magnitude lower than the limits set above (Murray and Riley, 1973; Pearson and McConnell, 1975; Bianchi *et al.*, 1989; Bianchi *et al.*, 1991; Dawes and Waldock, 1994; Dewulf *et al.*, 1995). The same is true for concentrations in biota with the exception of benzene concentrations reported by Yashura and Morita (1987). The authors reported concentrations of 7 µg/g benzene in the edible tissue of the blue mussel (Mytilus edulis) which is higher than the HC5 of 5.29 µg/g .

Another possibility is described by Mathiessen *et al.* (1993) who applied a safety factor of 100 to acute toxicity data to establish safe levels of chronic exposure (see earlier). The safety levels set with this method are several orders of magnitude lower. For instance the HC5 for chloroform is 1.67 mg/l were Mathiessen *et al.* (1993) calculated a safe level of 0.28 µg/l.

It is evident that a discrepancy exists between both methods with the more pragmatic approach of Mathiessen *et al.* (1993) resulting in the lowest safety levels. Other method will,

more than likely, lead to other safety levels. Only a more profound study of these contaminants can lead to a better understanding of their behaviour in the environment and their potential treat to organisms. It must further be stressed that concentrations thus far reported do exceed or approach the levels set by both methods which certainly validates a more profound study.

I.4.3.5.4. Establishing safe levels for human consumption

The daily consumption of contaminated fish and shellfish by humans can result in long term or acute effects. It is evident that, in view of the concentrations that are found in the environment, the risk of acute effects is negligible. However, a long term exposure to small doses can result in severe effects such as leukaemia in the case of benzene. It is therefore important to determine the maximum allowable concentration in sea food that will not result in chronic effects. Due to the limited availability of chronic exposure data for humans, it is often necessary to rely on experimental data for other mammals. One method of deriving threshold values is described by Sittig (1980). Based on the maximum no effect or minimum toxic doses, reported in literature, it is possible to calculate the maximum daily intake for a given contaminant. For instance, the lowest reported dose in rats that caused toxic effects for 1,1,1-trichloroethane is 750 mg/kg body weight (National Cancer Institute (1978) in Sittig (1980)) administered 5 days a week. However, the lowest toxic dose for humans can be lower or even higher. A safety factor of 1000 is therefore appropriate. Assuming an average body weight of 70 kg for humans results in a maximum allowable daily intake (MADI) of

$$\frac{750\ mg.kg^{-1} x\ 70\ kg\ x\ 5/7\ day}{1000} = 37.5\ mg.day^{-1} \qquad (I.4.7)$$

Assuming an average daily consumption of 100 g of fish (based on the values reported for fish rich diets in GESAMP (1988)), the maximum allowable concentration (MAC) in sea food can be calculated according to

$$\frac{37.5\ mg.day^{-1}}{100\ g.day^{-1}} = 375\ \mu g/g \qquad (I.4.8)$$

Using this principle, the MAC was calculated for a number of CHCs and MAHs and is given in Table I.4.10.

Table I.4.10: Maximum daily intake and maximum concentration in edible seafood for CHCs and MAHs.

Chemical	$MADI_1$ [1] in mg/day	MAC_1 [2] in mg/kg	$MADI_2$ [3] in mg/day	MAC_2 [4] in mg/kg	$MADI_3$ [5] in mg/day	MAC_4 [6] in mg/kg
Trichloromethane	11.9	119			59.76	598
Tetrachloromethane			2.04	20.4	76.8	768
1,1-Dichloroethane						
1,2-Dichloroethane	5.35	53.5			9.84	98.4
1,1,1-Trichloroethane	37.5	375	7.21	72.1		
Trichloroethene					105.2	1052
Tetrachloroethene			350	3500		
Benzene	0.032	0.32	3.92	39.2	12	1.2
Toluene	29.5	295			27.58	275.8
o-Xylene					31.75	317.5
p-Xylene						
m-Xylene						
Ethylbenzene	1.6	16	2.45	24.5		

[1] Maximum allowable daily intake according to Sittig (1980), [2] Maximum allowable concentration according to Sittig (1980), [3] Maximum allowable daily intake according to the alternative method 1, [4] Maximum allowable concentration according to the alternative method 1, [5] Maximum allowable daily intake according to the alternative method 2, [6] Maximum allowable concentration according to the alternative method 2.

Alternatively, the maximum allowable daily intake could be derived from acute toxicity data by applying a safety factor of 100 for chronic exposure (sea earlier). Again, in view of the potential differences between humans and the test animals, a safety factor of 1000 could be used. Thus by dividing the acute doses reported for test animals the maximum daily intake can be calculated, for according to

$$\frac{AD \; x \; 70 \; kg}{100\,000} = MADI \qquad \text{(I.4.9)}$$

were AD is the reported acute dose in mg per kg body weight. Again, an average body weight of 70 kg is assumed for humans. The maximum allowable concentration in sea food can than be calculated according to Eqn I.4.8. Using the acute data reported in Tables I.4.4 and I.4.5, the MADI and MAC were calculated and are given in Table I.4.10.

Finally, when acute or chronic data are available for humans, it is preferable to base the calculations on this basis. Levels in air resulting in symptoms of illness in humans were

already reported in Tables I.4.4 and I.4.5. Using a safety factor of 100, as before, for the acute concentration the chronic safety level in air can be calculated. Assuming an average respiratory rate of 24 $m^3.day^{-1}$ the maximum daily intake can be calculated according to

$$\frac{ADai}{100} \times 24\ m^3.day^{-1} = MADI \quad (I.4.10)$$

were AD_{air} is the acute dosis in air in $mg.m^{-3}$. The maximum allowable concentration for seafood is again calculated according to Eq I.4.8. The results of these calculations are given in Table I.4.10.

To conclude, based on the different methods described above the maximum allowable concentrations in seafood vary between 0.32 ppm for benzene and 3500 ppm for tetrachloroethane. Looking at the concentrations reported in Tables I.4.2 and I.4.3 it becomes evident that man is not threatened through the consumption of sea food as far as most CHCs and MAHs are concerned. The only exception is benzene for which concentrations have been reported that either exceed or approach the levels calculated above. On the whole, no serious problems should be expected when consuming sea food.

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