3.2 Measurement of volatile organic compounds in sediments of the Scheldt estuary and the southern North Sea[††]

Summary

The concentrations and distribution of 13 priority volatile organic compounds (VOCs) were determined in sediments of the Scheldt estuary and the Belgian continental shelf, using a modified Tekmar LSC 2000 purge-and-trap system coupled to GC-MS. The method allows a sample intake of up to 50 g wet weight and detection limits are between 0.003 ng/g (tetrachloromethane) and 0.16 ng/g (m- and p-xylene). The repeatability (n=5) varied between 4% (benzene) and 17% (toluene) and the recoveries ranged from 59% (1,1-dichloroethane) to 99% (tetrachloromethane). Because of the nature of the contaminants, special attention was paid to analyte losses and contamination of the samples during storage aboard the research vessel. Spiked sediment samples were prepared in the laboratory and stored aboard under the same conditions as the environmental samples. The recoveries for these samples varied between 94% and 130%, which suggests that storage had no adverse effect on the samples. No detectable VOC concentrations were found for most of the sampling stations. However, in the Antwerp harbour area, significant concentrations of VOCs were found. The sorption behaviour as predicted from laboratory equilibrium partitioning experiments gives an indication of the *in situ* partitioning behaviour of VOCs. Although VOCs in sediments should, in general, not be regarded as a major problem in the marine environment, high local concentrations may be a cause of concern.

[††] From *Water Res.*, 35 (2001) 1478-1488.

3.2.1 Introduction

The presence and distribution of volatile organic compounds (VOCs) in marine and estuarine systems have so far received relatively little attention from the scientific community, as was recognised by the International Conferences on the Protection of the North Sea [1,2]. VOCs enter the marine environment through their use as solvents and in production processes; their formation during chlorination of drinking water and exploitation and use of fossil fuels [3,4]. Recent work showed the presence of VOCs in marine organisms from the Belgian coastal region at concentrations comparable to those of well-known contaminants such as PCBs [5]. The significance of these findings for e.g. reproductive success and survival of organisms is at present unknown. It can be assumed that organisms are mainly exposed to contaminants through contaminated water and by the ingestion of contaminated particles or sediment and through food. Dewulf et al. [6] determined 13 priority VOCs in water from the Belgian coastal region and found average concentrations ranging from 2.2 to 73 ppt over a period of 1.5 year. The water column can therefore be regarded as a potential source of VOCs for organisms, especially when one considers that these VOC concentrations are approximately 1000-fold higher than those of, for instance, individual PCB congeners [7]. The contribution of sediments to the presence of VOCs in organisms is at present unknown. Parameters reflecting the equilibrium partitioning over the different compartments (air, water, sediment and organisms), environmental degradation rates and intercompartment exchange velocity models provide information to establish models which can predict the environmental fate of organic pollutants [8]. A low sorption can be expected because of the low Kow (octanol-water partitioning coefficient) values of most VOCs and the low organic carbon content of marine sediments, since VOCs are thought to be mainly associated with the organic fraction of sediments [9]. Recent experiments seem to confirm this and sediments are, therefore, generally not regarded as major sinks for VOCs [3,9]. However, reported concentrations in sediments tend to be higher than those of the overlying water column [10,11]. Moreover, the nature of organic matter in soils, which are comparable to sediments, can vary substantially. The degree of aromaticity [12] or the polar-to-nonpolar group ratio (O+N)/C [13] influence the sorption equilibrium. Because of this and the inherent stability of VOCs, sediments cannot be ruled out as a local source of VOCs for organisms.

There appears to be no universally recognised and approved method for the determination of VOCs in sediment. A variety of methods were reported in the literature which are based on techniques such as solvent extraction [14,15], vacuum distillation [16,17] and supercritical fluid extraction (SFE) [21], but the most commonly used methods are based on either static [18-20] or dynamic [10,11,22-25] headspace techniques. The latter is sometimes preceded by a solvent extraction step, in which case the extract itself is then analysed using a dynamic headspace or purge-and-trap (P&T) technique [26,27]. Static headspace offers the advantage of lower cost, easy automation and rapid sample throughput [18]. The main disadvantage are the relatively high detection limits (LODs), although Bianchi and Varney [20] reported LODs below 0.5 µg/kg dry weight for VOCs in sediments. The best LODs are generally found for methods that use P&T techniques. For example, Al-Rekabi et al. [11] reported LODs of 40-50 ng/kg wet weight for various VOCs and Bianchi et al. [10] found LODs of 20-300 ng/kg dry weight when using a similar approach. The latter group determined a large number of VOCs in the Solent estuary (UK). The analyte recoveries and repeatabilities of the different methods vary considerably and depend on the methodology. Using solvent extraction or SFE, recoveries are generally better than 80% [14,21] with RSDs (Relative Standard Deviations) below 10%, while for vacuum extraction recoveries varied between 50 and 100% [17] and the RSDs between 20 and 30%. Voice and Kolb [19] obtained recoveries of over 70% and RSDs of 5-10% when using static headspace. These authors also demonstrated the superior performance of the latter technique compared to P&T. The large variability in both recoveries (30-100%) and RSDs (1 - >30%) of the P&T techniques is well known [10,11,20,23-25]. Operational parameters such as, especially, the purge temperature, influence the overall performance. Bianchi et al. [10] showed an improved performance of their method when the samples were purged at a temperature of 60 °C rather than 30 °C. The efficiency of the P&T technique appears not to be influenced by the sample composition or sample size [24], which is a distinct advantage.

For this work, a P&T method developed for the determination of 13 priority VOCs in biota [28] was evaluated for the analysis of sediment samples. This study is a follow up on recent studies on the analysis, concentration and distribution of VOCs in water, air and organisms in the Belgian coastal area that were initiated in the framework of a national research programme. It was undertaken in order to study the importance of sediment as a source for VOCs in organisms, to test the applicability of the methodology and to

establish concentrations in sediments of the Scheldt Estuary and the Belgian continental shelf. In addition the partitioning behaviour of VOCs in sediment was further investigated.

3.2.2 Materials and methods

Materials

All materials used for the various experiments and analyses were of research-grade quality. The chlorinated hydrocarbons (CHCs), chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene, and the monocyclic aromatic hydrocarbons (MAHs) benzene, toluene, ethylbenzene and the xylenes, were all from Merck (Darmstadt, Germany). Selection of the VOCs was based on international priority pollutant lists [1,2]. They were used without further purification. Methanol (Instra-analysed, J.T. Baker, Phillipsburg, USA) was used to prepare standard solutions. 1,1,1-Trifluorotoluene (Aldrich, Milwaukee, USA) was used as internal standard (IS). Vocarb 4000 traps (8.5 cm Carbopak C, 10 cm Carbopak B, 6 cm Carboxen 1000 and 1 cm Carboxen 1001) were obtained from Supelco (Bellefonte, USA) and used as adsorption traps (1/8" OD). Water used for the preparation of blanks and standards was obtained from J.T. Baker. Extra-pure sea sand for blanks and calibration was obtained from Merck.

Apparatus

A microprocessor-controlled P&T system, the Tekmar LSC-2000 (Tekmar, Cincinati, USA), was coupled to a GC-MS (Finnigan Magnum Ion Trap MS, Finnigan, San José, USA) via a heated transfer line terminating in a cryogenic focuser at the GC end. The internal lines of the P&T were constructed from glass-lined stainless steel and the transfer line and internal lines were connected via a heated 6-port switch valve. The standard needle sparger of the Tekmar was replaced with a system consisting of two needles (purge gas inlet and outlet) and a moisture trap, which was a 40-ml vial cooled to –10 °C (Roose and Brinkman, 1998b). The 40-ml open-hole screw cap vials (moisture trap and sample vials) and PTFE/silicone liners were from Alltech (Deerfield, USA).

Sampling and storage

Samples were collected during two periods (March 1997 and March 1998) aboard the Belgian oceanographic research vessel 'Belgica' at different locations (Figure 3.2.1)

using a Van Veen grab-sampler. Sampling locations were selected from among those of an ongoing sampling programme in such a way that both a more remote and a more coastal location were represented and that the salinity gradient in the Scheldt estuary was covered. Immediately after sampling, the sediment samples were taken from the central portion of the grab using all-glass vials, and without a headspace. The vials were immediately closed with a PTFE-lined screw cap (Alltech). Samples were stored at 4 °C in the absence of organic solvents. Upon their arrival in the laboratory the samples were stored in an airtight refrigerator located in a solvent-free area in a separate building.

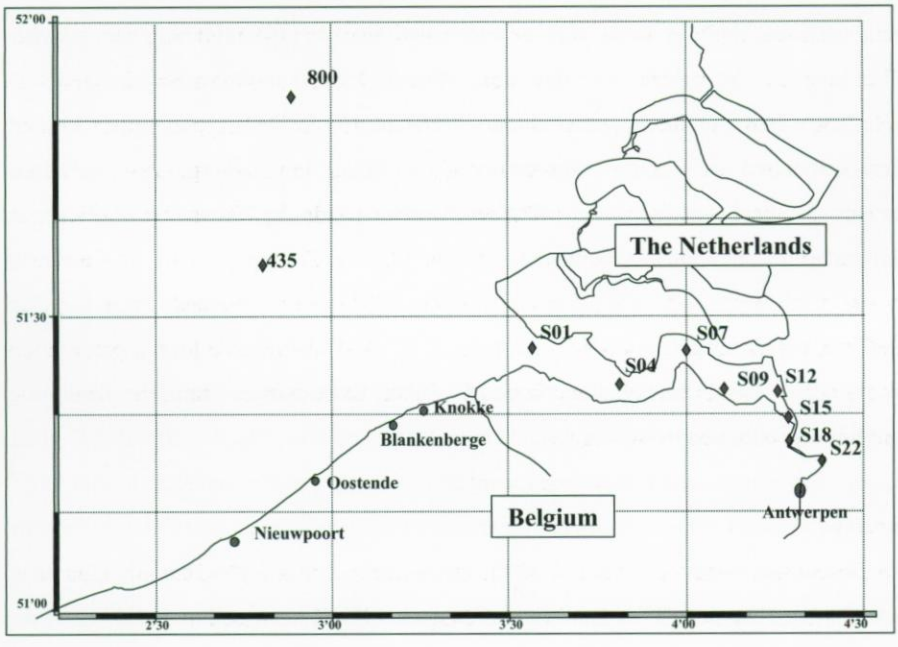

Figure 3.2.1: Sampling locations on the Belgian continental shelf and in the Scheldt estuary.

Analytical procedure

Preparation of blanks Water specially prepared for the analysis of VOCs (J.T. Baker) and extra-pure sea sand (Merck) were used to prepare blanks and standard solutions (see below). Both water and sediment were pre-treated by heating to 90°C with simultaneous purging with helium (N 7.0, l'Air Liquide, Liège, Belgium) or nitrogen (N 6.0, l'Air Liquide) in a glass sparger. As a routine, the latter were continuously purged during storage with helium or nitrogen. For the preparation of blank samples, 15 ml of the treated

water were drawn up in a 100-ml syringe and 1 µl of the internal standard was added by inserting a 10-µl HPLC syringe in the opening of the 100-ml syringe. The water was added to approx. 30 g of the blank sediment and the entire sample was then taken through the complete analytical procedure.

Preparation of standard solutions and spiked sediment samples A detailed description of the preparation of standard solutions is given elsewhere [5]. For calibration of the procedure, 1 µl of a methanolic solution containing 0.4-0.8 ng/µl of the various target compounds was injected with a 10-µl syringe in a 100-ml syringe containing 15 ml of blank water (see above). Next, 1 µl of a methanolic solution containing the internal standard (about 0.4 ng/µl) was also introduced into the 100-ml syringe with another 10-µl syringe. The water was then injected into a 40-ml sample vial filled with approx. 30 g of blank sediment and, after an equilibration period of 1 hour, the sample vial was connected to the on-line P&T set-up, pre-concentrated and analysed by GC-MS. An identical procedure was used for spiked sediment.

Sample pre-treatment and analysis

Approx. 30 g of sediment were transferred to a 40-ml sample vial. After the addition of 15 ml of organic-free water and internal standard, the vial was closed with a PTFE-lined screwcap. The glass vessel was then coupled to an impinger connected to the P&T system. The volatiles were forced out of the sediment by purging the sample for 30 min with a 20 ml/min stream of helium at 70°C (water bath). The analytes were trapped on a Vocarb 4000 sorbent trap mounted in the P&T apparatus, at a temperature of 45 °C. After purging, the trap was backflushed while being rapidly heated to 250 °C and the analytes were desorbed into a cryofocusing module cooled to -120°C and connected to the GC column. The analytes were injected into the column by rapidly heating the cryofocusing module from -120°C to 200 °C in 0.75 min. Separation was done on a 60 m x 0.32 mm i.d. (1.8 µm film) Restek, RTx-502.2 column. Temperature programming of the GC and data acquisition were started simultaneously. The temperature of the GC oven was held for 2 min at 40 °C and then increased from 40 °C to 200 °C at 10 °C/min. The final temperature was held for 5 min. Helium was used as the carrier gas with an inlet pressure of 16 psi.

Table 3.2.1: Retention windows, selected masses, recovery, repeatability and LOD of the target compounds.

Compound	Retention window (min)	Selected masses	Recovery[1] (%) (n=5)	RSD (%) (n=5)	LOD[2] (pg/g wwt)
1,1-Dichloroethane	4:30-4:50	63, 64	59	23	4
Chloroform	6:10-6:30	83, 85	88	16	90
Trichloroethane	6:40-6:60	61, 97, 99	97	17	4
Tetrachloromethane	7:00-7:20	117, 119	99	17	3
1,2-Dichloroethane	7:10-7:30	62	97	17	20
Benzene	7:10-7:30	78	92	4.3	50
Trichloroethene	8:00-8:20	60, 130	95	16	30
Toluene	9:45-9:65	91	86	17	100
Tetrachloroethene	10:40-10:60	91, 105	92	15	50
Ethylbenzene	12:00-12:20	91, 106	82	14	60
m&p-Xylene	12:05-12:25	91, 106	82	14	200
o-Xylene	12:45-12:65	91, 106	81	14	50

[1] Recoveries for a sediment sample spiked with concentrations ranging from 280 to 580 pg/g depending on the compound.
[2] LOD calculate for an average sample intake of 30 g.

The target compounds were identified on the basis of their retention times and mass spectra and quantified using the total mass abundance of selected ions (Table 3.2.1). The ion trap detector was operated in the electron ionisation (EI) mode with the multiplier voltage set at 2550 V, the axial modulation (A/M) amplitude at 4.0 V and the emission current at 13 μA. The manifold temperature was 220 ° C. The mass range was 50-250 amu and the scan rate 1000 ms. The filament delay was 180 s, and a mass defect of 50 mmass / 100 amu and a background mass of 45 amu were selected.

Analytical quality assurance

A blank sample was run with each series of samples. The peak heights of the analytes in the blank were compared with those in the standard solution used for calibration. Peak heights in the blank should at least be ten times lower than those in the standard solution (warning limit) and never be less than five times lower (control limit). A second quality assurance measure (QA) was to monitor the response factors of the different VOCs during the analysis of the standard solution used for calibration. Deviations of over 30% (± 2 sd) from the median response factor were considered as out of control. When the results of a test were out of control, a standard solution was treated as a sample and analysed as an

internal reference material (IRM). The test provides a way to determine whether the problem is MS or P&T related.

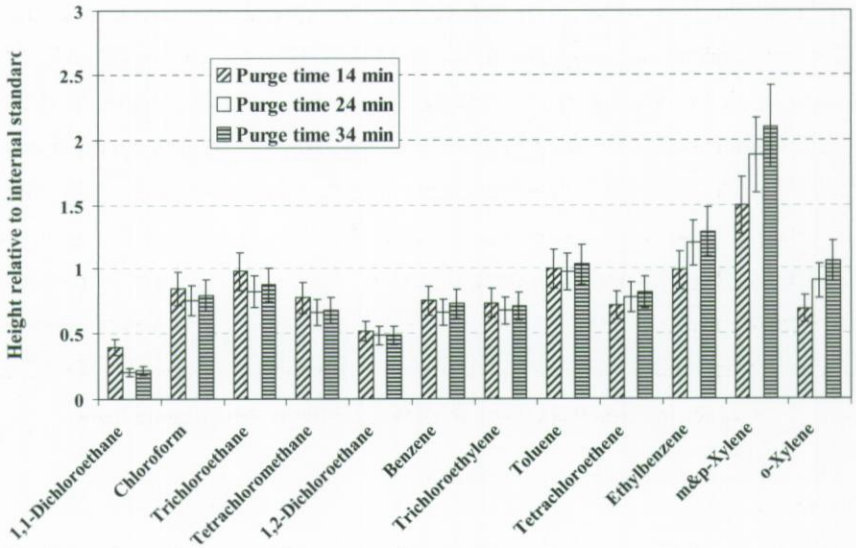

Figure 3.2.2: Effect of purge time on recovery of the analytes given in order of elution (n=3). The error bars represent the standard deviation.

3.2.3 Results

Analytical data

The P&T method developed earlier for the determination of 13 priority VOCs in biota [28] was slightly modified, viz. with respect to the sample preparation and sample intake. As there were practically no changes in the operational parameters of the earlier set-up, only the purge time was evaluated. To this end a spiked sediment sample was purged under otherwise identical conditions for different periods of time. The results are presented in Figure 3.2.2. For the compounds up to toluene no significant differences were observed between purge times of 14, 24 and 34 min, with the exception of 1,1-dichloroethane. The latter is clearly affected by longer purge times, presumably because 1,1-dichloroethane, with its high volatility, will break through the sorbent under these conditions. For the less volatile compounds such as tetrachloroethene, ethylbenzene and the xylenes, a substantial difference was observed between a purge time of 14 min and purge times of 24 min and 34 min. A purge time of 34 min was selected for all further work. To further test the method, both the repeatability (short-term precision) and the

recovery were determined by analysing five replicates of a spiked sediment sample. The results of the tests are given in Table 3.2.1. The recoveries varied between 80 and 99%, with one exception, 59%, for the highly volatile 1,1-dichloroethane, which can be explained by the 34-min purge time (cf. above). The repeatability, calculated as the RSD of five independent analyses, was between 14 and 17% for all but two VOCs. The deviating result for benzene cannot easily be explained. The much higher RSD for 1,1-dichloroethane is due to its less efficient recovery caused by the prolonged purging. The LODs were calculated for a standard sample of 30 g and were based on the analytical blank (blank + 3 sd) or a signal-to-noise ratio of 3 [5]. Considering that blank values range from 0.02 ng/g for tetrachloroethene to 0.08 ng/g wet weight for m&p-xylene, the method allows the detection of individual VOCs in sediments at concentrations varying from 0.004 ng/g for trichloroethane, for which no background levels were found, to 0.2 ng/g wet weight for m&p-xylene, with the above mentioned background levels.

Sample storage

Because of the volatility of the compounds of interest, analyte losses and sample contamination during storage aboard the research vessel and in the laboratory may well occur. Both sampling and storage were devised in such a way that contamination and losses would be minimised. To obtain an idea of both hazards, spiked sediment samples and blank sediment samples were prepared in the laboratory and stored aboard under the same conditions as the grab samples (1997 campaign). The prepared samples were then transported to and stored in the laboratory together with the sediment samples, again under identical conditions. The analyte recoveries for the spiked sediment samples varied between 94% and 130% (median: 102%); that is, they were within two standard deviations of the expected 100% recovery which proved that storage had no adverse effect on the samples. This was further confirmed by the fact that no significant differences were found between a laboratory blank and a set of blanks that were stored together with the environmental samples aboard and in the laboratory.

Sediment samples

P&T-GC-MS was used to analyse the samples collected at ten stations on the Belgian continental shelf and in the Scheldt estuary during two surveys in 1997 and 1998. The results of the analyses for both surveys are given in Table 3.2.2. For most of the sampling stations no detectable concentrations of the target compounds were found in 1997. Only

at sampling station S22, in the industrial region of Antwerp harbour (Figure 3.2.1), a marked presence of VOCs could be demonstrated. Even so, only the less volatile members of the group were present in the sediment but there was no clear relation between vapour pressure and sediment concentration. As every sampling station was independently sampled twice and the two samples were analysed individually, an idea of the sampling variability could be obtained. For obvious reasons this was only done for station S22.

Table 3.2.2: Concentration range and medians between brackets (where applicable) for VOCs in pg/g wet weight for the different sampling stations in the period 1997-1998.

Compound	Sampling station									
	800	435	S01	S04	S07	S09	S12	S15	S18	S22
1,1-Dichloroethane	-	-	-	-	-	-	-	-	10[1]	-
Chloroform	-	100[1]	-	-	-	-	-	-	-	-
Trichloroethane	-	-	-	-	-	-	-	< 4 – 170 (90)	< 4 – 60 (15)	-
Tetrachloromethane	-	-	-	-	6[1]	4[1]	-	-	50[1]	-
1,2-Dichloroethane	-	-	-	-	-	-	-	-	-	-
Benzene	-	-	-	-	70[1]	70[1]	< 50 – 110 (90)	< 50 – 120 (100)	90 – 340 (200)	-
Trichloroethene	-	-	-	-	-	-	-	< 30 – 80 (40)	< 30 – 70 (50)	< 30 – 90 (60)
Toluene	-	-	-	-	-	-	-	< 100 - 750 (400)	280 – 810 (690)	180 – 910 (700)
Tetrachloroethene	109[1]	-	< 50 – 350 (240)	-	-	-	-	-	-	< 50 – 110 (80)
Ethylbenzene	-	-	-	-	-	-	-	70[1]	100[1]	< 60 – 130 (80)
m&p-Xylene	-	-	-	-	-	-	-	-	-	80 – 230 (150)
o-Xylene	-	-	-	-	-	-	-	30 – 50[2] (40)	-	< 50 –110 (90)

- Below detection limits as given in Table 3.2.1
[1] Cases where only one sample had levels above the LOD
[2] Lower LOD due to lower background levels or higher sample intake

Considering that the average repeatability of the analytical method is 15%, the variability as a result of sampling was negligible for compounds such as toluene (17%), with concentrations well above the detection limit. When concentrations are near the detection limits the variability markedly increased (30-80%). During the 1998 survey, the VOCs were detected at the sampling stations S12, S15, S18 and S22 upstream the Scheldt river,

with the highest concentrations being found at stations S15 and S18. During this survey every station was sampled five times and each sample was analysed individually. In contrast to the 1997 results, the variability for the independent grabs was rather high (20-120%), even for a compound such as toluene which was present at relatively high concentrations.

Table 3.2.3: Average VOC concentrations and standard deviations (n=8) in water (C_w), salinity (S), and temperature (T) at selected sampling stations.

Sample	C_w (ng/l)	S (g/l)	T (°C)	log K_{ow}	log $K_{oc,sw}$	log $K_{oc,(S=0)}$	log $K_{oc,sw,eq}$
CHCl3/S22	300 ± 70	1.45	11.4	1.93	1.81	1.81	1.36
/435	19 ± 9	35	11.0		3.64	3.55	
CCl4/S18	12 ± 13	5.38	11.6	2.73	2.04	2.02	1.67
DCE11/S18	21 ± 7	5.38	11.6	1.79	1.10	1.08	0.96
/S04	24 ± 19	24.7	10.2	1.47	1.65	1.60	
/S12	80 ± 61	11.0	11.4		0.60	0.58	
/S15	100 ± 65	8.65	11.8		1.10	1.08	
/S18	158 ± 77	5.38	11.6		0.26	0.24	
/S22	63 ± 21	1.45	11.4		1.67	1.67	
TRI/S07	12 ± 6	20.8	10.2	2.48	1.85	1.76	1.5
/S15	84 ± 55	8.65	11.8		2.14	2.10	
/S18	163 ± 107	5.38	11.6		0.60	0.57	
/S22	266 ± 212	1.45	11.4		0.78	0.77	
TCE/S07	18 ± 21	20.8	10.2	2.42	2.34	2.26	1.58
/S15	67 ± 45	8.65	11.8		1.99	1.96	
/S18	134 ± 66	5.38	11.6		0.94	0.92	
/S22	222 ± 60	1.45	11.4		1.83	1.82	
TTCE/S01	5.0 ± 3.5	29.5	10.2	2.88	3.53	3.39	2.14
/800	6.0 ± 7.5	35	10.9		3.97	3.81	
BENZ/S07	70 ± 114	20.8	10.2	2.13	2.55	2.47	
/S09	36 ± 39	16.4	10.7		3.02	2.97	
/S12	58 ± 72	11.3	11.4		2.21	2.17	
/S15	55 ± 64	8.65	11.8		2.38	2.35	
/S18	39 ± 53	5.38	11.6		2.11	2.09	
/S22	102 ± 240	1.45	11.4		2.40	2.39	
TOL/S07	29 ± 13	20.8	10.2	2.69	3.03	2.96	1.6
/S12	71 ± 58	11.0	11.4		2.32	2.28	
/S15	66 ± 64	8.65	11.8		2.99	2.96	
/S18	64 ± 35	5.38	11.6		2.37	2.35	
/S22	56 ± 43	1.45	11.4		3.23	3.22	
ETBEN/S12	35 ± 34	11.0	11.4	3.15	2.16	2.11	2.03
/S15	32 ± 39	8.65	11.8		2.36	2.32	
/S18	23 ± 17	5.38	11.6		1.81	1.78	
MPXYL/S04	33 ± 38	24.7	10.2	3.19	2.61	2.51	
/S15	37 ± 37	8.65	11.8		2.47	2.44	
/S18	34 ± 41	5.38	11.6		1.89	1.87	
OXYL/S01	15 ± 9	29.5	10.2	3.12	2.16	2.02	2.02
/S04	22 ± 13	24.7	10.2		2.62	2.50	
/S15	31 ± 30	8.65	11.8		2.25	2.21	
/S18	40 ± 52	5.38	11.6	±	1.52	1.49	

Log K_{ow}, logarithm of the calculated in situ partitioning coefficient; log $K_{oc/sw}$, logarithm of the calculated *in situ* partitioning coefficient at zero salinity; log $K_{oc,(S=0)}$ and logarithm of the equilibrium partitioning coefficient for salt water log $K_{oc,eq}$ [9].

The concentrations of VOCs found in sediment can be related to those observed in the water column. In order to study this, the *in situ* sediment/water partitioning of VOCs was compared with equilibrium partitioning. In 40 cases, concentrations of VOCs in the sediment layer were above the limit of detection during this study (Table 3.2.2). At the same sites VOC concentrations in the water column were determined in the period 1994-1997, as described in previous papers [4,6]. Average water column concentrations for these sites are presented in Table 3.2.3. From the experimental sediment layer concentration ($C_{s,meas}$), the organic carbon fraction of the sediment (f_{oc}), and the water concentration ($C_{w,meas}$) $K_{oc/sw}$ values were calculated (Table 3.2.3). $K_{oc/sw}$, the *in situ* partitioning coefficient of VOCs between the organic carbon fraction of the sediment and salt water, is defined as

$$K_{oc,sw} = \frac{C_{oc,meas}}{C_{w,meas}} = \frac{C_{s,meas}}{C_{w,meas}} . f_{oc} \qquad (1)$$

with $C_{oc,meas}$ the experimentally determined concentration of VOCs in the organic carbon fraction of the sediment. Indeed, given that VOCs in sediment are mainly associated with the organic fraction of the sediment, concentrations of VOCs in sediment can be expressed on the basis of the organic carbon fraction.

In the literature *in situ* partitioning coefficients are often compared with K_{ow} (octanol/water equilibrium partitioning coefficient) values [29]. However for the marine environment the *in situ* partition coefficient $K_{oc/sw}$ cannot be immediately compared with K_{ow} because of salinity. Indeed, K_{ow} represents the partition behaviour between an organic phase (octanol) and (deionised) water, whereas $K_{oc/sw}$ represents a partitioning process between an organic phase and salt water. Dewulf *et al.* [9] have shown that $K_{oc,sw}$ can be converted into a partitioning coefficient $K_{oc,(S=0)}$, reflecting the partitioning between organic carbon and deionised water by means of: $K_{oc,(S=0)} = K_{oc/sw} . (H/H_{sw})$ where H and H_{sw} are the dimension-less Henry's law coefficients of the compound of interest for deionized and salt water, respectively. By considering the average salinities and temperatures at the different locations, and data for H and H_{sw} as a function of temperature and salinity from Dewulf *et al.* [9], the *in situ* partitioning coefficient at zero salinity $K_{oc,(S=0)}$, can be calculated and the results are given in Table 3.2.3. In Figure 3.2.3

$K_{oc, (S=0)}$ is plotted in function of K_{ow}. It is obvious that there is a large scatter in the data points, which cannot be attributed to the rather large number of measurements close to the LOD. Even so, linear regression shows a positive relation between log $K_{oc, (S=0)}$ and log K_{ow} data with a slope of 0.58 and an intercept of 0.64 with r = 0.39 (n = 40), which is significant at $\alpha = 0.05$ (P = 0.012). In other words, although the scatter is large, the log K_{ow} data gives an indication of the *in situ* partitioning behaviour of the volatile organic compounds. The slope, with a value lower than unity, suggests that there is a difference in polarity between the organic matter in the sediment and octanol.

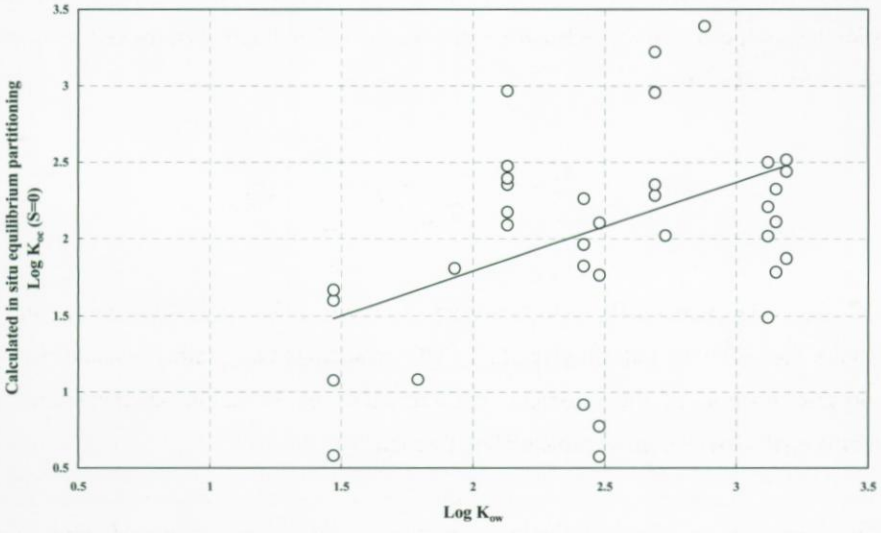

Figure 3.2.3: Relationship between K_{ow} (saltwater) and the *in situ* partitioning coefficient K_{oc} (S=0), determined with the present data set. (S = salinity)

In a second step, the *in situ* partitioning coefficients can be compared with experimental equilibrium partitioning coefficients in order to establish whether *in situ* partitioning is in equilibrium or disequilibrium. In a previous study experimental equilibrium partitioning coefficients of compounds of interest between organic matter in sea sediment and (deionized) water, $K_{oc,eq}$, were determined by Dewulf *et al.* [9] during their study of the sorption of VOCs onto marine sediments by using a miscible displacement technique. As before, the values were extrapolated to zero salinity to compensate for differences in salinity (e.g. Scheldt river versus North Sea). In Figure 3.2.4, the log $K_{oc, (S=0)}$ data are compared with experimental equilibrium partitioning coefficients at zero salinity ($K_{oc,eq,}$

$_{(S=0)}$). Linear regression now shows a slope of 0.89 and an intercept of 0.63 with r = 0.33. Although the linear regression is not significant at $\alpha = 0.05$ (P = 0.076), the value of the slope shows that the sorption behaviour of VOCs onto marine sediments as predicted from laboratory equilibrium partitioning experiments (cf. above) can be used to estimate the *in situ* partitioning behaviour.

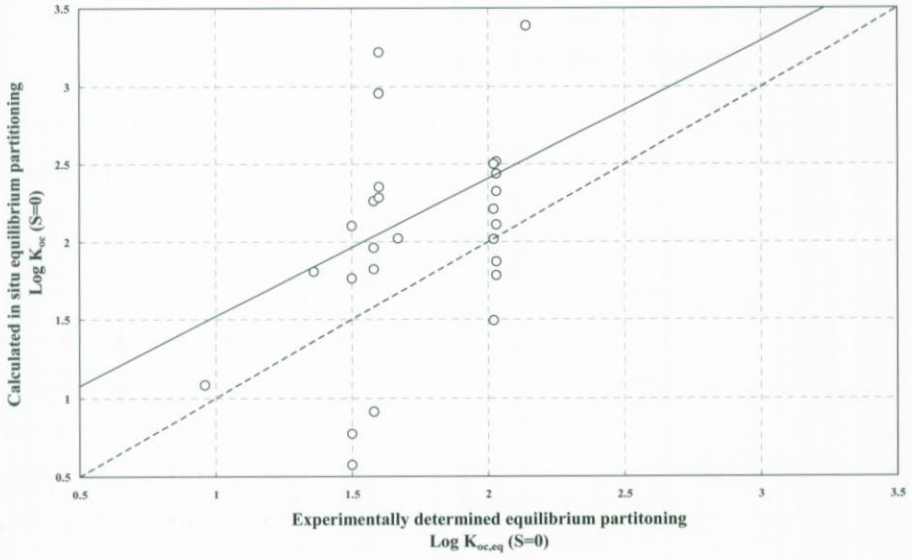

Figure 3.2.4: Relationship between the equilibrium partitioning coefficient $K_{oc,eq}$ (S=0), as determined by Dewulf *et al.* [9] and the *in situ* partitioning coefficient K_{oc}, determined with the present data set. (S= salinity)

The role of the sediment layer as a sink or source for VOCs can be assessed by comparing its role in partitioning with that of the water body and the atmosphere. From mass balances and equilibrium partitioning coefficients the fraction of a VOC in the sediment layer at equilibrium partitioning can be calculated from

$$M = C_{w,eq}.V_w+C_{s,eq}.V_s+C_{a,eq}.V_a, \qquad (2)$$

with M the total mass of a given VOC in the marine system, $C_{w,eq}$, $C_{s,eq}$, and $C_{a,eq}$ the concentrations at equilibrium in water, sediment and air, respectively, and V_w, V_s and V_a the volumes of the compartments water, sediment and air. With $H = C_{a,eq}/C_{w,eq}$ and K_{eq} =

$C_{s,eq}/C_{w,eq}$, with K_{eq} the equilibrium partitioning coefficient between sediment and water, the mass fractions of the VOCs at equilibrium in the water ($f_{w,eq}$), air ($f_{a,eq}$) and sediment ($f_{s,eq}$) compartments can be calculated from, respectively,

$$\frac{1}{f_{w,eq}} = 1 + K_{eq}.\frac{V_s}{V_w} + H.\frac{V_a}{V_w} \quad (3)$$

$$\frac{1}{f_{a,eq}} = 1 + \frac{V_w}{H.V_a} + \frac{K_{eq}.V_s}{H.V_a} \quad (4)$$

$$\frac{1}{f_{s,eq}} = 1 + \frac{V_w}{K_{eq}.V_s} + H.\frac{V_a}{K_{eq}.V_s} \quad (5)$$

K_{eq} can be calculated from $K_{eq} = \gamma.f_{oc}.K_{oc/sw,eq} + \theta$ with γ the apparent density of the sediment and θ the porosity of the sediment [9] and Henry's law coefficient is known from Dewulf *et al.* [30]. Considering an area of 1 km² and the same sediment and atmospheric heights as in the fugacity model of Mackay [31] and Mackay and Paterson [8,32,33] (1 cm and 2 km, respectively), and taking into account the depth of the water column at the sampling locations (30, 9 and 10.4 m for sampling locations 800, S15 and S22, respectively), the three fractions of interest can be calculated from equations 3 - 5. The results of these calculations are presented for tetrachloroethene in Figure 3.2.5. Tetrachloroethene was selected, because it is the only VOC for which measurable levels were found both in the sediment layer of the North Sea and of the Scheldt estuary.

Alternatively, the *in situ* partitioning can be studied by considering the VOC concentrations found in the sediment layer, the atmosphere and the water column. By substituting the actual concentrations of a VOC in water, sediment and air in Eq. 2, one finds

$$M = C_{w,meas}.V_w + C_{s,meas}.V_s + C_{a,meas}.V_a \quad (6)$$

with $C_{w,meas}$ and $C_{s,meas}$ as before and $C_{a,meas}$ the concentration measured in air. The mass fractions in each compartment can then be calculated by multiplying the concentration in each of these compartments with that compartment's volume, and dividing the outcome by the total mass of the VOC. The fractions were calculated using the sediment

concentrations from this work and the air and water column concentrations from previous work [6], and using the same volumes of the three compartments as above; the results are presented in Figure 3.2.5.

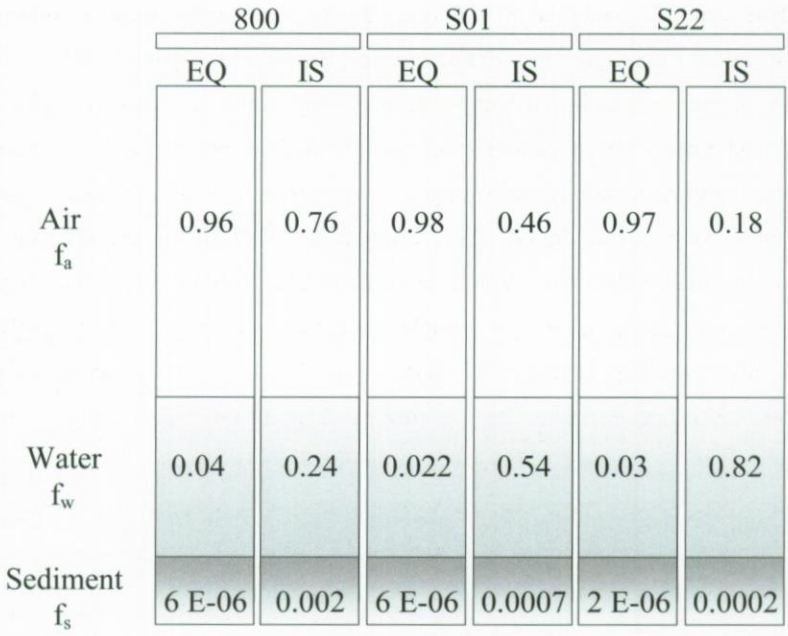

Figure 3.2.5: Comparison of the calculated fractions of tetrachloroethene in air, water and sediment at equilibrium (EQ) and *in situ* (IS) at the sampling locations 800, S01 and S22.

3.2.4 Discussion

After minor modification, the method used for the determination of VOCs in marine organisms [28] proved to be equally successful for the determination of VOCs in marine sediments. The repeatability, recoveries and LODs reported in this paper are similar to those reported in the literature (Table 3.2.1). The repeatability of the current method averaged around 15%, which is fully satisfactory compared to what is reported for similar P&T techniques (1-30%) [10,11]. With the current method the LODs ranged from 4 to 200 ppt, depending on the background concentrations and the characteristics of the analytes. Al Rekabi *et al.* [11] reported LODs between 40 and 50 ppt and Bianchi *et al.* [10] obtained LODs ranging from 20 to 30 ppt using P&T. The analyte recovery generally was above 80%. On the one hand, this is to be expected because a sandy sediment was

used which will not adsorb the VOCs as strongly as a sediment with a large clay or organic fraction. On the other hand, Charles and Simmons [24] found that neither sediment composition nor sample weight influenced the outcome of a P&T analysis. In any case, the choice of a sandy sediment for this study was deliberate. Most sediments we had to analyse were of a sandy nature and losses due to volatilisation were considered to be the most prominent danger [19]. Bianchi *et al.* [10] found comparable results when using the same approach as in our study, i.e. long purge times, a relatively high purge temperature and a minimum of sample handling. Most authors report special measures to minimise losses during sampling and storage, but the effect of these measures is hardly ever discussed. Siegrist and Jenssen [15] discussed the effects of several sampling methods on the determination of VOCs in contaminated soil in detail. The highest recoveries were obtained when the sample container was immersed in methanol immediately after sampling. Container headspace volume and soil disturbance contributed less to what they called negative bias (i.e. measured value lower than actual). For the present work, a zero headspace volume and an additional sealing with Teflon tape was applied to minimise losses. The analyte recoveries of over 90% obtained after storage of a spiked sandy sediment sample certainly illustrate the adequacy of these measures.

The results of the environmental analyses show that VOC concentrations are below the detection limits at nearly all sampling stations with the exception of those in the Antwerp harbour area (Table 3.2.2). At a first glance, this is somewhat surprising because the river Scheldt is regarded as being a heavily polluted stream and the major source of contamination of the Belgian coastal waters [7]. However, sediments are not widely regarded as a major source or sink of VOCs. As K_{ow} is low for most VOCs, significant sorption is not expected [3,9]. The present experimental results seem to support this thesis. A positive relation was found between log $K_{oc,\,(S=0)}$, determined *in situ*, and log K_{ow} (Figure 3.2.3). This indicates that the *in situ* partitioning behaviour of the volatile organic compounds can be predicted from their K_{ow}. The lower-than-unity slope suggests a polarity difference between octanol and the organic carbon fraction of the sediment, in the sense that VOCs apparently have a lower affinity for the organic carbon fraction of sediment than for octanol.

No significant relationship between $K_{oc,(S=0)}$ and $K_{oc,eq,(S=0)}$ could be demonstrated at α = 0.05 (P = 0.076) (Figure 3.2.4). The value of the slope suggests that the sorption

behaviour of VOCs onto marine sediments as predicted from laboratory equilibrium partitioning experiments can be used to estimate the *in situ* partitioning behaviour. However, the regression line is found above the bisector. This suggests that the sediment layer is 'oversaturated' by VOCs when compared to the aqueous layer. In other words, the sediment layer may act as a source of VOCs. The latter can be studied in more detail by using the model of Dewulf [34], who developed a dynamic exchange model for VOCs in the North Sea and the Scheldt estuary and estimated that only 0.0006% of the total VOC burden is present in the sediment fraction. This conclusion is confirmed when the mass fractions of tetrachloroethene in air, water and sediment are calculated according to this model (Figure 3.2.5). The results indeed show that the role of the sediment as a sink is of minor importance. However, when calculating the mass fractions of tetrachloroethene based on the *in situ* concentrations [34], the *in situ* partitioning into the sediment layer and, especially, the water column is higher than expected from equilibrium partitioning calculations (Figure 3.2.5). This may signify that there are additional sources in the sediment or in the water column. Additional sources are highly likely in the Scheldt estuary and can be attributed to anthropogenic activities along the river. However, even for the more remote sampling location 800, the role of the sediment layer and water body are underestimated. Direct anthropogenic inputs, as in the Scheldt estuary, are rather unlikely for this location. However, several alternatives can be suggested. Firstly, long-range aqueous transport from riverine inputs discharged into the North Sea can explain these relatively high water and sediment concentrations. Secondly, in the literature a number of biogenic marine sources have been mentioned for tetrachloroethylene [4]. Finally, the history of the sediment may play a role. Finally, but less likely, the higher (local) anthropogenic emissions in marine waters may have led to a relatively high accumulation in the sediment layer, from which the VOCs are, subsequently slowly, released.

Finally, although the current findings allow suggesting that the marine environment as a whole, and marine organisms in particular, are not threatened by the presence of VOCs in sediment, some caution is warranted. The results show that VOCs are mainly associated with the organic carbon fraction of the sediment. Considering that this fraction is primarily associated with the fine fractions of sediments, it should be noted that the concentrations of VOCs normalised for the fine-fraction content of sediments are similar to those of contaminants such as PCBs [35]. The fine fraction is, in addition, the most

important one for organisms. Many conveyer belt species or funnel feeders prefer ingesting and reworking the finer fraction of sediments. Contaminated-deposit-feeding organisms may significantly contribute to the dietary uptake of toxic chemicals by demersal fish, which will result in a food web transfer [36]. In other words, VOCs in sediment could contribute to, or be a main source of, VOC levels found in fish and higher organisms.

3.2.5 Conclusions

The current analytical methodology allows the determination of VOCs in marine and estuarine sediments with an acceptable recovery and reproducibility. Although the VOC levels in many sediments are at or below the detection limits, improving the detection limit is not urgently required. The current study illustrates that the sorption behaviour of VOCs in sediments, determined by laboratory experiments, can be used to estimate their behaviour under environmental conditions. Because of this, it can be assumed that the concentrations in marine sediments will be low and that, in general, VOCs in sediments should not be regarded as a major problem in the marine environment. However, the present study also shows that local situations cannot solely be explained by an equilibrium partitioning approach and that local high concentrations may be a cause for concern, especially with regard to organisms.

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