

**Impulse Programme Marine Sciences 1992-1996**

**Project n° 4**

**Intercompartment distribution of  
monocyclic aromatic hydrocarbons  
and C<sub>1</sub>-C<sub>2</sub> organochlorines  
in the North Sea environment**

**Part IV  
Physicochemical behaviour of the  
target compounds**

**Department of Organic Chemistry**

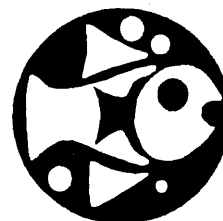
**Faculty of Agricultural & Applied  
Biological Sciences**

**University of Gent**



**Fisheries Research Station**

**Centre for Agricultural Research  
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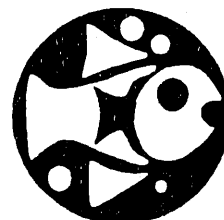
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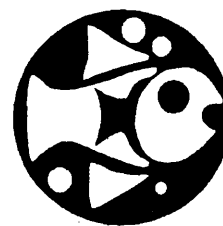
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## IV. PHYSICOCHEMICAL BEHAVIOUR OF THE TARGET COMPOUNDS

### IV.1. AIR/WATER EQUILIBRIUM DISTRIBUTION

#### IV.1.1. INTRODUCTION

The air/water equilibrium partitioning is expressed by the Henry's law. The Henry's law states that the ratio between the air concentration and the water concentration is a constant (Henry's law constant,  $H$ ) for a given compound at a defined temperature. Several methods are applied to study the air-water partitioning. Firstly a simple calculation using vapor pressure and maximum solubility gives a rough approximation of  $H$ . Secondly a multiple phase equilibration of VOCs in an air-water system within a syringe can be used (Mc Auliffe, 1971; Hunter-Smith et al., 1983). Thirdly, measurement of infinite dilution activity coefficients was carried out by gas chromatography (Tse et al., 1992; Orbey and Sandler, 1991) or by using a differential static cell equilibrium apparatus (Wright et al., 1992). Fourthly, a dynamic system can be used. A vessel containing VOCs enriched water is purged with a pure gas stream and the gas effluent concentration is analysed as function of time. Assuming defined and constant conditions (isotherm system, well mixed vessel, equilibration is attained at the top of the water column, ...)  $H$  can be calculated (Mackay et al., 1979; Lincoff & Gossett, 1984; Nicholson et al., 1984; Dunnivant et al., 1988).

Last, static systems with a liquid and a gaseous phase exist in several forms. The first is headspace analysis, calibrating it with an external calibration series. Knowing the mass of VOCs added to the system  $H$  is calculated (Przyjazny et al., 1983). Sampling both the gas and the liquid phase gives directly the  $H$  constant (Tancredi & Yanagisawa, 1990). In the Vapor Phase Calibration method (VPC method) a solute is injected in a two phase system and in a one phase gas system. Both headspaces are analysed and the latter is used as external standard (Kolb et al., 1992). Finally, different liquid/gaseous volume ratio's are used as in the Phase Ratio Variation method (Ettre et al., 1993) and as in the Static Headspace Method of Robbins et al. (1993). In these methods an increasing volume of water with the same concentration of VOCs is added to a series of bottles. By plotting  $1/C_g$  ( $C_g$  = the measured equilibrium gas phase concentration) against  $V_g/V_w$  (volume gas phase/ volume liquid phase), the  $H$ -coefficient is calculated from the linear regression parameters ( $H$ =slope/intercept). The correlation

coefficient is given as criterion for precision. In the EPICS-method (Equilibration Partitioning In Closed systems) (Lincoff & Gossett, 1984) two bottles, into which an equal mass of VOCs is added, but with a different gas/water volume ratio, are incubated. H is calculated from measurement of the headspace concentration ratio. In the modified EPICS-procedure (Gossett, 1987) the VOCs masses added are not necessarily the same. This EPICS-techniques give the possibility of several estimations of H with relatively few analyses.

Considering the simplicity of the method and the applicability to expected H-values at very low temperatures (to 2°C), the modified EPICS-method (Gossett, 1987) was further developed with higher difference in gas/liquid content in closed systems and using one stock solution.

#### **IV.1.2. MEASUREMENT RESULTS FOR HENRY'S LAW CONSTANT**

For the thirteen target VOCs nine experimental determinations for Henry's Law Constant (H) at all combinations of three salt concentrations (0.0, 17.5 and 35.0 g.L<sup>-1</sup>) and at five temperatures (2.0, 6.0, 10.0, 18.2 and 25.0 °C) were carried out by means of the EPICS technique (Equilibrium Partitioning In Closed Systems). The obtained mean H values (n=9) and the SD (in %, %SD) are given in Table IV.1.1.

**Table IV.1.1.** Measured values of Henry's law constant H vs. temperature and salt concentration.

VOC	temperature (°C)	salt concentration (g.L <sup>-1</sup> )	H (dimensionless)	%SD
chloroform	2.0	0.0	0.0507	13.6
		17.5	0.0490	8.7
		35.0	0.0540	2.9
	6.0	0.0	0.0582	5.1
		17.5	0.0685	3.2
		35.0	0.0735	2.6
	10.0	0.0	0.0704	3.8
		17.5	0.0818	6.9
		35.0	0.101	9.7
	18.2	0.0	0.114	4.9
		17.5	0.123	2.7
		35.0	0.143	2.3
	25.0	0.0	0.153	2.1
		17.5	0.162	3.0
		35.0	0.177	0.7
tetrachloromethane	2.0	0.0	0.365	5.4
		17.5	0.400	4.4
		35.0	0.434	5.8
	6.0	0.0	0.393	2.8
		17.5	0.498	4.8
		35.0	0.547	1.4
	10.0	0.0	0.448	2.3
		17.5	0.654	6.5
		35.0	0.684	12.1
	18.2	0.0	0.795	1.2
		17.5	0.938	7.1
		35.0	1.009	2.5
	25.0	0.0	1.048	2.1
		17.5	1.266	2.2
		35.0	1.359	1.8
1,1-dichloroethane	2.0	0.0	0.0665	2.2
		17.5	0.0743	1.0
		35.0	0.0829	3.3
	6.0	0.0	0.0841	4.8
		17.5	0.101	3.5
		35.0	0.109	2.0
	10.0	0.0	0.0827	3.9
		17.5	0.121	4.6
		35.0	0.128	5.4
	18.2	0.0	0.153	3.6
		17.5	0.166	4.8
		35.0	0.187	0.7
	25.0	0.0	0.206	1.2
		17.5	0.232	1.7
		35.0	0.258	3.2
1,2-dichloroethane	2.0	0.0	0.0140	55.3
		17.5	0.0132	15.3
		35.0	0.0110	16.6

	6.0	0.0	0.0183	10.5
		17.5	0.0199	3.9
		35.0	0.0209	7.2
	10.0	0.0	0.0168	8.8
		17.5	0.0223	6.2
		35.0	0.0272	17.8
	18.2	0.0	0.0305	11.7
		17.5	0.0336	4.2
		35.0	0.0394	5.0
	25.0	0.0	0.0412	5.2
		17.5	0.0449	7.7
		35.0	0.0502	3.6
<b>1,1,1-</b>	2.0	0.0	0.196	2.3
<b>trichloroethane</b>		17.5	0.222	1.7
		35.0	0.277	9.6
	6.0	0.0	0.259	4.4
		17.5	0.283	1.8
		35.0	0.350	3.9
	10.0	0.0	0.284	2.8
		17.5	0.444	7.2
		35.0	0.412	2.8
	18.2	0.0	0.460	6.3
		17.5	0.532	1.3
		35.0	0.645	7.8
	25.0	0.0	0.608	2.3
		17.5	0.662	3.5
		35.0	0.753	3.0
<b>trichloroethylene</b>	2.0	0.0	0.101	4.2
		17.5	0.111	5.8
		35.0	0.129	3.5
	6.0	0.0	0.125	5.0
		17.5	0.152	3.5
		35.0	0.169	1.4
	10.0	0.0	0.139	3.8
		17.5	0.197	4.1
		35.0	0.210	4.2
	18.2	0.0	0.254	2.7
		17.5	0.285	4.0
		35.0	0.321	0.8
	25.0	0.0	0.351	0.8
		17.5	0.407	2.3
		35.0	0.442	2.1
<b>tetrachloroethylene</b>	2.0	0.0	0.157	4.8
		17.5	0.187	1.8
		35.0	0.237	6.1
	6.0	0.0	0.212	2.9
		17.5	0.245	3.6
		35.0	0.310	3.5
	10.0	0.0	0.256	4.0
		17.5	0.405	5.0
		35.0	0.377	2.8
	18.2	0.0	0.411	5.8
		17.5	0.512	1.7

	25.0	0.0	0.601	4.0
		17.5	0.669	3.8
		35.0	0.788	2.8
benzene	2.0	0.0	0.0706	3.9
		17.5	0.0720	3.5
		35.0	0.0895	11.5
	6.0	0.0	0.0897	4.5
		17.5	0.0954	4.1
		35.0	0.120	4.2
	10.0	0.0	0.0970	5.9
		17.5	0.134	6.7
		35.0	0.132	3.5
	18.2	0.0	0.151	6.9
		17.5	0.171	0.7
		35.0	0.204	5.2
	25.0	0.0	0.194	2.5
		17.5	0.211	2.6
		35.0	0.246	2.4
toluene	2.0	0.0	0.0767	19.4
		17.5	0.0832	5.7
		35.0	0.0892	3.1
	6.0	0.0	0.0875	6.9
		17.5	0.105	1.5
		35.0	0.120	1.7
	10.0	0.0	0.106	8.6
		17.5	0.128	3.3
		35.0	0.163	6.4
	18.2	0.0	0.175	4.1
		17.5	0.197	1.3
		35.0	0.238	2.0
	25.0	0.0	0.224	1.9
		17.5	0.248	1.8
		35.0	0.290	1.8
ethylbenzene	2.0	0.0	0.0786	6.5
		17.5	0.0891	13.0
		35.0	0.112	6.3
	6.0	0.0	0.0837	7.5
		17.5	0.113	9.0
		35.0	0.131	2.8
	10.0	0.0	0.109	8.4
		17.5	0.162	3.4
		35.0	0.174	4.5
	18.2	0.0	0.205	8.9
		17.5	0.234	6.9
		35.0	0.268	3.0
	25.0	0.0	0.270	4.2
		17.5	0.321	1.8
		35.0	0.362	1.9
o-xylene	2.0	0.0	0.0582	14.2
		17.5	0.0655	19.2
		35.0	0.0817	9.6

	6.0	0.0	0.0507	11.2
		17.5	0.0715	13.1
		35.0	0.0834	4.5
	10.0	0.0	0.066	10.5
		17.5	0.115	9.9
		35.0	0.117	6.6
	18.2	0.0	0.134	16.8
		17.5	0.153	11.4
		35.0	0.176	6.8
	25.0	0.0	0.173	11.0
		17.5	0.200	2.4
		35.0	0.227	2.8
m-xylene	2.0	0.0	0.0913	6.2
		17.5	0.109	16.5
		35.0	0.102	4.7
	6.0	0.0	0.0877	13.9
		17.5	0.116	7.6
		35.0	0.116	4.0
	10.0	0.0	0.112	12.5
		17.5	0.142	5.4
		35.0	0.181	6.7
	18.2	0.0	0.195	7.2
		17.5	0.231	3.4
		35.0	0.271	3.3
	25.0	0.0	0.248	3.5
		17.5	0.274	5.0
		35.0	0.329	3.6
p-xylene	2.0	0.0	0.0771	14.0
		17.5	0.0816	5.7
		35.0	0.0922	15.6
	6.0	0.0	0.0681	6.1
		17.5	0.105	13.9
		35.0	0.134	5.6
	10.0	0.0	0.107	7.5
		17.5	0.168	11.2
		35.0	0.176	5.6
	18.2	0.0	0.193	4.9
		17.5	0.212	3.6
		35.0	0.275	5.8
	25.0	0.0	0.232	6.1
		17.5	0.267	6.7
		35.0	0.341	2.1



### IV.1.3. EXPECTED AND MEASURED STANDARD DEVIATIONS ON HENRY'S LAW CONSTANT

In the EPICS method two masses  $M_1$  and  $M_2$  are added to two bottles with liquid volumes  $V_{w1}$  and  $V_{w2}$  and headspace volumes  $V_{g1}$  and  $V_{g2}$ . The masses are distributed over the gas and the liquid phases in both systems:

$$M_1 = C_{g1} (V_{w1} / H + V_{g1})$$

$$M_2 = C_{g2} (V_{w2} / H + V_{g2})$$

where  $C_{g1}$  and  $C_{g2}$  = concentration of solute in the liquid phase (mole.L<sup>-1</sup>), and H = Henry's Law Constant (dimensionless). From this equations and if

$$r = \frac{C_{g1} / M_1}{C_{g2} / M_2}$$

one obtains for H:

$$H = \frac{V_{w2} - r \cdot V_{w1}}{r \cdot V_{g1} - V_{g2}}$$

Knowing that

$$V_{g1} + V_{w1} = V_{g2} + V_{w2} = V_b$$

H can be written as

$$H = \frac{V_{w2} - r \cdot V_{w1}}{V_b \cdot (r-1) - r \cdot V_{w1} + V_{w2}}$$

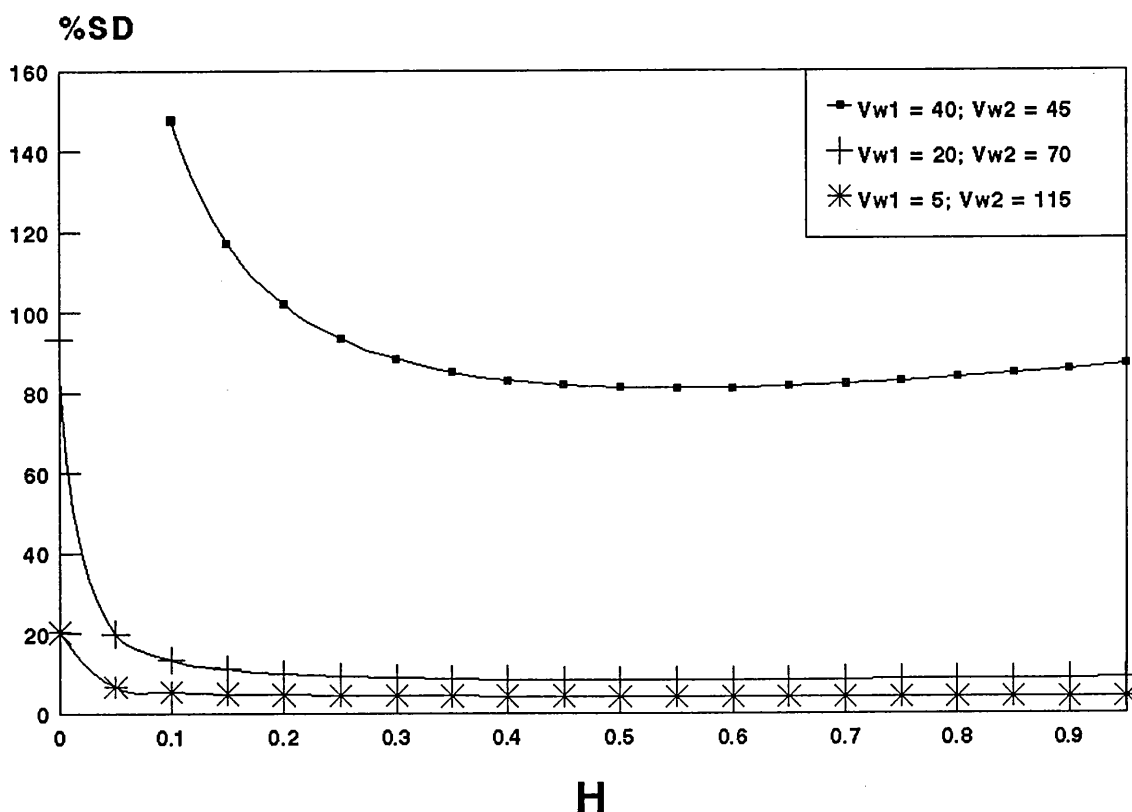
Gossett (1987) stated the standard deviation (SD) on H is mainly due to the factor r. The variance on H can be written as

$$\sigma^2 (H) = \left( \frac{\partial H}{\partial V_{w1}} \right)^2 \cdot \sigma^2 (V_{w1}) + \left( \frac{\partial H}{\partial V_{w2}} \right)^2 \cdot \sigma^2 (V_{w2}) + \left( \frac{\partial H}{\partial V_b} \right)^2 \cdot \sigma^2 (V_b) + \left( \frac{\partial H}{\partial r} \right)^2 \cdot \sigma^2 (r)$$

From this equation together with r as a function of H:

$$r = \frac{V_b - V_{w2} + V_{w2} / H}{V_b - V_{w1} + V_{w1} / H}$$

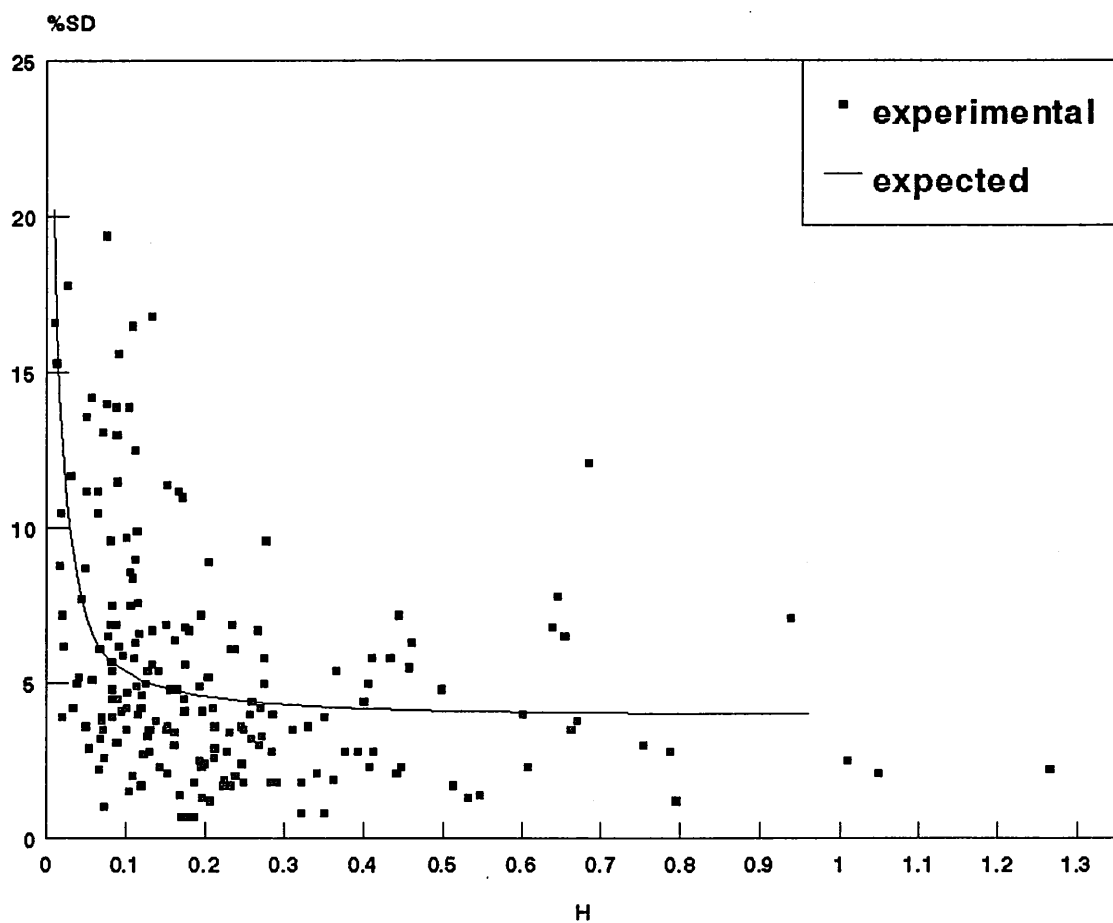
and calculating the variance of  $r$  as a function as a function of the variances on  $C_{g1}$ ,  $C_{g2}$ ,  $M_1$  and  $M_2$  (Table IV.1.2.), an estimation of the expected SD on  $H$  can be made. From Figure IV.1.1. it is clear that the larger the difference in liquid content is between the two bottles, the smaller is the SD on  $H$ . This was suggested earlier by Lincoff and Gossett (1984). A second conclusion is that for low  $H$ -values the SD is exponentially increasing with decreasing  $H$ . This is depending on the  $V_{w1}/V_{w2}$  ratio. In order to accurately measure at low temperatures and at expected low  $H$ -values, the volumes of  $V_{w1} = 5\text{mL}$  and  $V_{w2} = 115\text{mL}$  were used ( $V_b=118\text{ mL}$ ). Figure IV.1.2. shows that the general trend predicted by the calculations is good, but the variation on the experimental SD is quite large. This can be due to differences in precision of the measured headspace concentrations between the different VOCs.



**Figure IV.1.1.** Expected standard deviation (in %, %SD) of Henry's law constant  $H$  (dimensionless) in function of  $H$  and the applied liquid volume ratio (total volume of the bottle  $V_b=118\text{mL}$ ; volumes of liquid contents  $V_{w1}$  and  $V_{w2}$  in mL).

**Table IV.1.2.** Standard deviation ( in %, %SD) on factors affecting the standard deviation of the Henry's constant H, measured experimentally (n=5).

factor(s)	%SD
$C_{g1}, C_{g2}$	$\leq 2.50$
$M_1, M_2$	0.83
$V_{w1} = 5\text{mL}$	0.22
$V_{w2} = 115\text{mL}$	0.028
$V_b$	0.23



**Figure IV.1.2.** Expected and experimental standard deviation (in %, %SD) of Henry's law constant H (dimensionless) in function of H (Liquid volumes  $V_{w1} = 5\text{mL}$  and  $V_{w2} = 115\text{mL}$ )

**IV.1.4. COMPARISON WITH LITERATURE DATA (AT 25°C)**

The values obtained are compared in Table IV.1.3. to literature data from experimental work or from calculations. The measured data agree well for the C<sub>1</sub> and C<sub>2</sub> organochlorines. For the monocyclic aromatic hydrocarbons less data are available, so comparison is more difficult.

**Table IV.1.3.** Comparison of measured Henry's law constant with literature data (H dimensionless at 25.0°C).

VOC	measured	literature data
chloroform	0.153	0.163 <sup>1</sup> ; 0.159 <sup>2</sup> ; 0.146 <sup>3</sup> ; 0.152 <sup>4</sup> ; 0.172 <sup>5</sup> ; 0.159 <sup>6</sup> ; 0.199 <sup>7</sup>
tetrachloromethane	1.048	0.981 <sup>1</sup> ; 0.874 <sup>2</sup> ; 1.220 <sup>3</sup> ; 1.285 <sup>4</sup> ; 0.978 <sup>7</sup> ; 1.16 <sup>8</sup>
1,1-dichloroethane	0.206	0.246 <sup>1</sup> ; 0.222 <sup>3</sup> ; 0.243 <sup>4</sup>
1,2-dichloroethane	0.0412	0.0438 <sup>1</sup> ; 0.0409 <sup>2</sup> ; 0.0451 <sup>4</sup>
1,1,1-trichloroethane	0.608	0.798 <sup>1</sup> ; 0.683 <sup>3</sup> ; 0.652 <sup>4</sup> ; 0.683 <sup>5</sup> ; 0.697 <sup>6</sup> ; 0.532 <sup>7</sup> ; 0.513 <sup>9</sup>
trichloroethylene	0.351	0.438 <sup>1</sup> ; 0.383 <sup>3</sup> ; 0.367 <sup>4</sup> ; 0.411 <sup>5</sup> ; 0.353 <sup>6</sup> ; 0.310 <sup>8</sup> ; 0.420 <sup>10</sup>
tetrachloroethylene	0.601	1.127 <sup>1</sup> ; 0.710 <sup>3</sup> ; 0.707 <sup>5</sup> ; 0.619 <sup>6</sup> ; 0.550 <sup>8</sup> ; 0.499 <sup>9</sup> ; 0.697 <sup>10</sup>
benzene	0.194	0.225 <sup>1</sup> ; 0.230 <sup>2</sup> ; 0.216 <sup>10</sup> ; 0.227 <sup>11</sup> ; 0.230 <sup>12</sup>
toluene	0.224	0.277 <sup>1</sup> ; 0.277 <sup>2</sup> ; 0.260 <sup>9</sup> ; 0.263 <sup>10</sup> ; 0.272 <sup>11</sup> ; 0.261 <sup>12</sup> ; 0.272 <sup>13</sup>
ethylbenzene	0.270	0.325 <sup>1</sup> ; 0.348 <sup>2</sup> ; 0.318 <sup>10</sup> ; 0.345 <sup>11</sup>
o-xylene	0.173	0.283 <sup>1</sup>
m-xylene	0.248	0.298 <sup>10</sup>
p-xylene	0.232	0.210 <sup>1</sup> ; 0.189 <sup>10</sup>

<sup>1</sup>Schwarzenbach et al., 1993 (calculated values); <sup>2</sup>Schwarzenbach et al., 1993 (experimental values); <sup>3</sup>Gossett, 1987; <sup>4</sup>Wright et al., 1992; <sup>5</sup>Lincoff and Gossett, 1984 (EPICS method); <sup>6</sup>Lincoff and Gossett (batch air stripping); <sup>7</sup>Hunter-Smith et al., 1983; <sup>8</sup>Tancrède and Yanagisawa, 1990; <sup>9</sup>Kolb et al., 1992; <sup>10</sup>Robbins et al., 1993; <sup>11</sup>Mackay et al., 1979; <sup>12</sup>Ettre et al., 1993; <sup>13</sup>McAuliffe, 1971.

#### IV.1.5. BIFUNCTIONAL RELATIONSHIP BETWEEN H AND TEMPERATURE AND BETWEEN H AND SALINITY

Since theoretically a linear relationship between  $\ln H$  and  $T^{-1}$  ( $T$ = absolute temperature, K), and between  $\ln H$  and  $Z$  ( $Z$ =salinity, in  $g.L^{-1}$ ) was expected (Stumm and Morgan, 1981; Schwarzenbach et al., 1993), double linear regression was used (Table IV.1.4.):

$$\ln H = a \cdot \left(\frac{1}{T}\right) + b \cdot Z + c$$

The correlation was checked by a t-test to the two independent variables and confirmed (Table IV.1.4). Only the coefficient for salinity ( $b$ ) of 1,2-dichloroethane and for trichloroethylene was not confirmed by a t-test at the  $\alpha = 0.05$  level.

**Table IV.1.4.** Double linear regression for  $\ln H$  ( $H$  dimensionless) and the variables  $T^{-1}$  ( $K^{-1}$ ) and  $Z$  ( $g.L^{-1}$ ):  $\ln H = a.T^{-1} + b.Z + c$  with  $275 \leq T \leq 298$  and  $0.0 \leq Z \leq 35.0$ .

VOC	a	b	c
chloroform	- 4142 ± 153	0.00588 ± 0.00109	12.012 ± 0.539
tetrachloromethane	- 4073 ± 161	0.00814 ± 0.00114	13.722 ± 0.564
1,1-dichloroethane	- 3975 ± 167	0.00768 ± 0.00119	11.727 ± 0.587
1,2-dichloroethane	- 4329 ± 343	0.00473 ± 0.00244*	11.377 ± 1.205
1,1,1-trichloroethane	- 3834 ± 210	0.00897 ± 0.00149	12.351 ± 0.738
trichloroethylene	- 3648 ± 655	0.00813 ± 0.00465*	11.121 ± 2.301
tetrachloroethylene	- 4528 ± 214	0.01080 ± 0.00152	14.655 ± 0.752
benzene	- 3640 ± 168	0.00786 ± 0.00119	10.577 ± 0.592
toluene	- 4064 ± 143	0.00834 ± 0.00102	12.150 ± 0.504
ethylbenzene	- 4567 ± 178	0.01047 ± 0.00126	14.001 ± 0.624
o-xylene	- 4232 ± 317	0.01115 ± 0.00225	12.400 ± 1.114
m-xylene	- 4026 ± 256	0.00846 ± 0.00182	12.123 ± 0.899
p-xylene	- 4479 ± 315	0.01196 ± 0.00224	13.597 ± 1.107

\*This regression coefficient exceeds the critical value in a t-test for  $\alpha = 0.05$ .

#### IV.1.6. MEASUREMENT OF HENRY'S LAW CONSTANT FOR NATURAL SEA WATER

The Henry's law constant of the VOCs was measured for natural seawater (North Sea water) at 6.0 and 25.0°C (Table IV.1.5). Comparing the values obtained with natural sea water (salinity 35g.L<sup>-1</sup>) and the values of artificial sea water with a salt concentration of 35.0g.L<sup>-1</sup> it is clear that there is no systematic deviation. A t-test ( $\alpha = 0.05$ ) indicated in 17 of the 26 cases no significant difference, in four cases the natural sea water H value seemed to be larger and in five cases the inverse situation was observed (table IV.1.5).

Referring to the UN-report GESAMP n°38 (1989) the values of H for C<sub>1</sub> and C<sub>2</sub> organochlorines for sea water are a factor of  $1.301 \pm 0.085$  higher than for distilled water at 6.0 and at 25.0°C. For the monocyclic aromatic hydrocarbons a general correction factor is doubtful because the variation of this factor is quite large ( $1.401 \pm 0.233$ ).

**Table IV.1.5.** Measurements of Henry's constant H (dimensionless) for natural sea water.

VOC	temperature (°C)	H (dimensionless)	%SD	t-test *
chloroform	6.0	0.0762	5.2	=
	25.0	0.179	3.9	=
tetrachloromethane	6.0	0.578	1.4	>
	25.0	1.359	1.8	=
1,1-dichloroethane	6.0	0.106	2.8	=
	25.0	0.253	4.4	=
1,2-dichloroethane	6.0	0.0241	11.9	>
	25.0	0.0495	5.1	=
1,1,1-trichloroethane	6.0	0.345	1.8	=
	25.0	0.811	3.0	>
trichloroethylene	6.0	0.164	2.3	<
	25.0	0.433	3.7	=
tetrachloroethylene	6.0	0.309	2.2	=
	25.0	0.775	4.3	=
benzene	6.0	0.115	2.3	<
	25.0	0.247	2.6	=
toluene	6.0	0.121	4.9	=
	25.0	0.282	5.2	=
ethylbenzene	6.0	0.130	4.7	=
	25.0	0.338	1.9	<
o-xylene	6.0	0.0814	6.5	=
	25.0	0.200	3.6	<
m-xylene	6.0	0.128	7.3	>
	25.0	0.311	5.0	=
p-xylene	6.0	0.137	1.1	=
	25.0	0.308	6.3	<

\*= means not significantly different, < means H for natural sea water bigger than for artificial, and > means the inverse of the latter.

## IV.1.7. CONCLUSIONS

A complete field description of the Henry's constant as a function of temperature (2 - 25°C) and salinity (0 - 35.0g.L<sup>-1</sup>) was constructed. This confirmed relationships expected from theoretical considerations.

Measurement of Henry's constants in sea water indicated no systematic deviation when compared with values in artificial sea salt. This means that the parameters salinity and temperature are sufficient to determine the H-value in a marine system for gas-water exchange of VOCs. The obtained correction factor for sea water compared to distilled water exceeds the 20% correction factor proposed in the UN-report GESAMP n°38.

## IV.1.8. METHODS AND MATERIALS

### IV.1.8.1. Volatile organic compounds

The C<sub>1</sub>- and C<sub>2</sub>-organochlorines chloroform, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene (Janssen) and tetrachloromethane (Merck), and the monocyclic aromatic hydrocarbons benzene, toluene (Merck), ethylbenzene and m-, p- and o-xylene (Aldrich) were used as VOCs in this experiments. They were applied without further purification. The solvent methanol was obtained from Merck (for Chromatography, 99.8%).

### IV.1.8.2. Artificial sea water

The artificial sea water was prepared with deionized water and commercial sea salt (Marine Sea Salt HW, Wiegandt, Germany). The major elements of the sea salt are chlorine (54.93%), sodium (30.53%), sulphate (7.67%), magnesium (3.68%), cadmium (1.18%) and potassium (1.11%).

### IV.1.8.3. Mixtures used in the experiments

At every temperature and salt concentration four or five compounds were used together in one mixture. Compounds in one mixture were selected so that no GC-separation problems



occurred. The use of mixtures, including methanol (maximally 1% v/v), did not influence significantly the data obtained. This was checked by using separate compounds and in multiple combinations, and confirms earlier results (Gossett, 1987). Mixture A contained chloroform, 1,2-dichloroethane, toluene and m-xylene; mixture B 1,1-dichloroethane, tetrachloromethane, trichloroethylene, ethylbenzene and o-xylene; mixture C finally contained 1,1,1-trichloroethane, benzene, tetrachloroethylene and p-xylene.

Mixtures were prepared from a stock solution in methanol (20 to 200 $\mu$ L, depending on the H values of the compounds, in 25mL MeOH).

Mixtures of 4 or 5 VOCs were tested. Table IV.1.6 illustrates that using chloroform in this method separately or in combination with the other VOCs does not influence H.

**Table IV.1.6.** Measurements of Henry's constant (dimensionless) of chloroform at 25.0°C in presence of different cosolutes.

H	cosolutes
0.148 $\pm$ 1.8%	none
0.151 $\pm$ 2.1%	toluene
0.152 $\pm$ 1.3%	1,2-dichloroethane
0.153 $\pm$ 2.1%	toluene, 1,2-dichloroethane, m-xylene

#### IV.1.8.4. Procedure of the modified EPICS-technique

Into three dry bottles with a volume of 118mL, 5mL demineralised water or demineralised water with 17.5 or 35.0g.L<sup>-1</sup> artificial sea salt were pipeted. Into three similar bottles 115 mL of the same solution was pipeted. Approximately 50 $\mu$ L of the stock solution was weighted with an accuracy of 0.0001g. The syringe content was added to the bottle under the water surface, the bottle was immediately closed with a Mininert-valve (Alltech Ass.), and the syringe was reweighed after drying the needle.

The bottles were incubated in a thermostatic water bath (at  $\pm$  0.1°C) upside down, to get minimal diffusion losses (Gossett et al., 1985). Bottles were normally incubated overnight without any mixing; in a few cases incubation lasted only 5.5h. Earlier studies indicate that this time is sufficient for attaining equilibrium (Gossett,1987; Lincoff & Gossett, 1984).

The chromatographic analysis was done on a Varian gas chromatograph model 3700 (injector

at 220°C, FID-detector at 270°C) with a fused silica column (RSL 150, 30m, film thickness 5µm, ID 0.53mm) with an HP3388A integrator. The GC oven temperature was kept at 50°C for five minutes, then followed by heating till 200°C at a rate of 7°C.min<sup>-1</sup>. He-carrier gas flow rate was 4 mL.min<sup>-1</sup>, the FID was fed with air at 400 mL.min<sup>-1</sup> and H<sub>2</sub> at 40 mL.min<sup>-1</sup>. 500 µL headspace (Syringe Pressure-Lok Series A, 500 µL) was taken by inverting the bottle and holding the neck of the bottle just above the water surface.

#### IV.1.8.5. Calculation of Henry's Law Constant from the experimental results

The modified EPICS-method (Gossett, 1987) of the original method (Lincoff & Gossett, 1984) is based upon addition of masses of a volatile solute to two sealed bottles incubated at a constant temperature with a different liquid content.

If the masses  $M_1$  and  $M_2$  are added respectively to two bottles with liquid volume  $V_{w1}$  (L) and  $V_{w2}$  (L) and headspace volumes  $V_{g1}$ (L) and  $V_{g2}$  (L), one gets

$$M_1 = C_{g1} (V_{w1} / H + V_{g1})$$

$$M_2 = C_{g2} (V_{w2} / H + V_{g2})$$

where  $C_{g1}$  and  $C_{g2}$  = concentration of solute in the liquid phase (mole.L<sup>-1</sup>), and  $H$  = Henry's law constant (dimensionless). By dividing equation 1 by  $M_1$  and equation 2 by  $M_2$  and if

$$r = \frac{C_{g1} / M_1}{C_{g2} / M_2}$$

then one obtains for  $H$ :

$$H = \frac{V_{w2} - r \cdot V_{w1}}{r \cdot V_{g1} - V_{g2}}$$

Knowing the volumes  $V_{w1}$ ,  $V_{w2}$ ,  $V_{g1}$  and  $V_{g2}$ , by weighing the added masses  $M_1$  and  $M_2$  and by measuring the headspace concentrations  $C_{g1}$  and  $C_{g2}$ ,  $H$  is determined. Using three bottles of each volume, nine determinations of  $H$  can be made.

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## IV.2. WATER/SEDIMENT EQUILIBRIUM DISTRIBUTION

### IV.2.1. INTRODUCTION

The sediment/sediment equilibrium distribution is determined by the solid phase/water equilibrium partitioning coefficient  $K_p$  (mole.kg<sup>-1</sup> over mole.kg<sup>-1</sup>). To study the equilibrium distribution ratio  $K_p$ , column experiments are widely applied (miscible displacement technique), but also techniques as the gas-purge technique (Wu and Gschwend, 1986), the batch equilibrium technique (Means et al., 1980; Schwarzenbach and Westall, 1981, Piwoni and Banerjee, 1989), a headspace technique (Garbarini and Lion, 1985; Garbarini and Lion, 1986) and a single-pellet technique (Cabbar et al., 1994) are described. The miscible displacement technique is to be preferred above gas purge experiments for systems of low to moderate sorptivity (Brusseu et al., 1990). The obtained breakthrough curves are interpreted via models describing the behaviour of the VOCs during percolation. Models are based on linear sorption equilibrium, or on non-equilibrium sorption like two-site models, two-region models and intrasorbens diffusion models (Rao et al., 1979; Schwarzenbach and Westall, 1981; Hutzler et al., 1986; Miller and Weber, 1988; van Genuchten and Wagenet, 1989; Nkedi-Kizza et al., 1989; Brusseau et al., 1989; Gamerdinger et al., 1990; Brusseau et al., 1990; Biswas et al., 1991; Gamerdinger et al., 1994).

### IV.2.2. RESULTS OF THE COLUMN EXPERIMENTS

The miscible displacement technique needs the determination of the porosity of the column used and the determination of the breakthrough volumes of the VOCs in order to calibrate the sorption constants of the VOCs. In this work the porosity was determined by means of a tracer and the detection of the tracer and of the VOCs was done by means of on-line UV-detection and off-line GC-detection (*see* Experimental section).

#### IV.2.2.1. Determination of the porosity: tracer experiments

The porosity was determined by applying a non-sorbing tracer, pentafluorobenzoic acid (PFBA) (Bowman, 1984). For three experiments (flow rate  $Q \leq 0.270 \text{ mL} \cdot \text{min}^{-1}$ ) the asymmetry coefficient  $A_s$  (dimensionless), defined as (Sewell and Clarke, 1987)

$$A_s = \frac{t_{90\%BT} - t_{50\%BT}}{t_{50\%BT} - t_{10\%BT}}$$

was below 1.15. The  $t_{10\%BT}$ ,  $t_{50\%BT}$  and  $t_{90\%BT}$  values are the times after which 10, 50 and 90% of the input concentration is measured at the column outlet. Sewell and Clarke (1987) considered  $A_s$  values below 1.30 as symmetric for chromatographic columns. Our fourth experiment showed  $A_s=1.42$ , which was explained by the higher flow rate ( $0.806\text{mL}\cdot\text{min}^{-1}$ ). However, all 50% breakthrough points were all within a small range:  $0.348\pm 0.005\text{mL}$  (1.5%SD) ( $n=4$ ).

The symmetric breakthrough curves indicate local sorption equilibria and confirm the suitability of the local equilibrium sorption model. This observation supports the statement of Schwarzenbach and Westall (1981). They concluded that at flow rates below  $10^{-3}\text{cm}\cdot\text{s}^{-1}$  sorption reactions are near equilibrium at every point on the column when the organic carbon (O.C.) is below 0.1%. The determined column characteristics are presented in Table IV.2.1. The volume occupied by PFBA ( $33.07\text{mL}$ ) was 97% of the entire water volume of the column ( $34.10\text{mL}$ ). Dispersion coefficients ( $D$ ) in experiments 1, 2 and 3 were  $1.54 \cdot 10^{-8}$ ,  $1.24 \cdot 10^{-8}$  and  $5.82 \cdot 10^{-8} \text{m}^2\cdot\text{s}^{-1}$ . Tracer experiment 4 showed  $D=1.98 \cdot 10^{-7} \text{m}^2\cdot\text{s}^{-1}$ . Miller and Weber (1988) and Gamedinger et al. (1990) found similar  $D$  values at comparable flow rates.

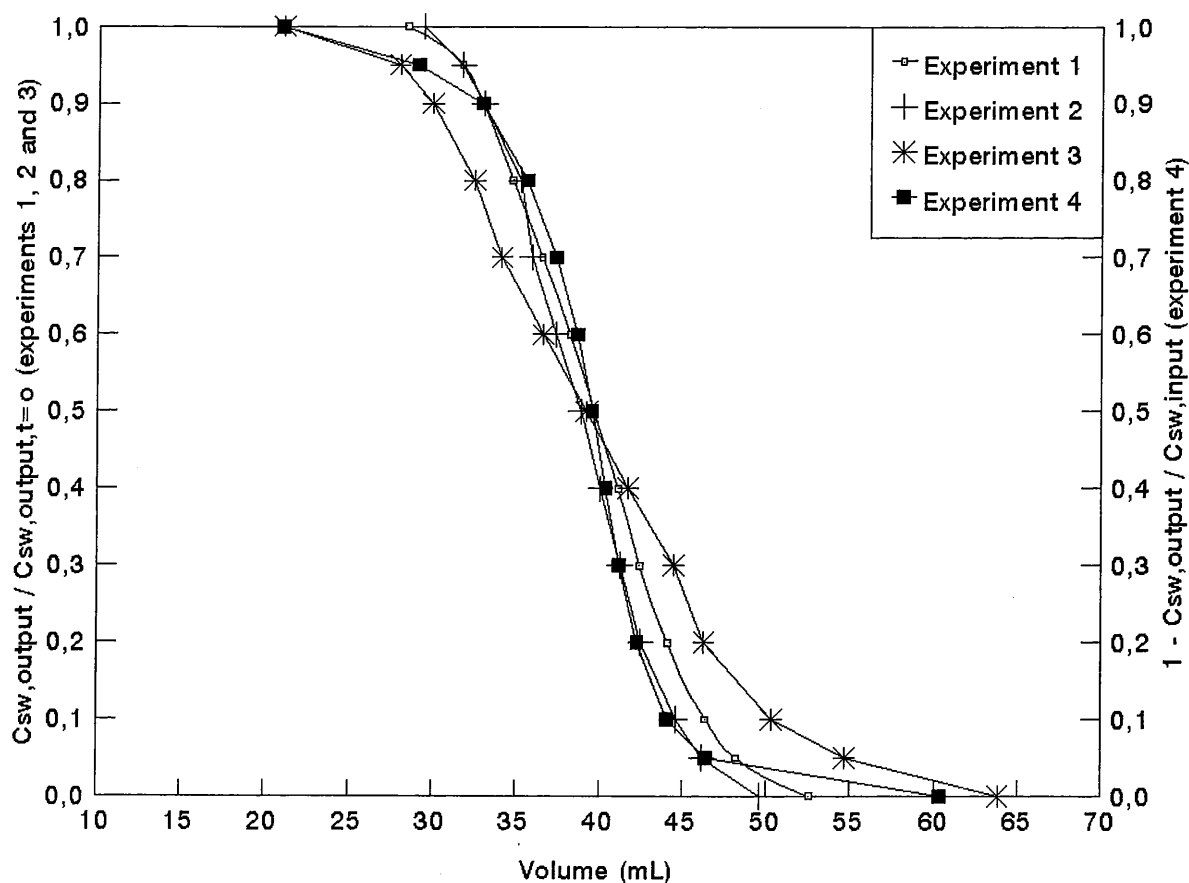
**Table IV.2.1.** Column characteristics

Total volume (mL)	95.03
Total wet mass (g)	182.25
Dry matter (g)	147.47
Water content (g)	34.78
Water volume (mL)*	34.10
Porosity (-)	0.359
Apparent density ( $\text{kg}\cdot\text{m}^{-3}$ )	1552

\* Density of salt water ( $35\text{g}\cdot\text{L}^{-1}$ ) at  $25^\circ\text{C}$  :  $1020\text{kg}\cdot\text{m}^{-3}$  (Perry, 1984)

### IV.2.2.2. Column experiments with on-line UV-detection

Column experiments with on-line UV-detection avoid losses of VOCs, but they are limited to U.V.-detectable compounds and only one VOC can be studied in one run. Figure IV.2.1 illustrates the breakthrough curves for experiments 1, 2 and 3 by plotting the output concentrations  $c_{w,o}$ , relative to the initial aqueous column concentration  $c_{w,o,t=0}$  as a function of time. In addition, 1 minus the output concentration  $c_{w,o}$ , relative to the input concentration  $c_{w,o,x=0}$ , is plotted as a function of time for the desorption experiment (experiment 4). In this way the reversibility of the sorption and desorption processes are illustrated. The results are presented in Table IV.2.2.



**Figure IV.2.1.** Experimental breakthrough curves for m-xylene with on-line UV-detection. Experiments 1, 2 and 3 are desorption experiments; experiment 4 is a sorption experiment.



**Table IV.2.2.** Results of the m-xylene sorption experiments and simulations with  $K_p$ =solid phase/aqueous phase partitioning coefficient,  $D$ =dispersion coefficient,  $SSQ$ =sum of squares of deviations of the curve fitting and  $Q$ =flow rate

experiment	$K_p$ ( $m^3.kg^{-1}$ )	$D$ ( $m^2.s^{-1}$ )	$SSQ$ (-) (n=12)	$Q$ ( $mL.min^{-1}$ )
1 (desorption)	$4.73 \cdot 10^{-5}$	$4.40 \cdot 10^{-8}$	$4.65 \cdot 10^{-3}$	0.15
2 (desorption)	$4.23 \cdot 10^{-5}$	$2.96 \cdot 10^{-8}$	$7.05 \cdot 10^{-3}$	0.13
3 (desorption)	$4.50 \cdot 10^{-5}$	$1.11 \cdot 10^{-7}$	$6.76 \cdot 10^{-3}$	0.15
4 (sorption)	$4.52 \cdot 10^{-5}$	$7.71 \cdot 10^{-8}$	$1.47 \cdot 10^{-2}$	0.48

The solid phase/aqueous phase partitioning coefficients  $K_p$  ( $mole.kg^{-1}$  over  $mole.kg^{-1}$ ) determined from sorption and desorption showed no difference, illustrating the reversibility of the sorption mechanism. The  $K_p$  value based on the desorption experiments was  $(4.49 \pm 0.25) \cdot 10^{-5} m^3.kg^{-1}$  (5.6%SD, n=3), whereas the sorption experiment showed  $K_p=4.52 \cdot 10^{-5} m^3.kg^{-1}$ . In the same way  $K_p$  values for tri- and tetrachloroethylene were determined via sorption and desorption experiments. The results are summarised in Table IV.2.3.

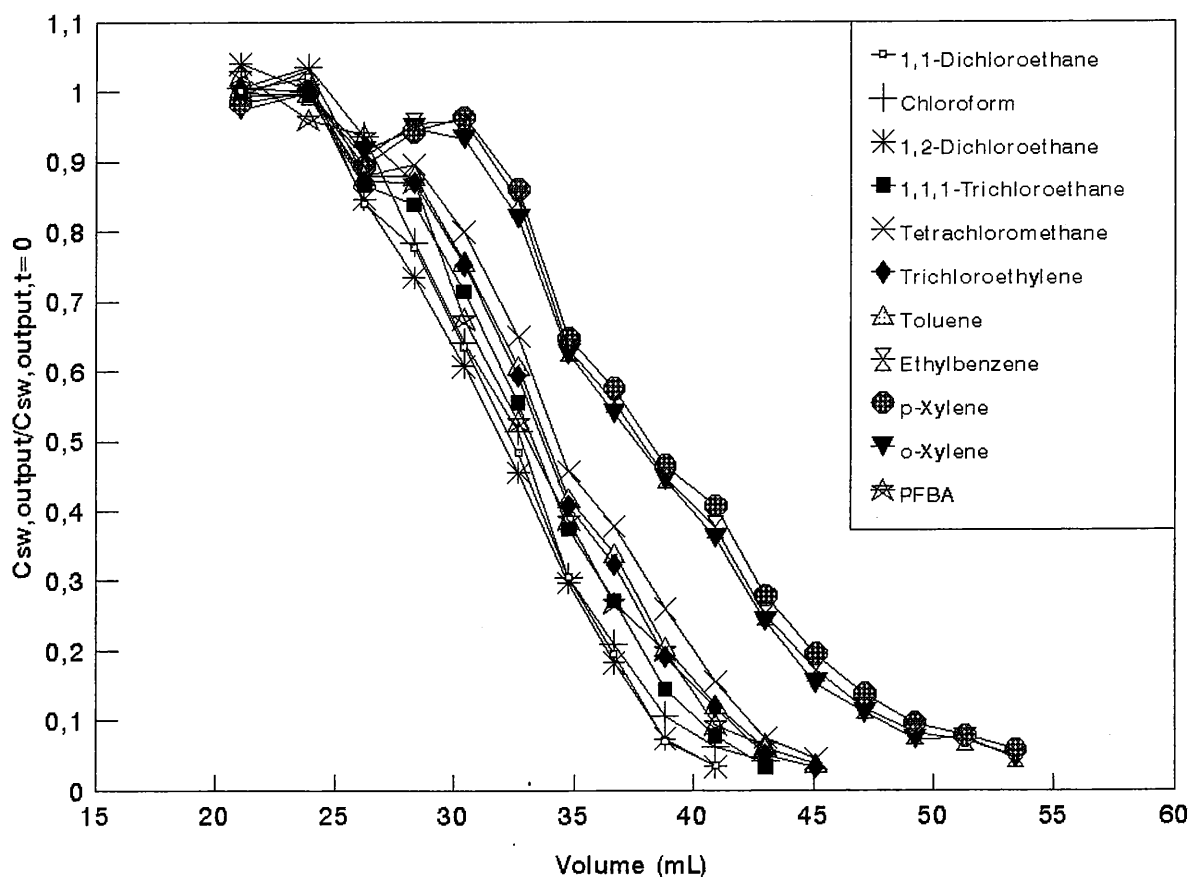
**Table IV.2.3.** Results of the sorption and desorption experiments (with UV-detection) and simulations with  $K_p$ =solid phase/aqueous phase partitioning coefficient,  $SD$ =standard deviation on  $K_p$ , %SD=relative standard deviation on  $K_p$  in % and  $n$ =number of experimental determinations.

VOC	$K_p$ ( $m^3.kg^{-1}$ )	$SD$ ( $m^3.kg^{-1}$ )	%SD	n
m-xylene	$4.49 \cdot 10^{-5}$	$0.20 \cdot 10^{-5}$	4.5	4
trichloroethylene	$9.87 \cdot 10^{-6}$	$0.84 \cdot 10^{-6}$	8.5	3
tetrachloroethylene	$5.47 \cdot 10^{-5}$	$0.05 \cdot 10^{-5}$	0.9	2

The higher relative standard deviation on trichloroethylene can be explained by the lower sorption. Small time deviations on the breakthrough curves result in larger deviations on  $K_p$  for less sorbing compounds.

### IV.2.2.3. Column experiments with off-line GC-detection

Discontinuous sampling at the output combined with headspace analysis allowed simultaneous determination of 10 VOCs (chloroform, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, toluene, ethylbenzene, o-xylene and p-xylene). The tracer PFBA, run at the same time, was measured afterwards with UV-detection after purging the samples in order to volatilize the VOCs. The breakthrough curves obtained at a flow rate of  $0.140\text{ mL}\cdot\text{min}^{-1}$  are presented in Figure IV.2.2.



**Figure IV.2.2.** Experimental breakthrough curves for 10 VOCs and PFBA, determined with off-line GC-analysis and off-line UV-detection respectively.

The breakthrough volumes of 1,1-dichloroethane, 1,2-dichloroethane and chloroform were smaller than the breakthrough volume of the tracer PFBA, run in the same experiment. One explanation could be the difference in aqueous volumes occupied by the tracer and these chlorinated compounds because of different lateral diffusivity into zones hard to reach. The volume occupied by 1,2-dichloroethane is 94% of the water content, where for PFBA 97% is found, as already mentioned before. But, since the diffusivities vary approximately inversely related to the square root of the molecular weight (Schwarzenbach et al., 1993), the opposite result has to be expected from this consideration. On the other hand, the retardation of PFBA can be explained by the very low sorption of the VOCs and by sorption effects of the tracer on the polar mineral surface. However, Bowman (1984) stated that PFBA does not sorb on soil material. Applications of PFBA as tracer for columns with low organic content are reported by Brusseau and Rao (1991) for sandy aquifer material with O.C.=0.13%; Brusseau (1991) studying the sorption of compounds including tetrachloroethylene and p-xylene on aquifer materials with O.C.<0.03% and by Gamerdinger et al. (1994) studying MAHs-sorption in columns with O.C.=0.066-0.074%. In the experiment presented here, PFBA does sorb at least as much as 1,1-dichloroethane, 1,2-dichloroethane and chloroform. In this respect 1,2-dichloroethane was considered to be more suitable as tracer in order to determine the  $K_p$  values. Based on the breakthrough volume of 1,2-dichloroethane, a porosity of 0.337 was calculated. Table IV.2.4 presents the determined  $K_p$ ,  $D$  and SSQ.

**Table IV.2.4.** Results from the column experiments with off-line detection with  $K_p$ =solid phase/aqueous phase partitioning coefficient,  $D$ =dispersion coefficient and SSQ=sum of squares of deviations of the curve fitting

VOC	$K_p$ ( $m^3.kg^{-1}$ )	$D$ ( $m^2.s^{-1}$ )	SSQ (-)
1,1-dichloroethane	$3.46 \cdot 10^{-6}$	$5.70 \cdot 10^{-8}$	$8.37 \cdot 10^{-3}$
chloroform	$7.98 \cdot 10^{-6}$	$6.42 \cdot 10^{-8}$	$1.57 \cdot 10^{-3}$
1,1,1-trichloroethane	$1.17 \cdot 10^{-5}$	$5.90 \cdot 10^{-8}$	$7.10 \cdot 10^{-3}$
trichloroethylene	$1.43 \cdot 10^{-5}$	$6.15 \cdot 10^{-8}$	$6.33 \cdot 10^{-3}$
toluene	$1.55 \cdot 10^{-5}$	$6.19 \cdot 10^{-8}$	$5.88 \cdot 10^{-3}$
tetrachloromethane	$1.83 \cdot 10^{-5}$	$6.31 \cdot 10^{-8}$	$1.04 \cdot 10^{-2}$
o-xylene	$4.08 \cdot 10^{-5}$	$7.68 \cdot 10^{-8}$	$1.52 \cdot 10^{-2}$
ethylbenzene	$4.30 \cdot 10^{-5}$	$7.51 \cdot 10^{-8}$	$2.00 \cdot 10^{-2}$
p-xylene	$4.55 \cdot 10^{-5}$	$8.05 \cdot 10^{-8}$	$2.39 \cdot 10^{-2}$

### IV.2.3. CALCULATION AND INTERPRETATION OF $K_{OM}$ DATA

If sorption of VOCs on sediment is due to sorption on the organic matter fraction, partitioning between the organic matter and (sea) water is established as

$$K_{om/sw} = \frac{K_p}{f_{om}} \cdot 1000$$

where  $K_{om/sw}$  is the organic matter/salt water partitioning coefficient (mole.kg<sup>-1</sup> over mole.L<sup>-1</sup>) and  $f_{om}$  is the organic matter fraction of the solids (kg.kg<sup>-1</sup>, 0.06%). The  $K_{om/sw}$  partitioning coefficient does not represent the equilibrium partitioning between deionized water and the organic matter as  $K_{om}$  does. Since solvated inorganic ions would not be expected to interfere or compete with the penetration of VOCs into natural organic matter, it is reasonable to assume that the salinity affect the values of  $K_{om}$  primarily through the water activity (Schwarzenbach et al., 1993). In this respect,  $K_{om}$  is calculated from  $K_{om/sw}$ :

$$K_{om} = K_{om/sw} \cdot \frac{H}{H_{sw}}$$

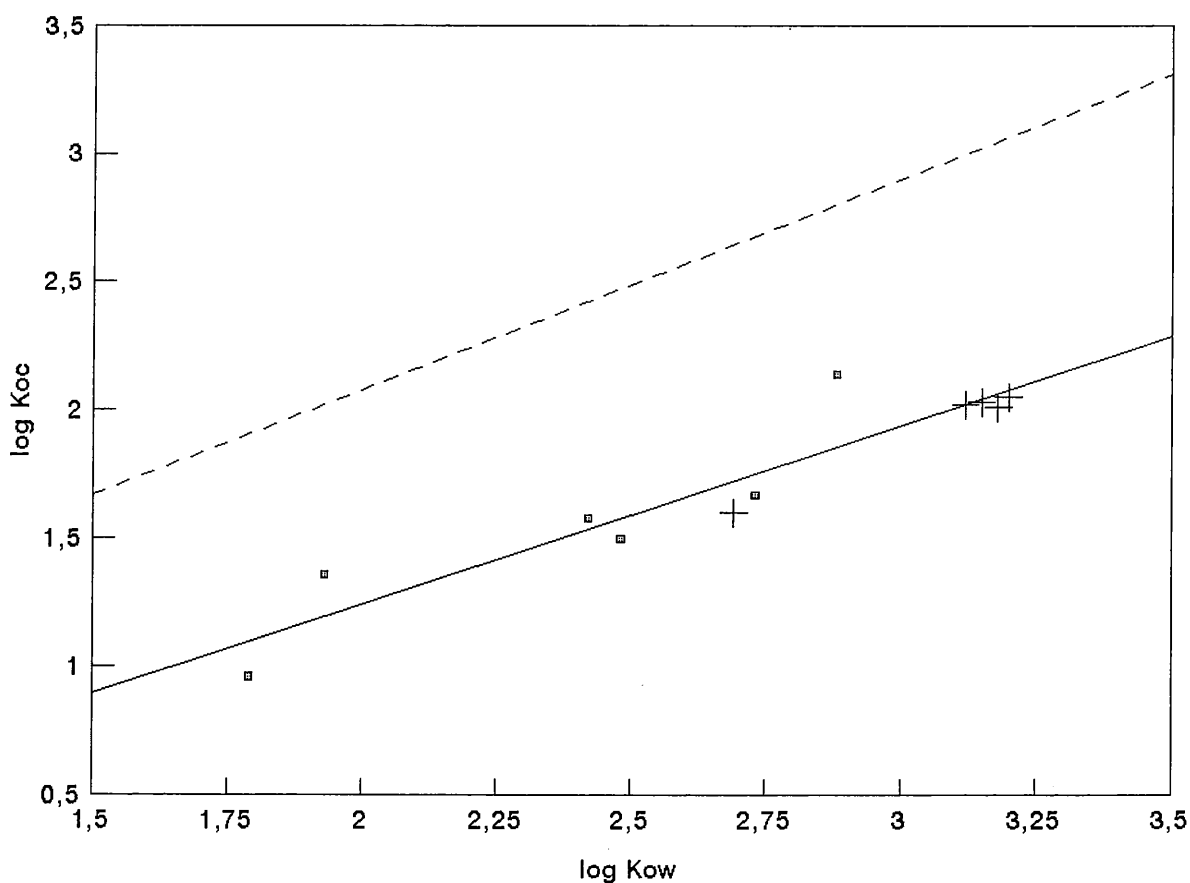
where  $H$  and  $H_{sw}$  are the dimensionless Henry's law constants of the VOC for deionized and salt water, respectively. With knowledge of Henry's law constants (Dewulf et al., 1995), the obtained  $K_{om}$  values are presented in Table IV.2.5.

**Table IV.2.5.**  $H$  and  $H_{sw}$  (dimensionless),  $K_{om/sw}$  and  $K_{om}$  (mole.kg<sup>-1</sup> over mole.L<sup>-1</sup>) and  $\log K_{om}$  and  $\log K_{ow}$  values

VOC	$H^*$	$H_{sw}^*$	$K_{om/sw}$	$K_{om}$	$\log K_{om}$	$\log K_{ow}^{**}$
chloroform	0.153	0.177	13.3	11.5	1.06	1.93
tetrachloromethane	1.048	1.359	30.5	23.5	1.37	2.73
1,1-dichloroethane	0.206	0.258	5.8	4.6	0.66	1.79
1,1,1-trichloroethane	0.608	0.753	19.5	15.8	1.20	2.48
trichloroethylene	0.351	0.442	23.8	18.9	1.28	2.42
tetrachloroethylene	0.601	0.788	91.2	69.5	1.84	2.88
toluene	0.224	0.290	25.8	20.0	1.30	2.69
et-benzene	0.270	0.362	71.7	53.5	1.73	3.15
o-xylene	0.173	0.227	68.0	51.8	1.71	3.12
m-xylene	0.248	0.329	74.8	56.4	1.75	3.20
p-xylene	0.232	0.341	75.8	51.6	1.71	3.18

\* Data from Dewulf et al. (1995). \*\* Data from Schwarzenbach et al. (1993) and Verschueren (1983).

A correlation between  $\log K_{om}$  and  $\log K_{ow}$  ( $K_{ow}$  = octanol/water partitioning coefficient in mole.L<sup>-1</sup> over mole.L<sup>-1</sup>) (Table IV.2.5) was examined. Linear regression, presented in Figure IV.2.3, showed a slope=0.70 and an intercept=-0.45 with  $r=0.94$  ( $n=11$ ). The slope (<1) indicates that the natural organic matter is less lipophilic than octanol since the increase of  $\log K_{om}$  is not proportional to the increase of  $\log K_{ow}$ . Moreover, the lower lipophilicity of the organic matter is clear from the low  $\log K_{om}$  values themselves, when compared with  $\log K_{ow}$  data. In addition, Figure IV.2.3 shows that the sorption on organic matter in this study is obvious lower than predicted by the relationship presented by Schwarzenbach et al. (1993). The source of differences in the sorption behaviour of sediment-associated organic matter may be in small differences in the overall structure of the complex, as suggested by Isaacson and Frink (1984).



**Figure IV.2.3.** Log  $K_{om}$  plot:  $\square$  CHCs,  $+$  MAHs. Solid line: linear regression, broken line: linear regression of Schwarzenbach et al., 1993

For the two VOCs for which the sorption on the sediment is not determined experimentally, it can be calculated from the relationship between  $\log K_{om}$  and  $\log K_{ow}$ . From the  $\log K_{ow}$  values of 1.47 and 2.13 for 1,2-dichloroethane and benzene respectively (Schwarzenbach et al., 1993), the  $K_{om}$  values are calculated as 3.79 and 10.99. The  $K_{om/sw}$  for 1,2-dichloroethane and benzene are 4.62 and 13.94 respectively, calculated from their Henry's law constant at 25°C for salinity 0g.L<sup>-1</sup> ( $H=0.0412$  and  $0.194$  resp.) and for salinity 35g.L<sup>-1</sup> ( $H_{sw}=0.0502$  and  $0.246$  resp.) (Dewulf et al., 1995).

#### IV.2.4. IMPLICATIONS FOR THE MARINE ENVIRONMENT

If the partitioning of the VOCs between 1m<sup>3</sup> sea water and 1m<sup>3</sup> wet sediment (as *in situ*) is considered, an equilibrium partitioning coefficient  $K_{sed}$  between wet sediment and the water column (mole.m<sup>-3</sup> over mole.m<sup>-3</sup>, dimensionless) is defined

$$K_{sed} = \gamma \cdot K_p + \theta$$

where  $\gamma=1552\text{kg.m}^{-3}$  (apparent density) and  $\theta=0.348$  (volumetric water content). The  $K_p$  values for 11 of the 13 target compounds are given in Table IV.2.3. and Table IV.2.4. For 1,2-dichloroethane and benzene,  $K_p$  is calculated from  $K_{om/sw}$  and the equation

$$K_p = \frac{K_{om/sw} \cdot f_{om}}{1000}$$

So  $K_p$  is  $2.8 \cdot 10^{-6}$  and  $8.4 \cdot 10^{-6} \text{ m}^3.\text{kg}^{-1}$  for 1,2-dichloroethane and benzene respectively. The obtained  $K_{sed}$  values for all VOCs are presented in Table IV.2.6. From these values it is concluded that, at equilibrium, the volumetric sediment concentrations are only 35.2 (1,2-dichloroethane) to 43.3% (tetrachloroethylene) of the water concentrations. Consequently, the marine sediment compartment will not be a major sink for the investigated VOCs since they do not really accumulate in the sediment. In addition, these anthropogenic compounds are brought into the marine environment by atmospheric transport or via water transport. The mechanism to bring them in the sediment phase must be exchange with the water column. It is clear that this process is slow when compared with other exchange processes (Mackay and Paterson, 1991). In this respect, it is concluded that the equilibrium partitioning between the aqueous phase and the sediment examined here, gives the upper limit for the sediment

concentrations.

**Table IV.2.6.**  $K_{sed}$  values for all target compounds

VOC	$K_{sed}$ (mole.m <sup>-3</sup> over mole.m <sup>-3</sup> )
Chloroform	0.360
Tetrachloromethane	0.376
1,1-Dichloroethane	0.353
1,2-Dichloroethane	0.352
1,1,1-Trichloroethane	0.366
Trichloroethylene	0.370
Tetrachloroethylene	0.433
Benzene	0.361
Toluene	0.372
Ethylbenzene	0.412
o-Xylene	0.411
m-Xylene	0.418
p-Xylene	0.419

## IV.2.5. MATERIALS AND METHODS

### IV.2.5.1. Materials

CHCs studied were chloroform, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene (Janssen) and tetrachloromethane (Merck). MAHs were toluene (Merck), ethylbenzene and m-, p- and o-xylene (Aldrich). They were applied without further purification. Pentafluorobenzoic acid (PFBA), used as tracer, was obtained from Fluka. Stock solutions were prepared in methanol (Merck, for Chromatography, 99.8%) at about 20  $\mu\text{L.L}^{-1}$ . Concentrations were below one tenth of the maximum water solubility. Karickhoff (1981) demonstrated that sorption is to be considered linear if concentrations are below one half the maximum water solubility.

The artificial sea water was prepared from deionized water and commercial sea salt at 35g.L<sup>-1</sup> (Marine Sea Salt HW, Wiegandt, Germany). The major elements of the sea salt were chlorine (54.93%), sodium (30.53%), sulphate (7.67%), magnesium (3.68%), cadmium (1.18%) and

potassium (1.11%).

The sediment was taken in the North Sea on the Belgian Continental Shelf (51°28.83N, 2°27.00E) in October 1993. It was sieved over a 0.5mm sieve before it was used to fill up the column. The organic carbon (O.C.) content of the sea sediment was determined with the method of Walkley and Black (Page, 1982). Because of the low organic content 5 grams of sediment were analysed. The O.C. measured was  $0.030 \pm 0.004\%$  (w/w) (n=3).

#### IV.2.5.2. Experimental setup

A 2.5L flask was completely filled up with artificial sea water (containing the VOCs in sorption experiments or not in desorption experiments), closed with a GC-septum (Alltech) and a screw-cap. Through the screw-cap and the septum a glass syringe of 100mL was mounted in a vertical position. It continuously filled up the withdrawn aqueous solution. The solution, withdrawn from the flask, was pumped through the column at a flow rate of 0.1 to  $0.3 \text{ mL} \cdot \text{min}^{-1}$  by a HPLC-pump (Water Associates, model 6000A) for sorption and desorption experiments, whereas for the desorption experiments a peristaltic pump (Pharmacia, model P-1) was used as well. The column was a HPLC-column (Alltech) with an inner diameter of 22mm and a length of 250mm. At the entrance of the column a frit and distributor was installed in order to obtain a plug flow input. At the end of the column only a frit was placed. The column temperature was kept at  $25.0 \pm 0.3^\circ\text{C}$  by means of a thermostatic water bath. In on-line detection experiments, the column output was led through a UV-detector (Varian, model UV50), equipped with a Varian recorder, model 25A. m-Xylene and PFBA were detected at 254nm, trichloroethylene at 212nm and tetrachloroethylene at 215nm. For experiments carried out with off-line discontinuous detection, a 5mL glass syringe was attached to the column output via a union where at one site the syringe was pierced through a septum. This was necessary in order to avoid volatilization of the VOCs. The sampling syringe was filled up and after 15 to 20 minutes it was replaced by another one. The collected column output sample was transferred to a 25mL glass flask which was immediately closed with a Mininert stopper (Mininert valve; Alltech). In this way, closed two phase systems (CTS) samples were obtained on which static headspace analysis was done.



### IV.2.5.3. The stability of the experimental setup

Since VOCs are used in a polar water phase, losses due to volatilisation have to be considered, especially at the output when discontinuous output samples are taken (Brusseau et al., 1990). Therefore, five VOCs (tetrachloromethane, 1,1-dichloroethane, trichloroethylene, ethylbenzene and o-xylene) were pumped through the system without inserting the column. Four discontinuous output samples, taken over a 24 hours period, did not show any decrease in concentration. The standard deviations in percent (%SD) on the four samples were of the same order of magnitude (<3.4%) as the %SD values on multiple analysis of one sample (<2.4%, n=4).

### IV.2.5.4. Analysis of the discontinuous column output

5  $\mu$ L methanol, containing 0.1  $\mu$ L tetrachloroethylene, was added as internal standard to each CTS sample. The bottles were incubated ( $25.0 \pm 0.3^\circ\text{C}$ ) upside down in order to minimise diffusion losses (Gossett et al., 1985). After reaching the air-water equilibrium partitioning overnight (Lincoff and Gossett, 1984; Gossett et al., 1985) 500  $\mu$ L headspace was taken with a gas tight syringe (500  $\mu$ L, Pressure-Lock Series A) and analysed on a Varian Gas Chromatograph (model 3700), equipped with a HP3388A integrator and with a 30m RSL150 column (100% polydimethylsiloxane, film thickness 5  $\mu$ m, ID 0.53mm). Injector and detector temperature were 220 and 270  $^\circ\text{C}$ , respectively. The GC-oven was kept at 40  $^\circ\text{C}$  for 5 minutes, followed by a temperature rise at 5  $^\circ\text{C}\cdot\text{min}^{-1}$  till 150  $^\circ\text{C}$ . Helium carrier gas flow rate was 4  $\text{mL}\cdot\text{min}^{-1}$ , the flame ionization detector was fed with air at 400  $\text{mL}\cdot\text{min}^{-1}$  and with hydrogen gas at 40  $\text{mL}\cdot\text{min}^{-1}$ .

The aqueous concentration of the VOCs in the column output samples was calculated from the headspace analyses. Knowing the volumes of the two phases of the CTS, knowing Henry's law constant of all VOCs and of the internal standard (Dewulf et al., 1995), relative output concentrations could be calculated from the absolute integration areas of the VOCs and of the internal standard in the input and output samples.

### IV.2.5.5. Determination of breakthrough volumes

Van Genuchten and Wagenet (1989) derived an equation governing linear equilibrium sorption

based on Fickian diffusion and including degradation:

$$R \cdot \frac{\partial C_w}{\partial t} = D \cdot \frac{\partial^2 C_w}{\partial x^2} - v \cdot \frac{\partial C_w}{\partial x} - \mu \cdot C_w$$

where

$$R = 1 + \frac{\rho \cdot K_p}{\theta}$$

$$\mu = \mu_l + \frac{\rho \cdot \mu_s \cdot K_p}{\theta}$$

with  $\theta$ =volumetric water content ( $\text{m}^3 \cdot \text{m}^{-3}$ ),  $t$ =time (s),  $\rho$ =soil (or sediment) bulk density ( $\text{kg} \cdot \text{m}^{-3}$ ),  $x$ =distance (m),  $D$ =the dispersion coefficient ( $\text{m}^2 \cdot \text{s}^{-1}$ ),  $v=q \cdot \theta^{-1}$ =the average pore water velocity if  $q$ =the volumetric water flux density ( $\text{m} \cdot \text{s}^{-1}$ ),  $\mu_l$ =first-order decay coefficient for degradation from the liquid phase ( $\text{s}^{-1}$ ) and  $\mu_s$ =first order sorbed phase degradation coefficient ( $\text{s}^{-1}$ ).

This transport equation was simulated by means of a FORTRAN 77 programme based on the Crank-Nicholson method (Crank, 1967), omitting degradation. In this approach, the column is divided into  $n$  slices with thickness  $h$  (m) and with an average liquid concentration  $(c_w)_i$  for each layer  $i$ . With the approximations applied in the Crank-Nicholson method and after rearrangement one obtains the concentrations in all layers at time  $t+\Delta t$  as a function of the concentrations at time  $t$ :

$$\begin{aligned} & (c_w)_{i-1}^{t+\Delta t} \cdot \left( -\frac{D}{2 \cdot R \cdot h^2} + \frac{v}{4 \cdot R \cdot h} \right) + (c_w)_i^{t+\Delta t} \cdot \left( \frac{1}{\Delta t} + \frac{D}{R \cdot h^2} \right) + (c_w)_{i+1}^{t+\Delta t} \cdot \left( -\frac{D}{2 \cdot R \cdot h^2} - \frac{v}{4 \cdot R \cdot h} \right) \\ & = (c_w)_{i-1}^t \cdot \left( \frac{D}{2 \cdot R \cdot h^2} - \frac{v}{4 \cdot R \cdot h} \right) + (c_w)_i^t \cdot \left( \frac{1}{\Delta t} - \frac{D}{R \cdot h^2} \right) + (c_w)_{i+1}^t \cdot \left( \frac{D}{2 \cdot R \cdot h^2} + \frac{v}{4 \cdot R \cdot h} \right) \end{aligned}$$

The equations can be written as a matrix

$$[X] \cdot [C] = [Y]$$

with solution

$$[C] = [X]^{-1} \cdot [Y]$$

The additional conditions for a sorption experiment are

$$t = 0 : x > 0 ; c = 0$$

$$t > 0 : x = 0 ; c = c_0$$

whereas for desorption experiments the conditions are

$$t = 0 : x > 0 ; c = c_0$$

$$t > 0 : x = 0 ; c = 0$$

The third condition is a quadratic extrapolation of the concentration profile at the end of the column in order to avoid perturbation.

Fitting a simulation curve to the experimental breakthrough curves was done by varying  $K_p$  till the 50% breakthrough point approached the 50% point of the experimental curve.  $D$  was estimated by minimising the sum of squares of deviations (SSQ).

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### IV.3. FUGACITY MODEL

#### IV.3.1. INTRODUCTION

The fugacity model (Mackay, 1979; Mackay and Paterson, 1981; Mackay and Paterson, 1982; Mackay and Paterson, 1991) allows to describe the partitioning and transport processes of organic compounds in an environment. It considers exchange between environmental compartments and transformation mechanisms within all compartments. The calculations made are based on the concept 'fugacity'. Fugacity  $f$  (Pa) in each compartment is related to the concentration  $c$  (mole.m<sup>-3</sup>)

$$C = f \cdot Z \quad (30)$$

where  $Z$  is the fugacity capacity of the compartment (mole.m<sup>-3</sup>.Pa<sup>-1</sup>).

The fugacity model can be applied on several levels. The level 1 fugacity model assumes an equilibrium partitioning between all environmental compartments. This means that all fugacities are equal and no exchange nor transformation processes are considered. The level 2 model considers a transformation of the compounds within each compartment, and equilibrium distribution between all compartments. The steady state is established by a steady state input to encounter the transformations, while no diffusive exchange processes are assumed. In the level 3 model equilibrium partitioning between all compartments is no longer assumed. By consequence, diffusive exchange between the compartments is added:

$$N = D \cdot (f_1 - f_2) \quad (31)$$

where  $N$ = diffusive compound exchange between two compartments (mole.s<sup>-1</sup>),  $D$ =exchange velocity constant (mole.Pa<sup>-1</sup>.s<sup>-1</sup>) and  $f_1$  and  $f_2$  the fugacities of the respective compartments.  $D$  is to be considered as a conductivity or the reciprocal of a resistance, consisting of two partial resistances in series:

$$\frac{1}{D} = \frac{1}{D_1} + \frac{1}{D_2} \quad (32)$$

where  $D_1=K_1.A. Z_1$  and  $D_2=K_2.A. Z_2$ .  $K_1$  and  $K_2$  are the compartment mass transfer



coefficients ( $\text{m}\cdot\text{s}^{-1}$ ) and  $A$  is the contact surface between the two compartments. Finally, the level 4 fugacity model incorporates non-steady state input, concentrations and fugacities. This approach is applied when e.g. a step function as input of a compound in an environment is considered. Concentration changes can then be described as a function of time.

## IV.3.2. MODEL DEVELOPMENT

### IV.3.2.1. Calculation of the fugacities and fugacity capacities

#### IV.3.2.1.1. Air

Since the compounds are VOCs, they are entirely present as gaseous compounds in the atmosphere since sorption on aerosols can be neglected (Bidleman, 1988). By consequence, the fugacity  $f_a$  (Pa) is equal to the partial pressure

$$f_a = C_a \cdot R \cdot T_a \quad (33)$$

where  $R$ = gas constant= $8.314 \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$  and  $T_a$ =air temperature (K). The fugacity capacity of the air compartment  $Z_a$  ( $\text{mole}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$ ) is defined by

$$Z_a = \frac{1}{R \cdot T_a} \quad (34)$$

#### IV.3.2.1.2. Water

The fugacity capacity for the VOCs in the water compartment is derived from the air/water equilibrium:

$$f_w = H \cdot C_w \cdot R \cdot T_w \quad (35)$$

with  $H$ = Henry's law constant (dimensionless),  $C_w$ =concentration of the VOC in the water column ( $\text{mole}\cdot\text{m}^{-3}$ ) and  $T_w$ =water temperature (K). The fugacity capacity for the water compartment is:

$$Z_w = \frac{1}{H \cdot R \cdot T_w} \quad (36)$$

#### IV.3.2.1.3. Sediment

The fugacity  $f_s$  of a VOC in the sediment compartment and the fugacity capacity  $Z_s$  of the sediment compartment are derived from the dimensionless (wet) sediment/water equilibrium partitioning coefficient  $K_{sw}$  (mole.m<sup>-3</sup> over mole.m<sup>-3</sup>, dimensionless):

$$f_s = C_s \cdot \frac{H \cdot R \cdot T_s}{K_{sw}} \quad (37)$$

$$Z_s = \frac{K_{sw}}{H \cdot R \cdot T_s} \quad (38)$$

with  $C_s$ = concentration in the sediment (mole.m<sup>-3</sup>) and  $T_s$ =temperature of the sediment (K).

#### IV.3.2.1.4. Biota

The fugacity  $f_b$  of the compounds in biota and the fugacity capacity  $Z_b$  of the biota compartment are based on the bioconcentration factor  $K_{bw}$  (mole.m<sup>-3</sup> over mole.m<sup>-3</sup>, dimensionless):

$$f_b = C_b \cdot \frac{H \cdot R \cdot T_b}{K_{bw}} \quad (39)$$

$$Z_b = \frac{K_{bw}}{H \cdot R \cdot T_b} \quad (40)$$

The fugacity capacity  $Z_b$  is linked to the octanol fugacity capacity  $Z_o$  if an octanol-equivalent

volume fraction  $L_o$  is governing the partitioning (Mackay, 1982; Connolly and Pedersen, 1988; Clark et al., 1990):

$$Z_b = L_o \cdot Z_o \quad (41)$$

with

$$Z_o = \frac{K_{ow}}{H \cdot R \cdot T_b} \quad (42)$$

where  $K_{ow}$  is the octanol/water partitioning coefficient.

### IV.3.2.2. Equilibrium distribution constants

#### IV.3.2.2.1. Air/water

The air/water equilibrium distribution is governed by Henry's law constant and is depending on the temperature of the air/water system and on the salinity of the water (Dewulf et al., 1995a):

$$H = \exp (a \cdot T^{-1} + b \cdot Z + c) \quad (43)$$

with  $T$ =temperature of the air/water system (K),  $Z$ =salinity ( $\text{g.L}^{-1}$ ) and  $a$ ,  $b$  and  $c$  constants are regression constants. The constants  $a$ ,  $b$  and  $c$  are known (Dewulf et al., 1995a) (Table IV.3.1) and by consequence the air/water equilibrium distribution can be calculated if temperature and salinity are measured.

If water and air temperature are different,  $H$  can be calculated, based on theoretical considerations. From the chemical potential of a gas  $\mu$  ( $\text{J.mole}^{-1}$ )

**Table IV.3.1.** Regression constants for the relationship  $H = \exp (a.T^{-1} + b.Z + c)$ 

VOC	a	b	c
chloroform	-4142	0.00588	12.012
tetrachloromethane	-4073	0.00814	13.722
1,1-dichloroethane	-3975	0.00768	11.727
1,2-dichloroethane	-4329	0.00473	11.377
1,1,1-trichloroethane	-3834	0.00897	12.351
trichloroethylene	-3648	0.00813	11.121
tetrachloroethylene	-4528	0.01080	14.655
benzene	-3640	0.00786	10.577
toluene	-4064	0.00834	12.150
ethylbenzene	-4567	0.01047	14.001
o-xylene	-4026	0.00846	12.123
m/p-xylene*	-4232	0.01115	12.400

\*averaged over m- and p-xylene

$$\mu = \mu^{\circ} + R.T.\ln\frac{P}{P^{\circ}} \quad (44)$$

where  $\mu^{\circ}$ =chemical potential in the reference conditions (J.mole<sup>-1</sup>), P and P<sup>o</sup> are the pressure of the gas and the pressure of the gas in the reference state respectively, and T is the temperature (K). If two gases at two different temperatures have the same chemical potential and if P<sup>o</sup>=1atm, then

$$T_1 . \ln P_1 = T_2 . \ln P_2 \quad (45)$$

or

$$P_1 = P_2^{T_2/T_1} \quad (46)$$

If  $T_2/T_1 \approx 1$ , then

$$P_1 = P_2 \quad (47)$$

This can be assumed since the difference between the air and water temperature is small at

one location (below 5.5°C during '93, '94 and '95 so that  $0.98 < T_2/T_1 < 1.02$ , Meteowing, 1996). So one obtains from this latter consideration and from the ideal gas law that for two gases with the same energy content:

$$C_1 \cdot T_1 = C_2 \cdot T_2 \quad (48)$$

$C_1$  and  $C_2$  are the respective gas concentrations (mole.m<sup>-3</sup>) at temperatures  $T_1$  and  $T_2$  (K). If now a system is considered with an air compartment at temperature  $T_1$  and with a concentration  $C_1$  in equilibrium with a water body at temperature  $T_2$  with concentration  $C_w$ , then an imaginary headspace volume at temperature  $T_2$  can be added. The concentration in the imaginary headspace ( $C_2$ ) at equilibrium would be obtained from Henry's law constant  $H'$  at temperature  $T_2$

$$H' = \frac{C_2}{C_w} = \exp (a \cdot T_w^{-1} + b \cdot Z + c) \quad (49)$$

Since the three compartments are in equilibrium, the concentration in the real headspace is calculated from the imaginary headspace concentration:

$$C_2 = C_1 \cdot \frac{T_1}{T_2} \quad (50)$$

or

$$C_2 = C_a \cdot \frac{T_a}{T_w} \quad (51)$$

So the *in situ* Henry's law constant  $H$  ( $=C_a/C_w$ ) is

$$H = H' \cdot \frac{T_w}{T_a} \quad (52)$$

or

$$H = \frac{T_w}{T_a} \cdot \exp (a \cdot T_w^{-1} + b \cdot Z + c) \quad (53)$$

**IV.3.2.2.2. Sediment/water**

The sediment/water equilibrium partitioning constant  $K_{sw}$  is depending on the solids/water partitioning constant  $K_p$  (mole.kg<sup>-1</sup> per mole.m<sup>-3</sup>), the apparent density  $\gamma$  (kg.m<sup>-3</sup>) and on the porosity of the sediment  $\theta$  (dimensionless):

$$K_{sw} = \gamma \cdot K_p + \theta \quad (54)$$

$K_{sw}$  values for 11 VOCs were determined experimentally (Dewulf et al., 1995b), while for 1,2-dichloroethane and benzene distribution constants can be calculated from the established regression (n=11, r<sup>2</sup>=0.94):

$$\log K_p = g \cdot \log K_{ow} + h \quad (55)$$

where  $K_{ow}$ =octanol/water equilibrium distribution constant (dimensionless) (Table IV.3.2) and  $g=0.70$  and  $h=-0.45$  are the regression constants. The  $K_{sw}$  data are presented in Table IV.3.3.

**Table IV.3.2.** Log  $K_{ow}$  distribution constants (Schwarzenbach et al., 1993; Verschueren, 1983)

VOC	Log $K_{ow}$
chloroform	1.93
tetrachloromethane	2.73
1,1-dichloroethane	1.79
1,2-dichloroethane	1.47
1,1,1-trichloroethane	2.48
trichloroethylene	2.42
tetrachloroethylene	2.88
benzene	2.13
toluene	2.69
ethylbenzene	3.15
o-xylene	3.19
m/p-xylene*	3.12

\* Averaged value.

**Table IV.3.3.**  $K_{ow}$  values, experimental determined, except for 1,2-dichloroethane and benzene which are calculated from the  $\log K_p/\log K_{ow}$  relationship (Dewulf et al., 1995b).

VOC	$K_{ow}$
chloroform	0.360
tetrachloromethane	0.376
1,1-dichloroethane	0.353
1,2-dichloroethane	0.352
1,1,1-trichloroethane	0.366
trichloroethylene	0.370
tetrachloroethylene	0.433
benzene	0.361
toluene	0.372
ethylbenzene	0.415
o-xylene	0.419
m/p-xylene*	0.411

Averaged value.

#### IV.3.2.2.3. Biota/water

The biota/water equilibrium partitioning coefficient  $K_{bw}$  (mole.m<sup>-3</sup> over mole.m<sup>-3</sup>) can be derived from the octanol/water equilibrium constant. The partitioning into biota is dominated by an octanol-equivalent volume fraction  $L_o$ . This octanol-equivalent volume fraction can be approximated by the lipid volume fraction, especially for compounds with  $\log K_{ow}$  below 4 (Connolly and Pedersen, 1988). Based on experimental values Mackay (1982) found the following relationship:

$$K_{bw} = L_o \cdot K_{ow} \quad (56)$$

with  $L_o=0.048$  and  $r^2=0.95$  ( $n=63$ ). However, for compounds with low  $K_{bw}$  (<10) or  $\log K_{ow}$  below 2.3 the amount of compound in non-lipid phases has to be considered. Assuming that the partitioning into the non-lipid fraction can be approximated by a water-equivalent partitioning, then the biota/water equilibrium partitioning can be calculated from

$$K_{Dw} = 0.952 + 0.048 \cdot K_{Ow} \quad (57)$$

From this an octanol-equivalent volume fraction  $L_o$  is calculated:

$$L_o = \frac{0.952 + 0.048 \cdot K_{Ow}}{K_{Ow}} \quad (58)$$

### IV.3.2.3. Determination of degradation rates

The degradation of the investigated compounds in the water and sediment compartment can be neglected when compared with other processes like exchange processes. From the stability of the compounds it is assumed that the degradation of the VOCs in biota can be ignored. The degradation process which has to be considered is the atmospheric degradation  $k_{a,DEGR}$  ( $s^{-1}$ ) of the VOCs (Dewulf et al., 1995c). Degradation rates are presented in Table IV.3.4.

Table IV.3.4. Atmospheric degradation rates

VOC	$k_{OH}$ ( $cm^3 \cdot radical^{-1} \cdot s^{-1}$ )	reference	$k_{a,DEGR}$ ( $s^{-1}$ ) *
chloroform	$11.4 \cdot 10^{-14}$	Davis et al., 1976	$1.14 \cdot 10^{-13}$
tetrachloromethane	$0.01 \cdot 10^{-14}$ **	Cox et al., 1976	$1.00 \cdot 10^{-16}$
1,1-dichloroethane	$26.0 \cdot 10^{-14}$	Howard and Evenson, 1976	$2.60 \cdot 10^{-13}$
1,2-dichloroethane	$22.0 \cdot 10^{-14}$	Howard and Evenson, 1976	$2.20 \cdot 10^{-13}$
1,1,1-trichloroethane	$0.95 \cdot 10^{-14}$	Talukdar et al., 1992	$9.50 \cdot 10^{-15}$
trichloroethylene	$286 \cdot 10^{-14}$	Edney et al., 1986	$2.86 \cdot 10^{-12}$
tetrachloroethylene	$12.0 \cdot 10^{-14}$	Franklin, 1994	$1.20 \cdot 10^{-13}$
benzene	$1.17 \cdot 10^{-12}$	Semadini et al., 1995	$1.17 \cdot 10^{-12}$
toluene	$6.03 \cdot 10^{-12}$	Semadini et al., 1995	$6.03 \cdot 10^{-12}$
ethylbenzene	$6.84 \cdot 10^{-12}$	Ohta and Ohyama, 1985	$6.84 \cdot 10^{-12}$
o-xylene	$13.2 \cdot 10^{-12}$	Ohta and Ohyama, 1985	$1.32 \cdot 10^{-11}$
m/p-xylene	$18.5 \cdot 10^{-12}$ ***	Ohta and Ohyama, 1985	$1.85 \cdot 10^{-11}$

\* Assuming  $[OH]=10^6$   $rad.cm^{-3}$  since Singh et al. (1985) estimated  $[OH]=2.5 \cdot 10^6$   $rad.cm^{-3}$  at day time and Prinn et al. (1992) estimated the global average OH concentration as  $0.91 \cdot 10^6$   $rad.cm^{-3}$ .

\*\* Maximum estimated value.

\*\*\* Average value of m- and p-xylene.



#### IV.3.2.4. Determination of compartment volumes and intercompartment contact surface areas

An evaluative 1km<sup>2</sup> area is used, as suggested by Mackay and Paterson (1991). Mean water depth is 30m\*. Air, sediment and biota volumes are chosen according to the suggestions of Mackay and Paterson (1991). The volumes applied and the intercompartment contact surfaces areas are presented in Table 5.

**Table IV.3.5.** Selected compartment volumes and surface areas.

	Area (m <sup>2</sup> )	Height (m)	Volume (m <sup>3</sup> )	Remarks
Air	10 <sup>6</sup>	2 10 <sup>3</sup>	2 10 <sup>9</sup>	Height as Mackay & Paterson, 1991
Water	10 <sup>6</sup>	*	3 10 <sup>7</sup>	* local water column height
Sediment	10 <sup>6</sup>	1 10 <sup>-2</sup>	1 10 <sup>4</sup>	thickness as Mackay & Paterson, 1991
Biota	-	-	3 10 <sup>1</sup>	1/10 <sup>6</sup> water body, as Mackay & Paterson, 1991

### IV.3.2.5. Diffusive transfers

#### IV.3.2.5.1. Air/water

The air/water transfer is limited by the air and water mass transfer resistances. However, for VOCs it is clear that the resistance is totally dominated by the water mass transfer if  $H > 0.02$ . In this respect one obtains

$$D_{aw} = \frac{K_w \cdot A}{H \cdot R \cdot T_w} \quad (59)$$

where  $D_{aw}$  = air/water exchange velocity constant ( $\text{mole} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ ) and A the air/water surface ( $\text{m}^2$ ). The water mass transfer coefficient  $K_w$  ( $\text{m} \cdot \text{s}^{-1}$ ) is deduced empirically from the water mass transfer coefficient of oxygen  $K_{w,O_2}$  ( $\text{m} \cdot \text{s}^{-1}$ ) (Holmén and Liss, 1984):

$$K_w = K_{w,O_2} \cdot \left( \frac{D_{w,VOC}}{D_{w,O_2}} \right)^{0.57} \quad (60)$$

with  $D_{w,VOC}$  and  $D_{w,O_2}$  the water diffusion coefficient ( $\text{m}^2 \cdot \text{s}^{-1}$ ) of the VOC and  $O_2$  in water, respectively.  $K_{w,O_2}$  is determined from the empirical relationship with  $u_{10}$ , the wind velocity 10m above the air/water surface ( $\text{m} \cdot \text{s}^{-1}$ ) (Schwarzenbach et al., 1993):

$$K_{w,O_2} = 4 \cdot 10^{-6} + 4 \cdot 10^{-7} \cdot u_{10}^2 \quad (61)$$

while the diffusion coefficients are calculated from the Othmer and Thakar equation (Schwarzenbach et al., 1993):

$$D_{w,VOC} = \frac{13.26 \cdot 10^{-9}}{\mu^{1.14} \cdot V^{0.589}} \quad (62)$$

with the water viscosity (centipoise) and V the molar volume of the VOC ( $\text{cm}^3 \cdot \text{mole}^{-1}$ ).

**IV.3.2.5.2. Water/sediment**

The water/sediment exchange velocity  $D_{ws}$  ( $\text{mole.Pa}^{-1}.\text{s}^{-1}$ ) depends on the partial exchange velocities:

$$D_w = \frac{K_w \cdot A}{H \cdot R \cdot T_w} \quad D_s = \frac{K_s \cdot A \cdot K_{sw}}{H \cdot R \cdot T_s} \quad (63)$$

So, the total water/sediment conductivity becomes

$$D_{ws} = \frac{A}{H \cdot R \cdot T_w} \cdot \frac{1}{\frac{1}{K_w} + \frac{1}{K_s \cdot K_{sw}}} \quad (64)$$

if  $T_s = T_w$ . The water mass transfer coefficients  $K_w$  is suggested to be  $0.01 \text{m.h}^{-1}$  (Mackay and Paterson, 1991). The sediment transfer coefficient is interpreted as being the result of ratio of the diffusion coefficient in the sediment and of the diffusion path length. The diffusion coefficient in the sediment  $D_{s,VOC}$  ( $\text{m}^2.\text{s}^{-1}$ ) is calculated from the Millington and Quirk expressions (Jury et al., 1983):

$$D_{s,VOC} = \theta^{4/3} \cdot D_{w,VOC} \quad (65)$$

The diffusion path length is suggested to be the half of the sediment thickness (Mackay and Paterson, 1991).

### IV.3.2.5.3. Biota/water

#### IV.3.2.5.3.1. The fish uptake model

The model for uptake of VOCs by fish is developed by Clark et al. (1990). A schematic representation is given in Figure IV.3.1. It represents uptake and loss via gills  $N_G$  (mole.h<sup>-1</sup>), uptake from food  $N_A$  (mole.h<sup>-1</sup>) and loss via egestion  $N_E$  (mole.h<sup>-1</sup>). To complete the model a degradation rate in the fish  $N_{DEGR}$  (mole.h<sup>-1</sup>) and a dilution loss by growth  $N_{GR}$  (mole.h<sup>-1</sup>) have to be added.

From these considerations, the accumulation in a fish  $N_{f,acc}$  (mole.h<sup>-1</sup>) is calculated from

$$N_{f,acc} = N_G + N_A - N_E - N_{DEGR} - N_{GR} \quad (66)$$

The uptake and loss via gills is regarded as a resistance model:

$$N_G = D_w \cdot (f_w - f_f) \quad (67)$$

where  $D_w$  is the overall rate parameter (mole.Pa<sup>-1</sup>.h<sup>-1</sup>) and  $f_f$  the fugacity in the fish (=f<sub>b</sub>). The overall resistance  $1/D_w$  consists of three resistances in series:

$$\frac{1}{D_w} = \frac{1}{D_v} + \frac{1}{D_{TO}} + \frac{1}{D_{TW}} \quad (68)$$

where  $1/D_v$  is the gill water flow resistance,  $1/D_{TO}$  the organic phase resistance for transfer between gill and lipid and  $1/D_{TW}$  the water phase resistance between gill and lipid (all in Pa.h.mole<sup>-1</sup>). The resistances can be written as resistances in h:

$$R_v = \frac{V_l \cdot Z_w}{D_v} ; R_{TO} = \frac{V_l \cdot Z_o}{D_{TO}} ; R_{TW} = \frac{V_l \cdot Z_w}{D_{TW}} \quad (69)$$

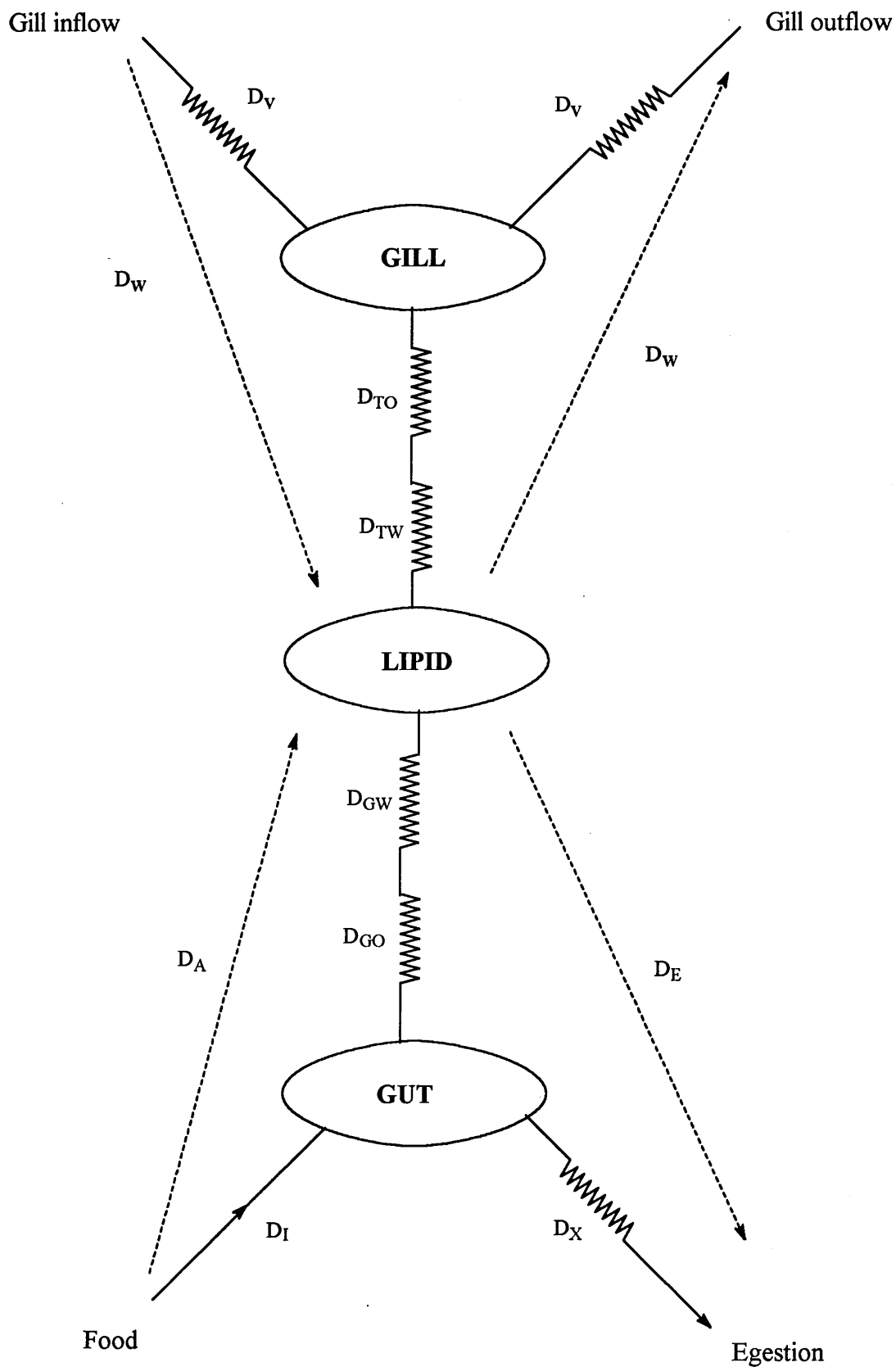


Figure IV.3.1. the fish uptake model of Clark et al. (1990)

with  $V_1$  the octanol-equivalent volume fraction ( $m^3$ ) ( $=V_f \cdot L_o$ ;  $V_f$  is the volume of the fish ( $m^3$ )),  $Z_w$  and  $Z_o$  the fugacity capacity of water and octanol respectively ( $mole \cdot m^{-3} \cdot Pa^{-1}$ ). When  $R_w = R_v + R_{tw}$ , one obtains

$$\frac{1}{D_w} = R_w \cdot \frac{1}{V_1 \cdot Z_w} + R_{T0} \cdot \frac{1}{V_1 \cdot Z_o} \quad (70)$$

$D_w$  is known when  $R_w$  and  $R_{T0}$  are estimated.

The loss via egestion  $N_E$  is calculated from

$$N_E = D_E \cdot f_f \quad (71)$$

where  $1/D_E$  is the overall egestion resistance ( $Pa \cdot h \cdot mole^{-1}$ ), consisting of a gut membrane water resistance  $1/D_{GW}$ , a gut membrane organic resistance  $1/D_{GO}$  and an egestion resistance  $1/D_X$  (Figure IV.3.1.):

$$\frac{1}{D_E} = \frac{1}{D_{GW}} + \frac{1}{D_{GO}} + \frac{1}{D_X} \quad (72)$$

Again, these resistances can be written in units of h:

$$R_{GW} = \frac{V_1 \cdot Z_w}{D_{GW}} ; R_{GO} = \frac{V_1 \cdot Z_o}{D_{GO}} ; R_X = \frac{V_1 \cdot Z_o}{D_X} \quad (73)$$

So

$$\frac{1}{D_E} = \frac{R_{GO}}{V_1 \cdot Z_o} + \frac{R_{GW}}{V_1 \cdot Z_w} + \frac{R_X}{V_1 \cdot Z_o} \quad (74)$$

$R_{GO}$  and  $R_{GW}$  can be estimated, where  $R_X$  is calculated from the food uptake rate and the digestion coefficient  $Q$  at steady state:

$$R_X = Q \cdot R_I \quad (75)$$

where  $R_I$  is the food uptake resistance:

$$R_I = \frac{V_1 \cdot Z_o}{G_i \cdot Z_A} \quad (76)$$

with  $G_i$  the feeding rate ( $m^3 \cdot h^{-1}$ ) and  $Z_A$  the fugacity capacity of the food.  $Z_A$  is depending on  $K_{ow}$  and the octanol-equivalent fraction of the food  $L_A$ :

$$Z_A = \frac{K_{ow} \cdot L_A}{H \cdot R \cdot T_w} \quad (77)$$

The uptake via food is calculated from

$$N_A = D_A \cdot f_A \quad (78)$$

where  $1/D_A$  is the food uptake resistance ( $\text{Pa.h.mole}^{-1}$ ) and  $f_A$  is the fugacity of the food (assumed to be equal to  $f_w^*$ ).  $D_A$  is obtained from

$$D_A = Q \cdot D_E \quad (79)$$

Finally the degradation loss  $N_{DEGR}$  and the growth dilution loss  $N_{GR}$  are calculated from

$$N_{DEGR} = D_R \cdot f_f = k_R \cdot V_f \cdot Z_f \quad (80)$$

$$N_{GR} = D_D \cdot f_f = k_D \cdot V_f \cdot Z_f \quad (81)$$

where  $k_R$  and  $k_D$  are the rates ( $\text{h}^{-1}$ ) for the degradation and growth dilution.

The parameters needed for the fish uptake model are listed in Table IV.3.6.

**Table IV.3.6.** Estimated parameters for the fish uptake model

Parameter	Formula <sup>1</sup> /value	Unit	Reference
$R_w$	$0.36 \log V_f - 0.81$	h	Clark et al., 1990
$R_{to}$	$0.29 \log V_f + 4.1$	h	Clark et al., 1990
$R_{go}$	2000	h	Clark et al., 1990
$R_{gw}$	$3 \cdot 10^{-5}$	h	Clark et al., 1990
Q	3	-	Clark et al., 1990
$G_i$	$0.02 V_f / 24$	$\text{m}^3 \cdot \text{h}^{-1}$	Clark et al., 1990
$k_D$	0	$\text{h}^{-1}$	Clark et al., 1990

<sup>1</sup>  $V_f$  is the volume of the fish in  $\text{m}^3$

### IV.3.2.5.3.2. Biota/water exchange

The exchange between water and biota  $N_{biota}$  (mole.s<sup>-1</sup>) is the sum of the exchange processes between the water body and each individual fish  $N_{fish}$  (mole.s<sup>-1</sup>). If an average volume for the fish  $V_f$  can be estimated, then the number of fishes  $NR_f$  is calculated from  $V_f$  and the total volume of biota  $V_b$ . So

$$N_b = NR_f \cdot N_{fish} \quad (82)$$

with  $N_{fish}$  the result of the exchange via gills, food and egestion for one fish:

$$N_{fish} = N_G + N_A - N_E \quad (83)$$

### IV.3.2.6. Non-diffusive transfers: dry deposition, transfer to higher altitudes and sediment burial

#### IV.3.2.6.1. Advection

Advection for the air and water compartment,  $N_{a,adv}$  and  $N_{w,adv}$  (mole.s<sup>-1</sup>), giving rise to an input, has to be considered. They cannot be estimated because knowledge about concentrations in the adjacent compartments are unknown and motion of the air and water masses are hard to estimate. By consequence they will be estimated from mass balances. Sediment advection is not to be considered while advection by biota can be neglected.

#### IV.3.2.6.2. Dry deposition

Deposition of aerosols in the aquatic compartment ( $N_{dry}$ , mole.s<sup>-1</sup>) is not important as an exchange process for VOCs because they are poorly distributed onto aerosols (Bidleman, 1988).

#### IV.3.2.6.3. Wet deposition

Deposition of VOCs into the aquatic compartment by rain can be calculated from the rain rate



$R$  ( $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ), the atmospheric concentration  $C_a$  ( $\text{mole} \cdot \text{m}^{-3}$ ) and Henry's law constant  $H$  (dimensionless) since rain drops are already in equilibrium with the air after a 10m fall with respect to the VOC absorption (Slinn et al, 1978). So the deposition by rain  $N_r$  ( $\text{mole} \cdot \text{s}^{-1}$ ) becomes

$$N_r = R \cdot C_a \cdot H \cdot A \quad (84)$$

$R$  is to be obtained from the meteorological database (Meteowind, 1996).

#### IV.3.2.6.4. Transfer to higher altitudes

Transfer from air to higher altitudes is assumed to occur at a velocity of  $K_{alt}=0.01\text{m} \cdot \text{h}^{-1}$ , as proposed by Mackay et al. (1985). The mass transfer to higher altitude  $N_{alt}$  ( $\text{mole} \cdot \text{s}^{-1}$ ) becomes

$$N_{alt} = K_{alt} \cdot C_a \cdot A \quad (85)$$

#### IV.3.2.7. Mass balances: total mass, mass balances, residence times

##### IV.3.2.7.1. Total masses

The total mass of VOCs  $M$  (mole) in the compartments air, water, sediment and biota can be estimated from the measured concentration  $C$  ( $\text{mole} \cdot \text{m}^{-3}$ ) and from the total volumes of the compartments  $V$  ( $\text{m}^3$ ):

$$M = C \cdot V \quad (86)$$

These masses will indicate where the major part of the VOCs is remaining.

##### IV.3.2.7.2. Mass balances

In order to establish a mass balance over a compartment, sources and degradations within the compartments and advective and diffusive exchange processes with adjacent compartments

are to be considered. These processes could give rise to a change in total mass in the compartment. But by reasons of simplifications and from observations, a dynamic steady state is to be applied, where all loss processes are encountered by input processes.

#### IV.3.2.7.2.1. Air

No sources of VOCs in the air compartment are known, while degradation processes by photochemical reactions are to be incorporated in the mass balance ( $k_{a,DEGR} \cdot C_a \cdot V_a$ ). Exchange processes are the diffusive exchange with the water body, exchange with higher altitudes ( $N_{alt}$ ), wet deposition ( $N_r$ ) and the net advective input ( $N_{a,ADV}$ ). The steady state mass balance becomes:

$$N_{a,ADV} = k_{a,DEGR} \cdot C_a \cdot V_a + D_{aw} \cdot (f_a - f_w) + N_r + N_{alt} \quad (87)$$

Photochemical degradation, diffusive exchange with the water column, wet deposition and exchange with the higher altitudes can be calculated. In this respect the net advective input into (or the net advective output from) the isolated marine air compartment can be estimated.

#### IV.3.2.7.2.2. Water

Degradation processes within the water body are to be neglected while sources for chloroform have to be considered. Input/output processes are diffusive exchange with the air and the sediment compartments, wet deposition and exchange with biota. So the net advective input (or the net advective output) can be calculated for all VOCs, except chloroform, from

$$N_{w,ADV} = D_{aw} \cdot (f_w - f_a) + D_{ws} \cdot (f_w - f_s) + N_b - N_r \quad (88)$$

For chloroform a source rate has to be added ( $k_{source}$ , in  $\text{mole} \cdot \text{s}^{-1} \cdot \text{m}^{-3}$ ). So the mass balance for chloroform becomes

$$N_{w,ADV} + k_{source} \cdot V_w = D_{aw} \cdot (f_a - f_w) + D_{ws} \cdot (f_w - f_s) + N_b - N_r \quad (89)$$

### IV.3.2.7.2.3. Sediment

The only process which can be quantified for the sediment compartment is the diffusive exchange with the water body. This input process will be encountered in a steady state by exchange to the underlying layers. This sediment burial  $N_{burial}$  (mole.s<sup>-1</sup>) is determined by a sediment burial rate per area unit ( $k_{burial}$ , in mole.s<sup>-1</sup>.m<sup>-2</sup>) and by the surface area. So the mass balance gives

$$N_{burial} = D_{ws} \cdot (f_w - f_s) \quad (90)$$

### IV.3.2.7.2.4. Biota

The biota mass balance at steady state is determined by the uptake and loss via gills, uptake from food and loss via egestion ( $=N_b$ , mole.s<sup>-1</sup>). If degradation and growth dilution are negligible, an accumulation  $N_{b,acc}$  (mole.s<sup>-1</sup>) is found:

$$N_{b,acc} = N_b \quad (91)$$

### IV.3.3. APPLICATION ON FIELD CONCENTRATION DATA

#### IV.3.3.1. Application field

The developed model includes the fugacity approach for the compartments air, water, sediment and biota. The model needs to be feeded by data on physico-chemical characteristics of the compounds, by concentration data in the different compartments and by environmental parameters.

The limiting factor for the application in this work is the availability of concentration data. Concentrations in air and water were simultaneously measured at 7 locations during 6 sampling campaigns (3rd and 4th campaign in 1994 and all 4 campaigns in 1995). The sampling locations are presented in Figure IV.3.2 and their coordinates are given in Table IV.3.7. An overview of the parameters of all simultaneous air and water samples is given in Table IV.3.8. Sediment and biota concentration data are too limited to be involved in the developed fugacity model. So this means that the application field concerns an air/water fugacity model for a dataset of 38 cases.

**Table IV.3.7.** Coordinates of the sampling locations of the monitoring campaigns.

Location	N	E
B07	51° 25.90	3° 17.80
S12	51° 21.90	4° 13.50
780	51° 28.27	3° 03.48
120	51° 11.10	2° 42.07
421	51° 28.83	2° 27.00
435	51° 34.84	2° 47.42
800	51° 50.83	2° 52.00

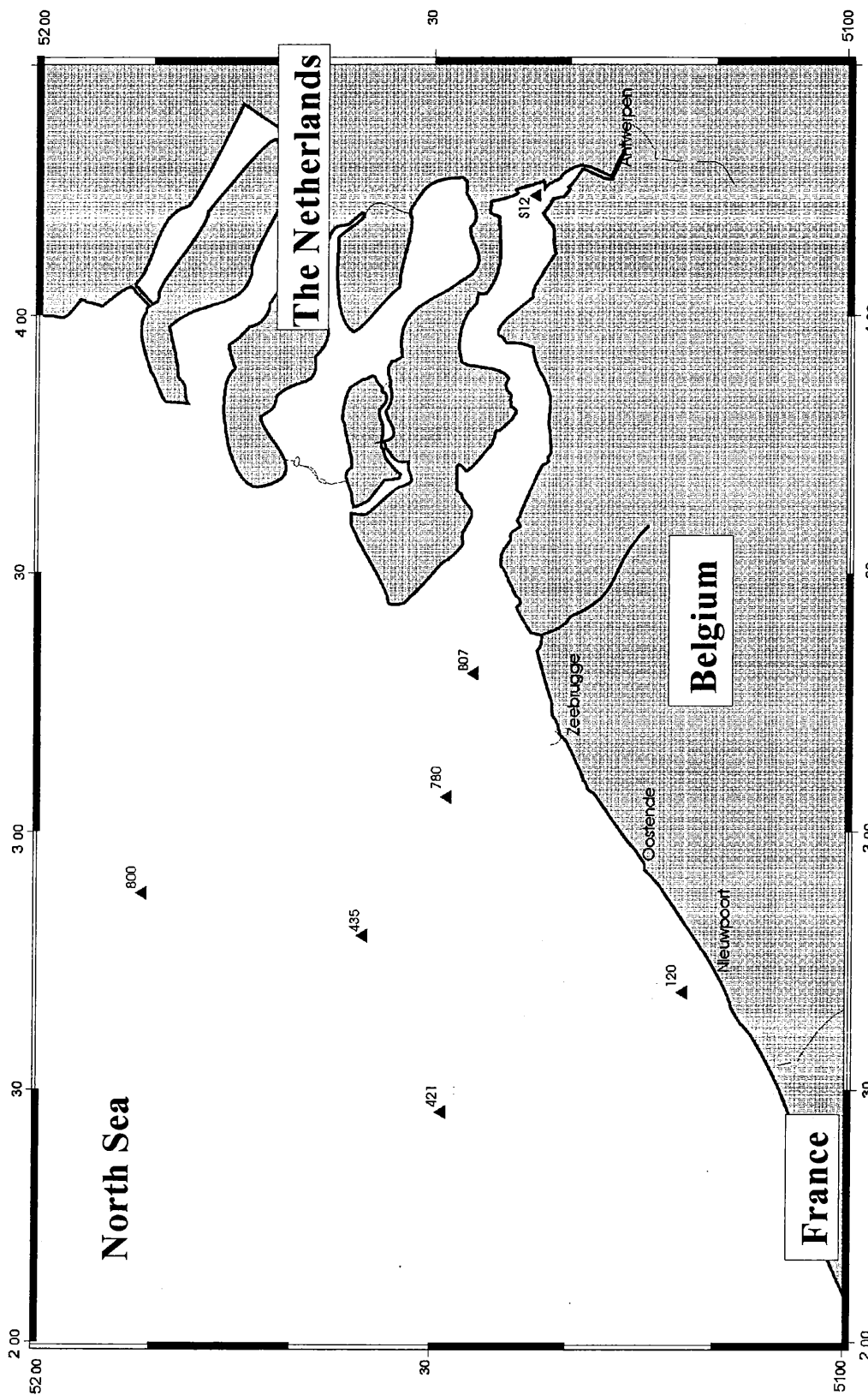


Figure IV.3.2. Map of the sampling locations on the Belgian continental shelf and in the Scheldt estuary

**Table IV.3.8.** Overview of samples taken in the monitoring campaigns: date, location, year, period of the year, code, wind velocity ( $u$ , in  $\text{m}\cdot\text{s}^{-1}$ ), wind direction ( $u$ , in  $^{\circ}\text{C}$ ), air temperature ( $T$ , in  $^{\circ}\text{C}$ ) and atmospheric pressure ( $P$ , in mbar)

Date	Location	Year	Period	Code	$u$ ( $\text{m}\cdot\text{s}^{-1}$ )	$u$ ( $^{\circ}$ )	$T$ ( $^{\circ}\text{C}$ )	$P$ (mbar)
20/09/94	B07	1994	3	B07/94/3	4.4	158	11.7	1004
20/09/94	S12	1994	3	S12/94/3	7.7	339	11.5	1005
15/09/94	120	1994	3	120/94/3	7.6	90	12.6	994
14/09/94	780	1994	3	780/94/3	0.9	222	14.0	1000
15/09/94	421	1994	3	421/94/3	11.5	25	14.5	995
19/09/94	435	1994	3	435/94/3	16.6	112	11.8	1014
22/09/94	800	1994	3	800/94/3	8.6	32	15.2	1022
5/12/94	B07	1994	4	B07/94/4	10.5	174	10.3	1015
5/12/94	S12	1994	4	S12/94/4	10.4	212	10.9	1011
7/12/94	120	1994	4	120/94/4	8.8	193	6.7	1011
28/03/95	B07	1995	1	B07/95/1	12.6	181	1.4	992
27/03/95	S12	1995	1	S12/95/1	14.8	332	5.3	1012
30/03/95	120	1995	1	120/95/1	7.4	247	11.0	1031
30/03/95	780	1995	1	780/95/1	1.8	74	5.3	1030
31/03/95	421	1995	1	421/95/1	3.8	227	7.6	1030
30/03/95	435	1995	1	435/95/1	4.4	222	6.7	1031
4/04/95	800	1995	1	800/95/1	6.2	10	9.0	1020
15/05/95	B07	1995	2	B07/95/2	5.9	272	12.2	1016
18/05/95	S12	1995	2	S12/95/2	6.4	351	8.6	1003
17/05/95	120	1995	2	120/95/2	5.6	176	10.9	997
17/05/95	780	1995	2	780/95/2	16.4	227	12.9	994
16/05/95	421	1995	2	421/95/2	8.3	60	15.0	1008
16/05/95	435	1995	2	435/95/2	6.6	98	12.5	1011

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continued

15/05/95	800	1995	2	800/95/2	2.7	146	9.9	1014
18/10/95	B07	1995	3	B07/95/3	5.1	298	15.7	1024
18/10/95	S12	1995	3	S12/95/3	5.2	335	14.6	1028
17/10/95	120	1995	3	120/95/3	4.2	184	17.2	1019
16/10/95	780	1995	3	780/95/3	2.7	182	15.4	1023
16/10/95	421	1995	3	421/95/3	7.3	140	16.5	1022
16/10/95	435	1995	3	435/95/3	5.4	130	16.7	1022
16/10/95	800	1995	3	800/95/3	4.3	182	15.4	1023
4/12/95	B07	1995	4	B07/95/4	12.2	80	1.9	1025
4/12/95	S12	1995	4	S12/95/4	5.2	43	1.7	1028
6/12/95	120	1995	4	120/95/4	8.9	77	-1.5	1019
5/12/95	780	1995	4	780/95/4	15.3	79	-1.4	1022
6/12/95	421	1995	4	421/95/4	8.5	90	-0.2	1017
7/12/95	435	1995	4	435/95/4	4.6	138	0.0	1016
7/12/95	800	1995	4	800/95/4	5.2	142	0.5	1016

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#### IV.3.3.2. Data to feed the model

The data to feed the model are physico-chemical characteristics, concentration data and environmental parameters. The physicochemical parameters are already discussed in the development of the model. The concentration data in air and water for the 13 target compounds for 38 samples are presented in Annex IV.3.1 and IV.3.2 respectively.

Environmental parameters were obtained from M.U.M.M. (Mathematical Unit of the North Sea Mathematical Models, Belgium) and the Meteowing (Belgian Air Force). They are listed in Annex IV.3.3. Salinity and depth for each sampling location are data averaged over a 5 years period (1990-1994). Monthly averaged data, obtained by the Meteowing during the month of sampling, are the water temperature, air temperature, wind speed and rain rate.

### IV.3.3.3. Application and interpretation of the fugacity model

The fugacity model was run for all 38 cases. An example of the model is given in Figure IV.3.3. All cases are given in Annex IV.3.4.

First, from the example in Figure IV.3.3, the abundancies of the compounds in each compartment are found. These are directly related to the concentrations and the volumes of the compartments. The masses of the VOCs in the water column are in the order of magnitude of  $10^1$  to  $10^2$ g for an evaluative  $1\text{km}^2$ , except for chloroform which is in the  $10^3$  order of magnitude. Air masses are for the CHCs in the order of  $10^1$  to  $10^3$ g, whereas all MAHs are in the order of  $10^3$ g. Due to the volumes and/or the lipophilicities of the compartments not considered (sediment and biota) it can be assumed that the air and water compartments are the main burdens for the VOCs.

Next to the abundancies of the compounds in the compartments, the model shows the dynamics of the compounds. All processes involved in the behaviour of the VOCs in air and water can be compared to each other to estimate their relative importance. Processes are diffusive exchange air/water, wet deposition, transport to higher altitude and atmospheric degradation. It can be seen that that water to air (or air to water) diffusive exchange is of the order of  $10^{-1}$  to  $10^1$   $\text{g}\cdot\text{day}^{-1}$  for  $1\text{km}^2$ . Wet deposition shows an averaged rate in the order of  $10^{-3}$  to  $10^{-5}$   $\text{g}\cdot\text{day}^{-1}$ . Transport to higher altitudes is in the order of  $10^{-1}$  to  $10^{-3}$   $\text{g}\cdot\text{day}^{-1}$  and atmospheric degradation in the order of  $10^{-3}$  to  $10^{-8}$   $\text{g}\cdot\text{day}^{-1}$ .

Next to the abundancies and individual dynamic processes, the fugacity model shows the dynamic input and output balances in each compartment by means of the mass balances, assuming a steady state. The advective input/output to (and sources in) the water compartment is (are) almost completely compensated by the diffusive air/water exchange (>99%). For the air compartment it can be seen that the mass balance is dominated by the diffusive air/water exchange and the transfer to higher altitudes (>99%). This means that what is entering (leaving) the air compartment from the water body by diffusive exchange is further exchanged to adjacent air compartments and to higher air layers.



sample: B07/94/3	1. CONCENTRATION DATA			2. DISTR. CONST.			3. TEMPERATURES AND SALINITY			4. COMPARTMENT VOLUMES			5. CONTACT SURF.		
	1.1. Ca	1.2. Cw	1.2. Cw	2.1. H	3.1. Ta	3.2. Tw	3.3. Z	4.1. Va	4.2. Vw	4.3. Vw	4.4. Vw	4.5. Vw	4.6. Vw	4.7. Vw	
	ng/m3	mole/m3	ng/l	-	K	K	g/l	m3	m3	m3	m3	m2	m2		
chloroform	42.70	3.57E-10	87.11	0.119	287	289	31.21	2E+09	1.2E+07	1E+06					
tetrachloromethane	238.20	1.55E-09	1.28	0.895	287	289	31.21	2E+09	1.2E+07	1E+06					
1,1-dichloroethane	3.60	3.64E-11	1.14	0.169	287	289	31.21	2E+09	1.2E+07	1E+06					
1,2-dichloroethane	15.30	1.55E-10	2.52	0.032	287	289	31.21	2E+09	1.2E+07	1E+06					
1,1,1-trichloroethane	678.10	5.08E-09	2.23	0.533	287	289	31.21	2E+09	1.2E+07	1E+06					
trichloroethylene	236.40	1.80E-09	0.51	0.289	287	289	31.21	2E+09	1.2E+07	1E+06					
tetrachloroethylene	608.90	3.67E-09	1.04	0.512	287	289	31.21	2E+09	1.2E+07	1E+06					
benzene	515.00	6.60E-09	9.33	0.171	287	289	31.21	2E+09	1.2E+07	1E+06					
toluene	3472.20	3.77E-08	23.45	0.193	287	289	31.21	2E+09	1.2E+07	1E+06					
ethylbenzene	2384.30	2.25E-08	8.87	0.230	287	289	31.21	2E+09	1.2E+07	1E+06					
m/p-xylene	1015.60	9.58E-09	15.33	0.215	287	289	31.21	2E+09	1.2E+07	1E+06					
o-xylene	658.90	6.22E-09	18.18	0.151	287	289	31.21	2E+09	1.2E+07	1E+06					

	6. FUGACITIES			7. FUGACITY CAPACITIES			8. MASS TRANSFER COEFF.			9. DIFF. EXCH. VELOCITIES			10. DIFFUSIVE EXCH. FLUXES			
	6.1. fa	6.2. fw	6.2. fw	7.1. Za	7.2. Zw	7.2. Zw	8.1. K	8.2. K	8.3. K	9.1. K	9.2. K	9.3. K	10.1. F	10.2. F	10.3. F	
	Pa	Pa	Pa	mole/m3	P mole/m3	Pa	m/s	m/s	m/s	mole/(Pa.s)	mole/(Pa.s)	mole/(Pa.s)	mole/s	mole/s	g/day	
chloroform	8.53E-07	2.08E-04	4.19E-04	3.50E-03	7.77E-06	2.72E-02	7.77E-06	7.77E-06	7.77E-06	2.72E-02	3.39E-03	3.39E-03	5.64E-06	4.82E-08	58.255	0.641
tetrachloromethane	3.69E-06	1.79E-05	4.19E-04	4.65E-04	7.30E-06	7.30E-06	7.30E-06	7.30E-06	7.30E-06	1.89E-02	1.89E-02	1.89E-02	8.64E-08	8.64E-08	0.739	0.739
1,1-dichloroethane	8.68E-08	4.66E-06	4.19E-04	2.47E-03	7.84E-06	7.84E-06	7.84E-06	7.84E-06	7.84E-06	1.02E-01	1.02E-01	1.02E-01	1.62E-07	1.62E-07	1.382	1.382
1,2-dichloroethane	3.69E-07	1.95E-06	4.19E-04	1.31E-02	7.17E-06	7.17E-06	7.17E-06	7.17E-06	7.17E-06	5.60E-03	5.60E-03	5.60E-03	5.18E-08	5.18E-08	0.597	0.597
1,1,1-trichloroethane	1.21E-05	2.14E-05	4.19E-04	7.80E-04	7.12E-06	7.12E-06	7.12E-06	7.12E-06	7.12E-06	1.03E-02	1.03E-02	1.03E-02	-1.64E-08	-1.64E-08	-0.186	-0.186
trichloroethylene	4.29E-06	2.69E-06	4.19E-04	1.44E-03	7.16E-06	7.16E-06	7.16E-06	7.16E-06	7.16E-06	5.82E-03	5.82E-03	5.82E-03	-6.16E-09	-6.16E-09	-0.088	-0.088
tetrachloroethylene	8.75E-06	7.69E-06	4.19E-04	8.12E-04	7.51E-06	7.51E-06	7.51E-06	7.51E-06	7.51E-06	1.83E-02	1.83E-02	1.83E-02	6.10E-07	6.10E-07	4.113	4.113
benzene	1.58E-05	4.91E-05	4.19E-04	2.16E-03	7.07E-06	7.07E-06	7.07E-06	7.07E-06	7.07E-06	1.53E-02	1.53E-02	1.53E-02	4.29E-07	4.29E-07	3.413	3.413
toluene	9.01E-05	1.18E-04	4.19E-04	1.81E-03	6.75E-06	6.75E-06	6.75E-06	6.75E-06	6.75E-06	1.22E-02	1.22E-02	1.22E-02	-8.94E-08	-8.94E-08	-0.819	-0.819
ethylbenzene	5.37E-05	4.63E-05	4.19E-04	1.94E-03	6.74E-06	6.74E-06	6.74E-06	6.74E-06	6.74E-06	1.30E-02	1.30E-02	1.30E-02	6.76E-07	6.76E-07	6.190	6.190
m/p-xylene	2.29E-05	7.47E-05	4.19E-04	1.94E-03	6.78E-06	6.78E-06	6.78E-06	6.78E-06	6.78E-06	1.87E-02	1.87E-02	1.87E-02	8.86E-07	8.86E-07	8.117	8.117
o-xylene	1.48E-05	6.23E-05	4.19E-04	2.75E-03	6.78E-06	6.78E-06	6.78E-06	6.78E-06	6.78E-06	1.87E-02	1.87E-02	1.87E-02	8.86E-07	8.86E-07	8.117	8.117

	11. WET DEPOSITION			12. TO HIGHER ALT.			13. ATMOS. DEGR.		
	R	H (dep)	Nr	Kalt	Nalt	Nalt	ka,degr	Na,degr	Na,degr
	m3/(m2.s)	(-)	mole/s	m/s	mole/s	g/day	1/s	mole/s	g/day
chloroform	3.78E-08	0.089	1.52E-12	2.78E-06	9.93E-10	1.02E-02	1.14E-13	8.15E-14	8.41E-07
tetrachloromethane	4.78E-08	0.625	4.63E-11	2.78E-06	4.30E-09	5.72E-02	1.00E-16	3.09E-16	4.12E-09
1,1-dichloroethane	4.78E-08	0.120	2.08E-13	2.78E-06	1.01E-10	8.64E-04	2.60E-13	1.89E-14	1.62E-07
1,2-dichloroethane	4.78E-08	0.025	1.82E-13	2.78E-06	4.29E-10	3.67E-03	2.20E-13	6.80E-14	5.82E-07
1,1,1-trichloroethane	4.78E-08	0.365	8.87E-11	2.78E-06	1.41E-08	1.63E-01	9.50E-15	9.65E-14	1.11E-06
trichloroethylene	4.78E-08	0.204	1.75E-11	2.78E-06	4.99E-09	5.67E-02	2.86E-12	1.03E-11	1.17E-04
tetrachloroethylene	4.78E-08	0.326	5.71E-11	2.78E-06	1.02E-08	1.46E-01	1.20E-13	8.80E-13	1.26E-05
benzene	4.78E-08	0.122	3.85E-11	2.78E-06	1.83E-08	1.24E-01	1.17E-12	1.55E-11	1.04E-04
toluene	4.78E-08	0.134	2.42E-10	2.78E-06	1.05E-07	8.33E-01	6.03E-12	4.55E-10	3.62E-03
ethylbenzene	4.78E-08	0.148	1.59E-10	2.78E-06	6.25E-08	5.72E-01	6.84E-12	3.08E-10	2.82E-03
m/p-xylene	4.78E-08	0.149	6.82E-11	2.78E-06	2.66E-08	2.44E-01	1.32E-11	2.53E-10	2.32E-03
o-xylene	4.78E-08	0.096	2.85E-11	2.78E-06	1.73E-08	1.58E-01	1.85E-11	2.30E-10	2.11E-03

Figure IV.3.3. Application of the fugacity model on sample B07/94/3, calculated by means of an EXCEL-programme (part I)

14. TOTAL MASS IN EACH COMPARTMENT		14.1. Wat		14.2. Air	
	mole	mole	g	g	g
chloroform	8.75E+00	7.15E-01	1.05E+03	8.54E+01	
tetrachloromethane	9.97E-02	3.09E+00	1.54E+01	4.76E+02	
1,1-dichloroethane	1.38E-01	7.27E-02	1.37E+01	7.20E+00	
1,2-dichloroethane	3.06E-01	3.09E-01	3.03E+01	3.06E+01	
1,1,1-trichloroethane	2.00E-01	1.02E+01	2.67E+01	1.36E+03	
trichloroethylene	4.65E-02	3.60E+00	6.12E+00	4.73E+02	
tetrachloroethylene	7.50E-02	7.34E+00	1.25E+01	1.22E+03	
benzene	1.44E+00	1.32E+01	1.12E+02	1.03E+03	
toluene	3.06E+00	7.55E+01	2.81E+02	6.94E+03	
ethylbenzene	1.00E+00	4.50E+01	1.06E+02	4.77E+03	
m/p-xylene	1.73E+00	1.92E+01	1.84E+02	2.03E+03	
o-xylene	2.06E+00	1.24E+01	2.18E+02	1.32E+03	

15. MASS BALANCES		15.1. Na,adv		15.2. Nw,adv	
	mole/s	mole/s	g/day	mole/s	g/day
	-5.64E-06	5.64E-06	-58.245		58.255
	-4.38E-08	4.81E-08	-0.583		0.640
	-8.63E-08	8.64E-08	-0.738		0.739
	-1.61E-07	1.62E-07	-1.378		1.382
	-3.76E-08	5.17E-08	-0.434		0.596
	2.14E-08	-1.64E-08	0.243		-0.186
	1.64E-08	-6.21E-09	0.235		-0.089
	-5.92E-07	6.10E-07	-3.989		4.113
	-3.24E-07	4.29E-07	-2.575		3.411
	1.52E-07	-8.96E-08	1.396		-0.821
	-6.49E-07	6.76E-07	-5.943		6.189
	-8.69E-07	8.86E-07	-7.956		8.117

Figure IV.3.3. Application of the fugacity model on sample B07/94/3, calculated by means of an EXCEL-programme (part 2)

In conclusion it can be stated that the main process determining the dynamics of the compounds in air and water is the air/water diffusive exchange. Moreover, this process can be assumed to be the main process with respect to the dynamics of the compounds in the whole marine environment since the mass transfer coefficients between other compartments (e.g. water/sediment) is far much lower. Transport to higher altitudes is the second important process. The rate of the atmospheric degradation and the wet deposition process is negligible to the rate of the air/water diffusive exchange.

#### **IV.3.3.4. Statistical approach**

##### **IV.3.3.4.1. Abundancies**

The abundancies calculated for the air compartment, the water compartment and the sum of both for all monitoring campaigns at all sampling locations are presented in Table IV.3.9, IV.3.10 and IV.3.11 respectively. The 5, 10, 25, 50, 75, 90 and 95 percentiles for the abundancies of each VOC are presented in Table IV.3.12. It can be seen that in the air compartment the 50 percentiles for the masses are below 0.15kg (for 1km<sup>2</sup>) for chloroform, 1,1-dichloroethane, 1,2-dichloroethane; between 0.5 and 0.6kg for trichloroethylene and tetrachloroethylene and from ±1 to ±2kg for tetrachloromethane, 1,1,1-trichloroethane and all MAHs except toluene, showing a 50 percentile of 5kg.

The 50 percentiles for the masses in water are below 0.15kg for all CHCs except chloroform. Chloroform and all MAHs show abundancies between 0.25 and 0.5kg in the water body.

The 50 percentiles for the sum of masses in air and water range for the CHCs from 0.05kg (1,1-dichloroethane) to 1.7kg (1,1,1-trichloroethane) whereas the MAHs are in the 1.8 to 2.6kg range except toluene (5.5kg).

**Table IV.3.9.a.** Masses (g) of the VOCs in air in an evaluative 1km<sup>2</sup> for each sample of the third campaign in 1994

	B07	S12	120	780	421	435	800
chloroform	85	104	145	178	139	91	452
tetrachloromethane	476	694	326	483	447	822	588
1,1-dichloroethane	7	18	22	7	28	31	23
1,2-dichloroethane	31	65	16	23	14	66	46
1,1,1-trichloroethane	1356	861	438	641	445	1310	614
trichloroethylene	473	399	213	159	115	596	157
tetrachloroethylene	1218	400	138	204	40	611	156
benzene	1030	1503	468	520	449	1508	1204
toluene	6944	5132	1246	2098	386	4976	2296
ethylbenzene	4769	7552	1262	2568	566	3190	2062
m/p-xylene	2031	2014	569	1089	215	1249	795
o-xylene	1318	1240	342	771	199	1057	549

**Table IV.3.9.b.** Masses (g) of the VOCs in air in an evaluative 1km<sup>2</sup> for each sample of the fourth campaign in 1994

	B07	S12	120
chloroform	106	100	83
tetrachloromethane	2289	1192	2092
1,1-dichloroethane	16	7	15
1,2-dichloroethane	110	91	87
1,1,1-trichloroethane	5600	1994	1694
trichloroethylene	1263	834	461
tetrachloroethylene	550	1063	350
benzene	1912	2149	1661
toluene	7435	6626	2377
ethylbenzene	2642	1342	827
m/p-xylene	4321	2022	1361
o-xylene	3449	1072	1366

**Table IV.3.9.c.** Masses (g) of the VOCs in air in an evaluative 1km<sup>2</sup> for each sample of the first campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	119	266	199	74	165	255	211
tetrachloromethane	1349	1153	1820	1626	2605	1026	1018
1,1-dichloroethane	17	10	19	12	23	7	9
1,2-dichloroethane	90	93	188	94	180	76	300
1,1,1-trichloroethane	2012	1300	2041	1515	2871	1092	1213
trichloroethylene	423	92	248	56	259	84	588
tetrachloroethylene	996	271	444	250	466	315	491
benzene	1739	1077	2245	1206	2491	1029	1238
toluene	10729	1994	3116	1183	2443	1315	3371
ethylbenzene	3575	1849	2458	1209	1118	1392	2083
m/p-xylene	3651	1191	3600	1142	663	2160	3787
o-xylene	2858	568	1585	378	301	829	2614

**Table IV.3.9.d.** Masses (g) of the VOCs in air in an evaluative 1km<sup>2</sup> for each sample of the second campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	123	128	83	156	141	538	127
tetrachloromethane	1209	1841	1569	937	812	2040	2129
1,1-dichloroethane	32	22	19	67	35	53	36
1,2-dichloroethane	96	187	60	181	252	642	82
1,1,1-trichloroethane	1375	1755	1723	1273	1232	2247	2278
trichloroethylene	739	587	707	1250	847	1469	591
tetrachloroethylene	508	610	883	1053	751	1159	585
benzene	1452	1434	1610	2170	3410	2709	1369
toluene	1189	2034	3145	3348	3567	6021	737
ethylbenzene	9769	962	1025	1697	12288	10575	2632
m/p-xylene	88529	1785	1833	3040	83596	37631	14174
o-xylene	51519	1525	1437	2698	58370	15751	5686

**Table IV.3.9.e.** Masses (g) of the VOCs in air in an evaluative 1km<sup>2</sup> for each sample of the third campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	83	86	197	412	96	83	83
tetrachloromethane	1369	1182	1001	1044	1120	759	1023
1,1-dichloroethane	12	15	16	24	19	13	13
1,2-dichloroethane	72	150	119	84	122	179	91
1,1,1-trichloroethane	1428	1734	1816	968	1590	1027	1139
trichloroethylene	1528	686	2454	2469	1935	762	901
tetrachloroethylene	428	430	1629	792	1185	821	964
benzene	1208	2003	3994	2032	3085	5868	2289
toluene	3284	4924	14035	6721	22448	11590	7108
ethylbenzene	549	759	2758	1682	3087	2936	2384
m/p-xylene	869	1011	2426	2223	2885	2548	2558
o-xylene	663	862	1901	1955	2258	1906	1882

**Table IV.3.9.f.** Masses (g) of the VOCs in air in an evaluative 1km<sup>2</sup> for each sample of the fourth campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	104	184	163	150	681	374	740
tetrachloromethane	1423	1479	1767	1583	2246	1617	1917
1,1-dichloroethane	20	22	7	14	12	13	13
1,2-dichloroethane	181	113	341	115	326	361	387
1,1,1-trichloroethane	1589	2012	1763	1843	2221	2107	1980
trichloroethylene	386	503	259	198	750	857	565
tetrachloroethylene	551	717	409	299	828	1191	733
benzene	6574	4497	5326	2978	10244	9748	9544
toluene	11520	8208	6348	5042	11333	15181	11253
ethylbenzene	1600	1528	1362	720	2907	2849	2446
m/p-xylene	1822	1754	1427	783	3999	3693	3701
o-xylene	1472	1266	1065	553	2625	2758	2340

**Table IV.3.10.a.** Masses (g) of the VOCs in water in an evaluative 1km<sup>2</sup> for each sample of the third campaign in 1994

	B07	S12	120	780	421	435	800
chloroform	1045	755	321	10603	650	695	988
tetrachloromethane	15	31	11	75	25	23	23
1,1-dichloroethane	14	73	14	86	36	34	34
1,2-dichloroethane	30	513	35	59	88	824	72
1,1,1-trichloroethane	27	695	25	74	122	56	76
trichloroethylene	6	406	53	129	560	437	167
tetrachloroethylene	12	1064	12	27	48	37	21
benzene	112	448	145	167	452	301	460
toluene	281	576	221	326	638	641	536
ethylbenzene	106	363	59	100	256	406	164
m/p-xylene	184	539	87	105	373	751	221
o-xylene	218	542	99	124	469	657	245

**Table IV.3.10.b.** Masses (g) of the VOCs in water in an evaluative 1km<sup>2</sup> for each sample of the fourth campaign in 1994

	B07	S12	120
chloroform	125	819	133
tetrachloromethane	13	38	19
1,1-dichloroethane	14	72	14
1,2-dichloroethane	65	682	46
1,1,1-trichloroethane	265	946	35
trichloroethylene	6	1039	6
tetrachloroethylene	27	1230	46
benzene	149	224	152
toluene	376	305	293
ethylbenzene	63	114	58
m/p-xylene	71	147	65
o-xylene	75	122	65

**Table IV.3.10.c.** Masses (g) of the VOCs in water in an evaluative 1km<sup>2</sup> for each sample of the first campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	6613	3134	313	170	797	980	738
tetrachloromethane	26	56	20	17	26	40	25
1,1-dichloroethane	24	126	18	11	37	39	36
1,2-dichloroethane	110	722	246	94	156	169	202
1,1,1-trichloroethane	48	1671	37	36	86	100	360
trichloroethylene	102	1600	78	133	219	454	671
tetrachloroethylene	37	1849	20	19	51	65	66
benzene	187	320	191	160	700	681	490
toluene	178	406	149	108	539	650	726
ethylbenzene	161	252	412	73	272	957	932
m/p-xylene	84	176	165	49	179	357	677
o-xylene	76	144	121	42	161	284	478

**Table IV.3.10.d.** Masses (g) of the VOCs in water in an evaluative 1km<sup>2</sup> for each sample of the second campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	65	1328	105	77	552	379	487
tetrachloromethane	20	80	24	15	49	58	134
1,1-dichloroethane	14	92	14	11	36	34	73
1,2-dichloroethane	86	2673	55	62	197	172	245
1,1,1-trichloroethane	48	1441	38	36	189	93	184
trichloroethylene	657	1279	257	122	527	676	600
tetrachloroethylene	25	1557	17	13	63	51	169
benzene	260	460	169	209	482	624	426
toluene	395	693	389	252	591	574	397
ethylbenzene	1302	892	624	449	1042	1736	1230
m/p-xylene	4105	2515	1709	1337	2287	4712	3363
o-xylene	1291	711	568	469	722	1368	1195



**Table IV.3.10.e.** Masses (g) of the VOCs in water in an evaluative 1km<sup>2</sup> for each sample of the third campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	130	876	80	135	571	505	4568
tetrachloromethane	23	82	20	18	186	66	155
1,1-dichloroethane	14	88	14	11	154	34	141
1,2-dichloroethane	58	3040	63	54	275	115	165
1,1,1-trichloroethane	43	1634	53	30	211	90	170
trichloroethylene	70	508	52	37	225	107	132
tetrachloroethylene	38	2448	50	27	184	99	570
benzene	150	325	170	68	601	268	426
toluene	452	1071	411	183	1150	669	1109
ethylbenzene	161	547	101	145	1089	961	782
m/p-xylene	274	1161	153	326	2301	2054	1440
o-xylene	210	862	124	260	2013	1873	1315

**Table IV.3.10.f.** Masses (g) of the VOCs in water in an evaluative 1km<sup>2</sup> for each sample of the fourth campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	84	1256	109	76	305	339	280
tetrachloromethane	20	48	19	15	51	67	34
1,1-dichloroethane	14	105	14	11	36	34	34
1,2-dichloroethane	132	1814	109	155	190	469	148
1,1,1-trichloroethane	33	867	32	26	77	87	53
trichloroethylene	109	663	37	41	84	101	67
tetrachloroethylene	39	3120	33	29	78	80	77
benzene	133	250	145	63	397	460	270
toluene	419	520	441	246	1194	1169	798
ethylbenzene	86	206	89	54	205	264	185
m/p-xylene	122	165	140	89	2343	403	265
o-xylene	87	211	115	59	254	356	214

**Table IV.3.11.a.** Total masses (g) of the VOCs in water and in air for an evaluative 1km<sup>2</sup> for each sample of the third campaign in 1994

	B07	S12	120	780	421	435	800
chloroform	1131	859	465	10781	789	786	1441
tetrachloromethane	492	725	337	559	471	845	611
1,1-dichloroethane	21	90	35	94	64	66	58
1,2-dichloroethane	61	578	51	82	102	890	118
1,1,1-trichloroethane	1383	1556	462	716	567	1365	690
trichloroethylene	479	805	266	288	675	1033	324
tetrachloroethylene	1230	1465	150	231	88	648	176
benzene	1142	1950	613	686	901	1809	1664
toluene	7226	5708	1467	2424	1024	5617	2832
ethylbenzene	4875	7915	1321	2668	822	3596	2226
m/p-xylene	2215	2553	656	1194	588	1999	1017
o-xylene	1536	1782	441	895	667	1714	794

**Table IV.3.11.b.** Total masses (g) of the VOCs in water and in air for an evaluative 1km<sup>2</sup> for each sample of the fourth campaign in 1994

	B07	S12	120
chloroform	231	918	216
tetrachloromethane	2302	1230	2111
1,1-dichloroethane	29	79	28
1,2-dichloroethane	175	773	133
1,1,1-trichloroethane	5864	2940	1730
trichloroethylene	1269	1873	468
tetrachloroethylene	577	2293	396
benzene	2060	2373	1814
toluene	7811	6931	2670
ethylbenzene	2706	1456	886
m/p-xylene	4393	2169	1425
o-xylene	3524	1194	1431

**Table IV.3.11.c.** Total masses (g) of the VOCs in water and in air for an evaluative 1km<sup>2</sup> for each sample of the first campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	6732	3400	511	244	962	1235	949
tetrachloromethane	1375	1209	1840	1642	2631	1066	1043
1,1-dichloroethane	41	136	37	23	60	46	45
1,2-dichloroethane	200	815	434	188	337	245	502
1,1,1-trichloroethane	2060	2971	2078	1551	2957	1192	1573
trichloroethylene	525	1691	327	189	478	538	1260
tetrachloroethylene	1033	2120	464	269	516	380	557
benzene	1926	1396	2436	1366	3191	1711	1728
toluene	10908	2400	3265	1291	2982	1965	4097
ethylbenzene	3736	2101	2870	1282	1391	2349	3015
m/p-xylene	3734	1367	3765	1192	842	2518	4464
o-xylene	2934	712	1706	420	461	1114	3092

**Table IV.3.11.d.** Total masses (g) of the VOCs in water and in air for an evaluative 1km<sup>2</sup> for each sample of the second campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	188	1456	188	233	693	917	615
tetrachloromethane	1229	1920	1593	952	861	2098	2263
1,1-dichloroethane	46	114	32	78	71	87	109
1,2-dichloroethane	181	2860	115	243	450	814	327
1,1,1-trichloroethane	1423	3195	1760	1310	1422	2341	2463
trichloroethylene	1395	1866	965	1372	1374	2145	1191
tetrachloroethylene	533	2167	900	1066	814	1210	754
benzene	1712	1894	1779	2379	3892	3334	1795
toluene	1584	2726	3534	3600	4159	6595	1134
ethylbenzene	11070	1854	1649	2146	13330	12311	3862
m/p-xylene	92634	4301	3542	4378	85882	42343	17537
o-xylene	52809	2236	2004	3168	59092	17119	6881

**Table IV.3.11.e.** Total masses (g) of the VOCs in water and in air for an evaluative 1km<sup>2</sup> for each sample of the third campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	213	962	277	546	667	588	4651
tetrachloromethane	1392	1264	1021	1062	1305	824	1178
1,1-dichloroethane	25	103	29	35	173	47	154
1,2-dichloroethane	130	3189	182	139	397	294	256
1,1,1-trichloroethane	1471	3367	1869	998	1801	1117	1309
trichloroethylene	1598	1195	2505	2506	2159	869	1033
tetrachloroethylene	466	2878	1679	819	1368	920	1534
benzene	1358	2328	4164	2100	3686	6136	2715
toluene	3735	5995	14445	6904	23599	12259	8217
ethylbenzene	710	1307	2859	1828	4176	3897	3166
m/p-xylene	1143	2173	2579	2549	5186	4602	3998
o-xylene	874	1724	2025	2215	4270	3779	3197

**Table IV.3.11.f.** Total masses (g) of the VOCs in water and in air for an evaluative 1km<sup>2</sup> for each sample of the fourth campaign in 1995

	B07	S12	120	780	421	435	800
chloroform	187	1441	272	227	986	713	1020
tetrachloromethane	1443	1526	1786	1598	2297	1684	1950
1,1-dichloroethane	34	127	21	25	48	48	47
1,2-dichloroethane	312	1927	450	270	516	830	535
1,1,1-trichloroethane	1622	2879	1795	1869	2297	2193	2033
trichloroethylene	495	1166	295	239	834	958	633
tetrachloroethylene	590	3836	442	328	906	1271	810
benzene	6707	4747	5472	3041	10641	10208	9814
toluene	11939	8728	6789	5287	12528	16351	12051
ethylbenzene	1685	1734	1450	773	3112	3114	2631
m/p-xylene	1945	1919	1566	873	6342	4097	3966
o-xylene	1559	1477	1180	612	2879	3114	2554

**Table IV.3.12.a.** Percentiles (g) of the masses in the air compartment for an evaluative 1km<sup>2</sup>

Compound	5	10	25	50	75	90	95
Chloroform	83	83	95	140	202	461	684
Tetrachloromethane	441	482	908	1201	1780	2141	2304
1,1-Dichloroethane	7	7	12	17	23	35	54
1,2-Dichloroethane	16	30	75	103	183	343	400
1,1,1-Trichloroethane	445	638	1195	1590	1999	2250	3007
Trichloroethylene	83	113	256	587	850	1569	2455
Tetrachloroethylene	133	199	388	568	903	1186	1239
Benzene	467	978	1231	1958	3166	6871	9773
Toluene	719	1188	2247	4950	7628	11834	15544
Ethylbenzene	565	755	1249	2072	2914	7774	10660
m/p-Xylene	551	771	1179	2027	3662	16520	83843
o-Xylene	296	374	815	1455	2617	6693	51861

**Table IV.3.12.b.** Percentiles (g) of the masses in the water compartment for an evaluative 1km<sup>2</sup>

Compound	5	10	25	50	75	90	95
Chloroform	75	80	132	496	902	3277	6813
Tetrachloromethane	13	15	20	26	57	87	157
1,1-Dichloroethane	11	11	14	34	72	107	142
1,2-Dichloroethane	35	53	65	152	253	923	2691
1,1,1-Trichloroethane	26	30	37	77	195	996	1636
Trichloroethylene	6	34	69	133	535	712	1295
Tetrachloroethylene	12	17	27	49	117	1586	2482
Benzene	68	131	158	264	454	603	682
Toluene	147	183	302	447	655	1113	1170
Ethylbenzene	58	63	105	254	810	1103	1323
m/p-Xylene	64	83	145	300	1507	2600	4135
o-Xylene	58	74	122	250	671	1320	1880

**Table IV.3.12.c.** Percentiles (g) of the sum of mass in air and water compartment for an evaluative 1km<sup>2</sup>

Compound	5	10	25	50	75	90	95
Chloroform	188	211	265	750	1048	3525	6934
Tetrachloromethane	464	552	929	1285	1800	2266	2318
1,1-Dichloroethane	21	25	34	48	88	128	155
1,2-Dichloroethane	61	100	166	303	546	994	2876
1,1,1-Trichloroethane	562	713	1351	1745	2308	2993	3492
Trichloroethylene	237	286	479	962	1379	2146	2505
Tetrachloroethylene	147	226	459	812	1295	2180	2926
Benzene	682	1118	1712	2080	3738	7018	10230
Toluene	1129	1449	2712	5452	8345	12720	16713
Ethylbenzene	770	880	1455	2490	3631	8231	12362
m/p-Xylene	653	870	1411	2551	4382	20018	86220
o-Xylene	440	597	1059	1753	3128	7905	53123

#### IV.3.3.4.1.1. Cluster analysis

A cluster analysis on all individual CHCs and a cluster analysis on all individual MAHs was carried out by means of the statistical package SPSS (*Statistical Package for Social Sciences*, originally developed for application in social sciences, but now extended for a broad range of applications). The obtained agglomeration schedules for both groups of VOCs for the dataset on air masses, water masses and the sum of both, are presented in Annex IV.3.5.

##### IV.3.3.4.1.1.1. CHCs

For the air masses of CHCs sample B07/94/4 is distinguished because of high masses of tetrachloromethane (2289g versus 75percentile 1780g), 1,1,1-trichloroethane (5600g versus 75percentile 1999g) and trichloroethylene (1263g versus 75percentile 850g). Next, three samples are separated : 120/95/3, 780/95/3 and 421/95/3, all samples from the third period in 1995. They show high masses of trichloroethylene (2454, 2469 and 1935g versus 75percentile 850g). The sample 780/95/3 showed also a high mass of chloroform (412g versus

75percentile 202g), whereas the samples 120/95/3 and 421/95/3 had in addition a high mass of tetrachloroethylene (1629 and 1185g versus 75percentile 903g).

The dataset on the water masses shows to groups to be separated. First the samples B07/95/1, 800/95/3 and 780/94/3 are clustered separately. They all have high masses of chloroform (6613, 4568 and 10603g versus 75percentile 902g). Next, the samples 780/94/3 and 800/95/3 have high masses of tetrachloromethane (75 and 155g versus 75percentile 57g) and of 1,1-dichloroethane (86 and 141g versus 75percentile 72g). The second group consists of all cases in the Scheldt estuary at location S12. All samples show masses of 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene above the 75 percentile levels, whereas also trichloroethylene showed masses above the 75 percentile in 4 cases.

The third cluster analysis, i.e. on the sum of masses in air and water, shows that the sample 780/94/3 is separated from the other samples because of high masses of chloroform (10781g versus 75percentile 1048g) and of 1,1-dichloroethane (94g versus 75percentile 88g).

#### IV.3.3.4.1.1.2 MAHs

The air masses in the three samples taken during the second sampling campaign in 1995 are clustered separately because of high concentrations of C<sub>2</sub>-substituted MAHs. The samples B07/95/2, 421/95/2 and 435/95/2 have high masses of ethylbenzene (9769, 12288, 10575g versus 75percentile 2914g), m/p-xylene (88529, 83596, 37631g versus 75percentile 3662g) and o-xylene (51519, 58370, 15751g versus 75percentile 2617g).

Also water samples taken during the second period of 1995 are clustered separately. The samples are B07/95/2, 435/95/2 and 800/95/2. They also show elevated concentrations of ethylbenzene (1302, 1736, 1230g versus 75percentile 1103g), m/p-xylene (4105, 4712, 3363g versus 75percentile 2600g) and o-xylene (1291, 1368, 1195g versus 75percentile 1320g).

Finally, the cluster analysis on the sum of masses in air and water shows the separate clustering of samples from the second period of 1995. The samples B07/95/2, 421/95/2 and 435/95/2 are the same samples as separated in the cluster analysis on air masses. It is clear that they show also high concentrations of C<sub>2</sub>-substituted MAHs (ethylbenzene: 11070, 13330, 12311g versus 75percentile 3631g; m/p-xylene: 92634, 85882, 42343g versus 75percentile 4382g; o-xylene: 52809, 59092, 17119g versus 75percentile 3128g).

#### IV.3.3.4.1.2. Principal component analysis

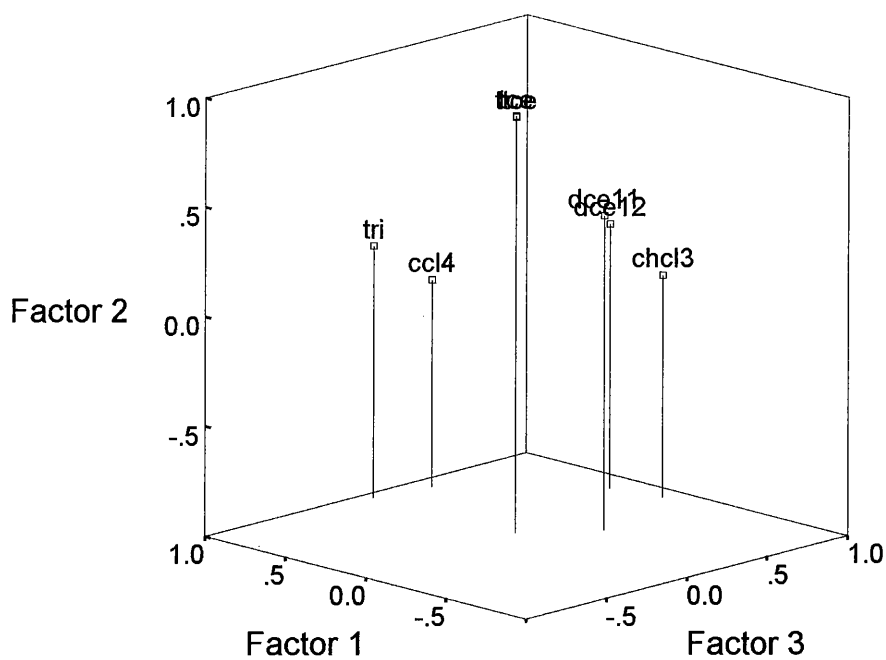
A principal component analysis (PCA) was done on the datasets of the abundancies of the CHCs and MAHs in the compartments air, water and the sum of both. This was done by means of the statistical package SPSS. The results are presented in Annex IV.3.6.

##### IV.3.3.4.1.2.1. CHCs

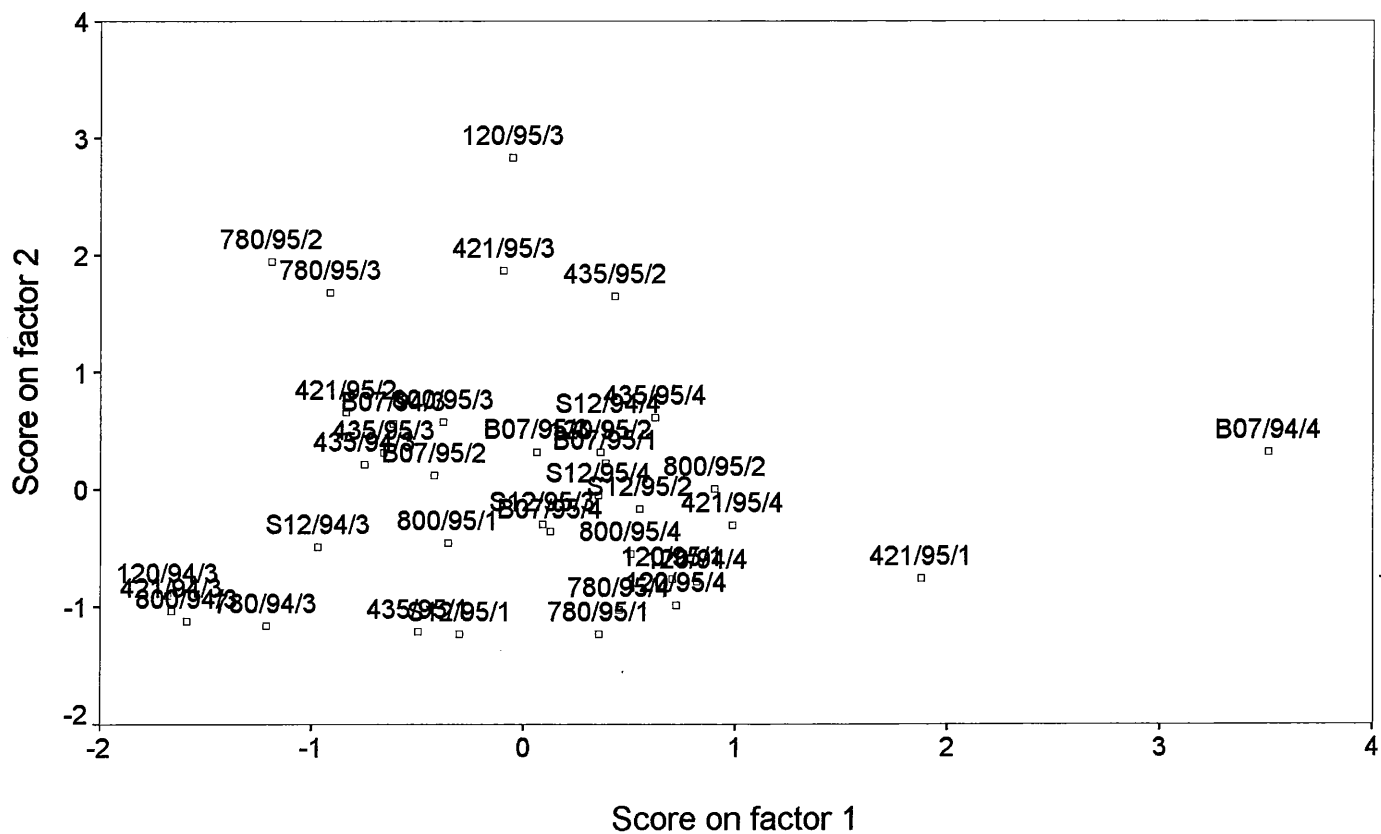
In the PCA on CHCs in the air compartment three factors with eigenvalues above 1 were found. Factor one was mainly loaded by tetrachloromethane (0.89) and 1,1,1-trichloroethane (0.94), factor 2 by trichloroethylene (0.90) and tetrachloroethylene (0.87) and factor 3 by chloroform (0.88) and 1,2-dichloroethane (0.83). Only 1,1-dichloroethane proved not to be well related to one single factor. The factor loadings are illustrated in Figure IV.3.4. The factor score plots are presented in Figure IV.3.5. Two samples are separated by a high score on factor 1, i.e. B07/94/4 and 421/95/1. They show high masses of tetrachloromethane (2289, 2605g versus 75 percentile 1780g) and 1,1,1-trichloroethane (5600, 2871g versus 75 percentile 1999g). According to factor two, five samples are remarked. These are samples from the second and third campaign in 1995: 780/95/2, 435/95/2, 120/95/3, 780/95/3 and 421/95/3. Their masses of trichloroethylene (1250, 1469, 2454, 2469, 1935g versus 75 percentile 850g) and tetrachloroethylene (1053, 1159, 1629, 792 and 1185g versus 75 percentile 903g) are elevated. Finally, three samples have high scores on factor 3. These samples are the samples from locations far from the coast: 435/95/2, 421/95/4 and 800/95/4. The masses of chloroform (538, 681, 740g versus 75 percentile 202g) and 1,2-dichloroethane (642, 326, 387g versus 75 percentile 183g) are high.

When the PCA on the water masses of the CHCs is considered, two groups of samples are separated according to two factors (Figure IV.3.6 and IV.3.7). The first factor is mainly loaded by 1,2-dichloroethane (0.89), 1,1,1-trichloroethane (0.96), trichloroethylene (0.79) and tetrachloroethylene (0.92), whereas factor 2 is mainly governed by chloroform (0.71), tetrachloromethane (0.85) and 1,1-dichloroethane (0.80). The first group remarked are all samples taken in the Scheldt estuary at location S12. They show high scores on factor 1 because 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene have masses above the 75 percentile in all cases, except trichloroethylene in two cases.





**Figure IV.3.4.** Factor loading plot of the PCA on the masses of CHCs in air (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, tce: tetrachloroethylene)



**Figure IV.3.5.a.** Factor score plot of the PCA on the masses of CHCs in air (factor 1 and 2)

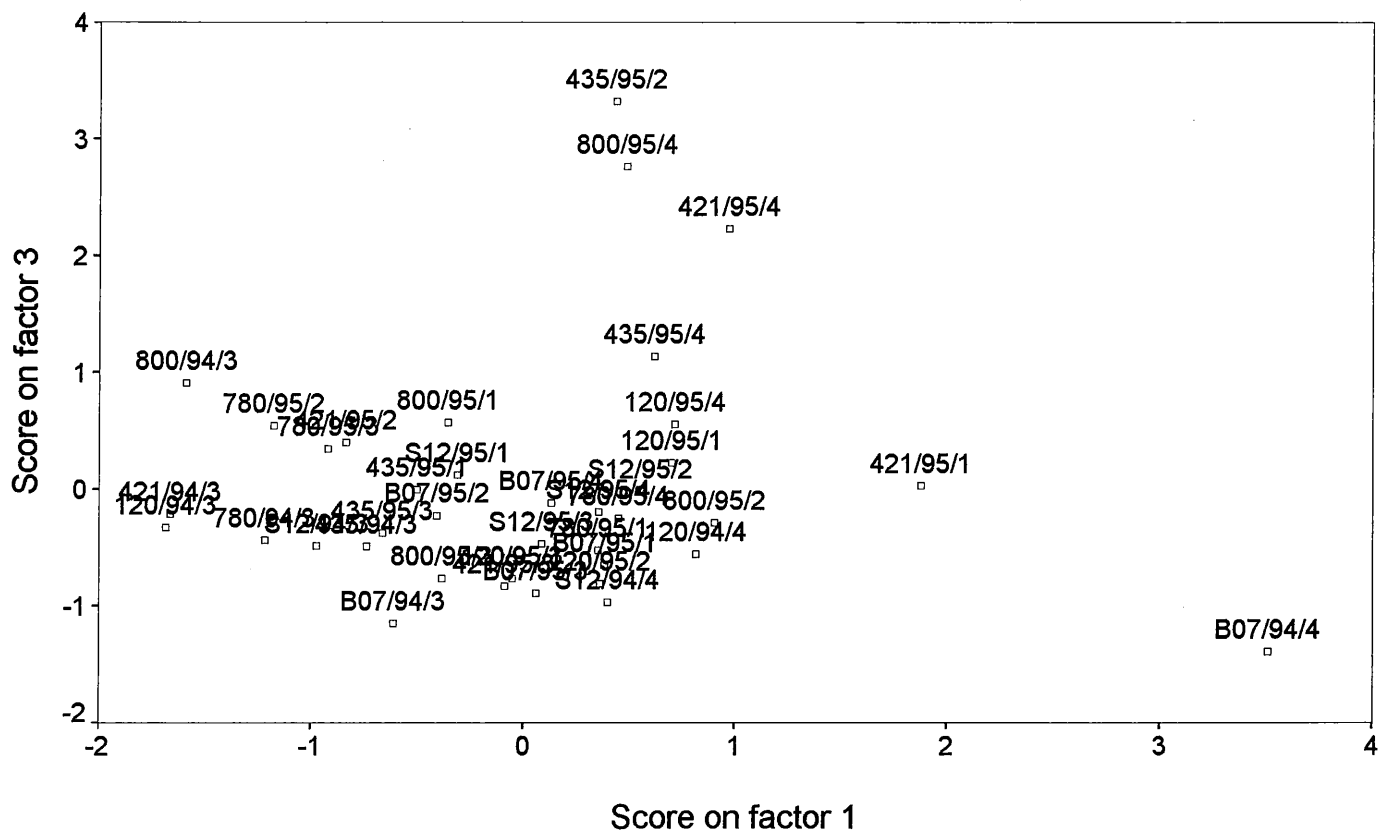
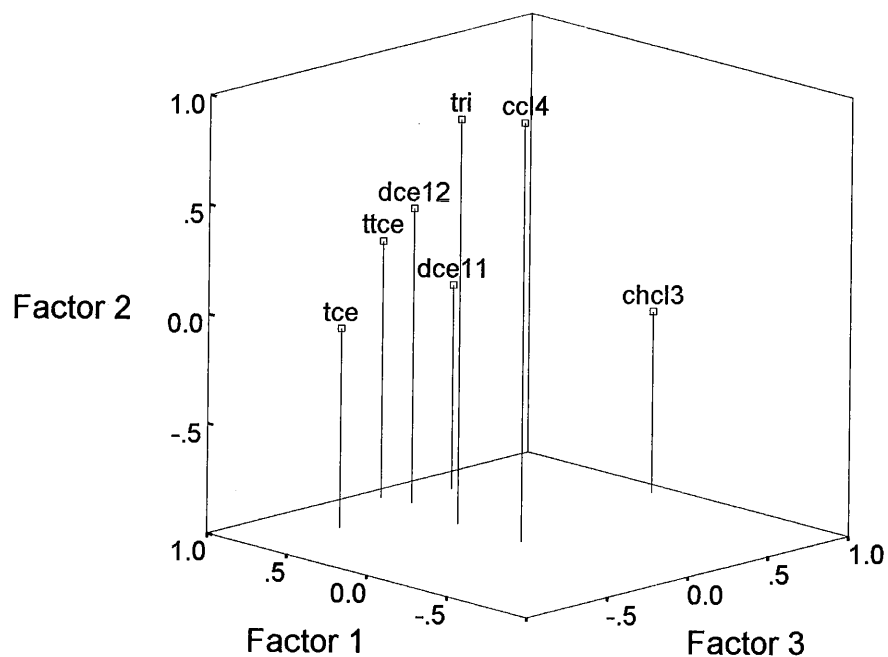
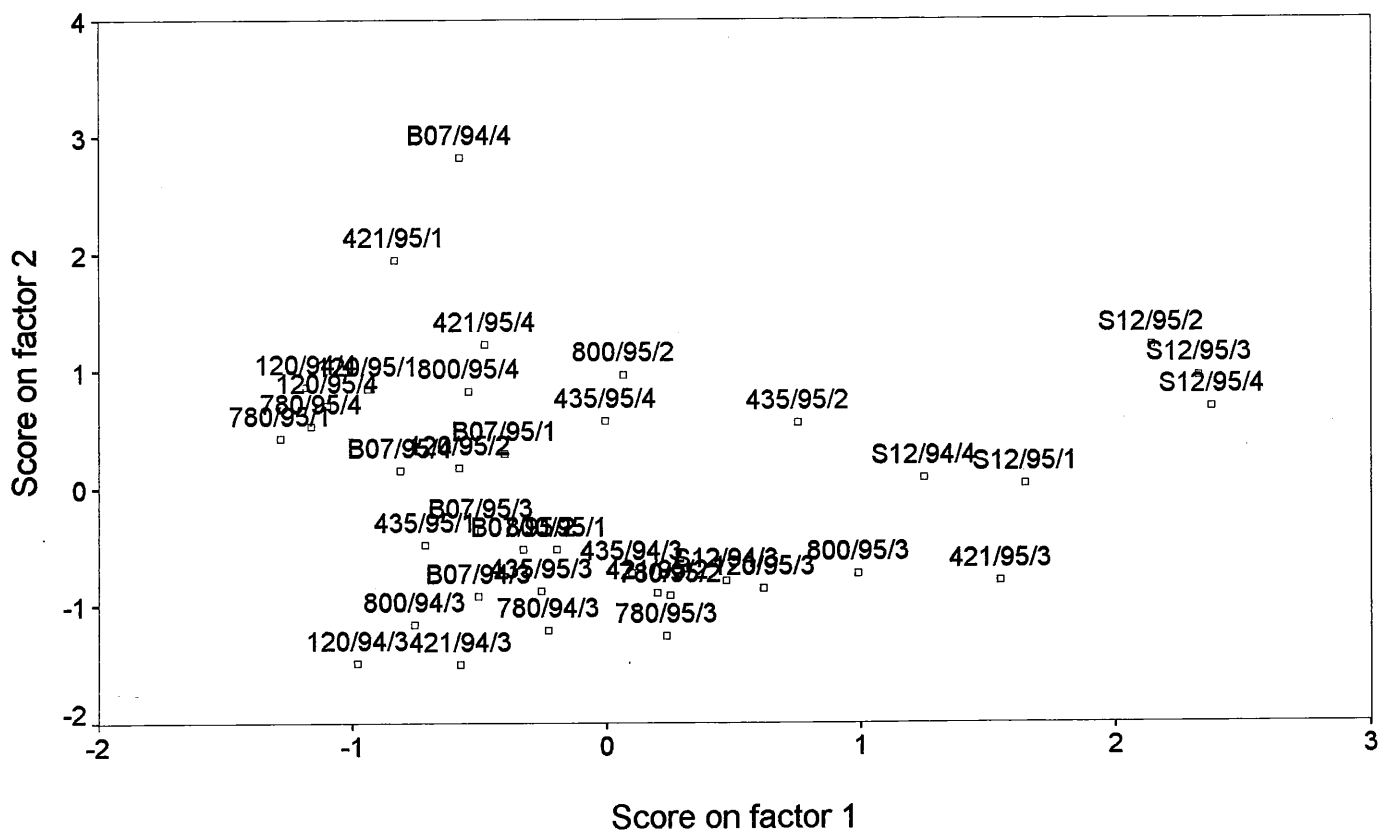


Figure IV.3.5.b. Factor score plot of the PCA on the masses of CHCs in air (factor 1 and 3)





**Figure IV.3.8.** Factor loading plot of the PCA on the masses of CHCs in air and water (chcl3: chloroform, cc4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttce: tetrachloroethylene)



**Figure IV.3.9.a.** Factor score plot of the PCA on the masses of CHCs in air and water (factor 1 and 2)

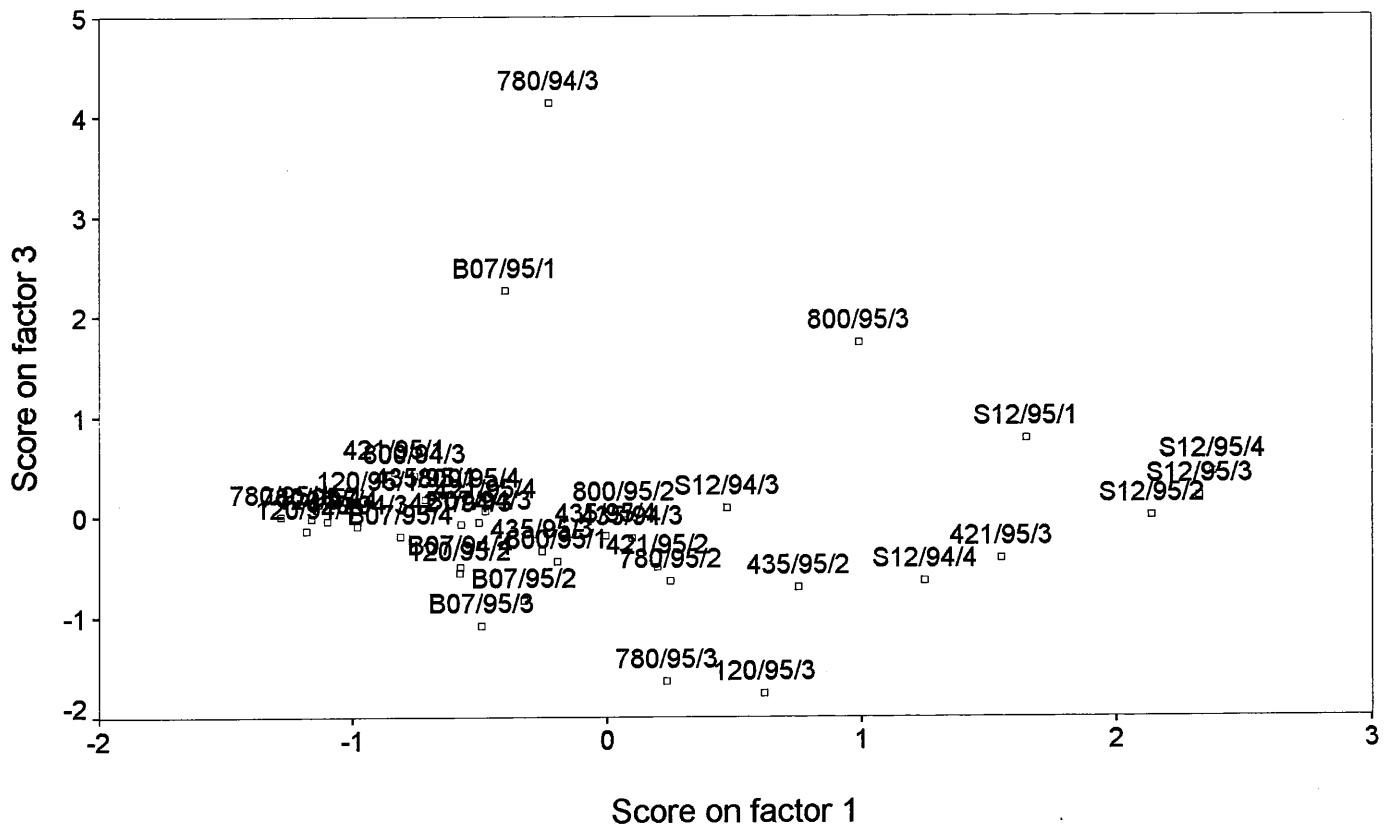


Figure IV.3.9.b. Factor score plot of the PCA on the masses of CHCs in air and water (factor 1 and 3)

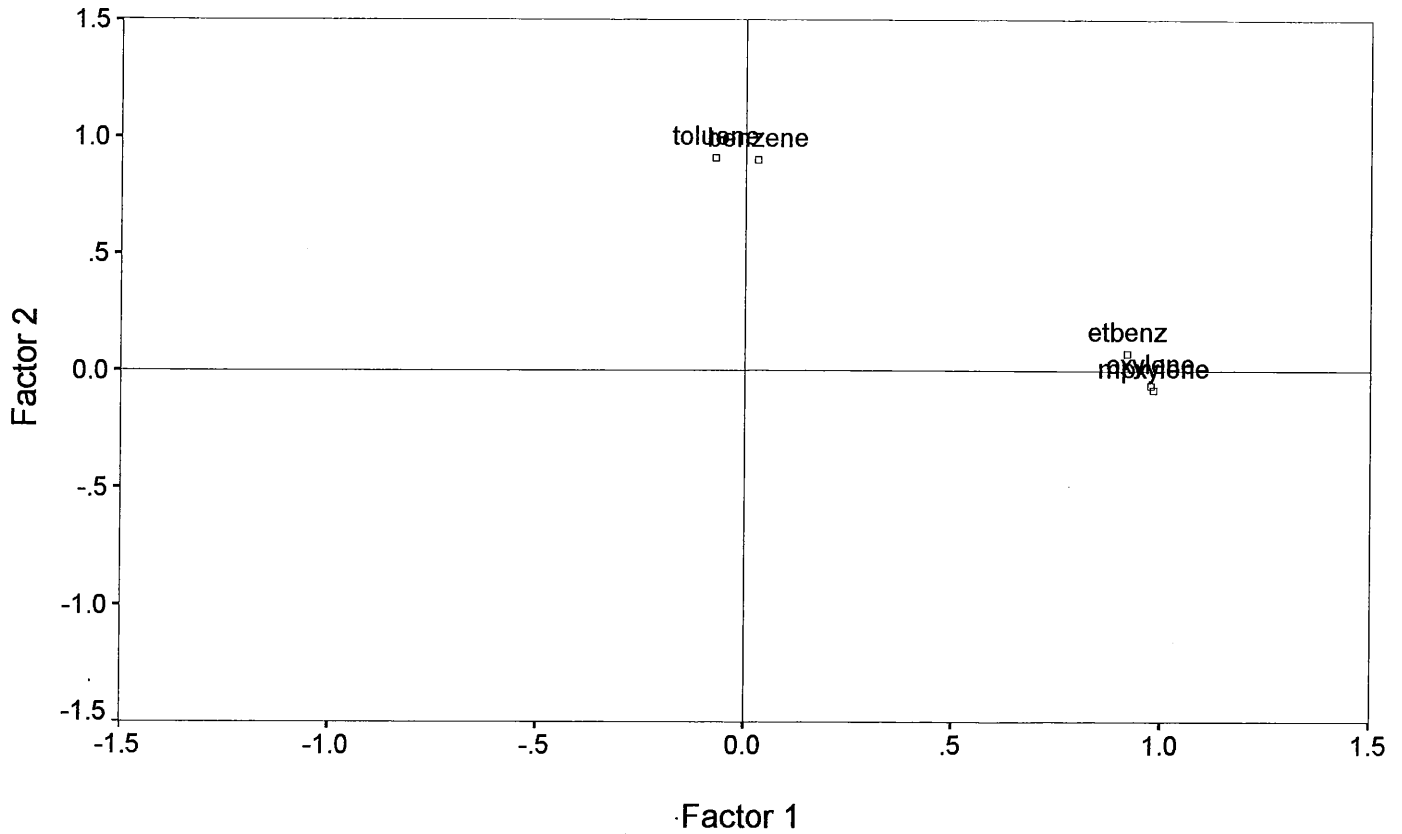
The second group shows scores on factor two above 2.5 and consists of the samples 780/94/3, 421/95/3 and 800/95/3. Their masses of chloroform, tetrachloromethane and 1,1-dichloroethane are elevated (chloroform: 10603, 571, 4568g versus 75 percentile 902g; tetrachloromethane: 75, 186, 155g versus 75 percentile 57g; 1,1-dichloroethane: (86, 154, 141g versus 75 percentile 72g).

The PCA on the sum of mass shows 3 factors with eigenvalues above 1. Factor 1 is mainly loaded by 1,1-dichloroethane (0.79), 1,2-dichloroethane (0.74), tetrachloroethylene (0.89), factor two by tetrachloromethane (0.91) and 1,1,1-trichloroethane (0.84) and factor 3 by chloroform (0.90) (Figure IV.3.8). Figure IV.3.9 shows that factor 1 is related to the first factor on CHCs in water samples, separating S12-samples (*See* Figure IV.3.7). According to factor 2, samples 421/95/1 and B07/94/4 are separated because of elevated concentrations of tetrachloromethane (2631g and 2302g, 75 percentile: 1800g) and 1,1,1-trichloroethane (2957g and 5864g, 75 percentile: 2308g). Finally, three samples (780/94/3, B07/95/1 and 800/95/3) show high scores on factor 3. These samples were already found to be separated by factor 2 in the analysis on CHCs in water samples (*See* Figure IV.3.7).

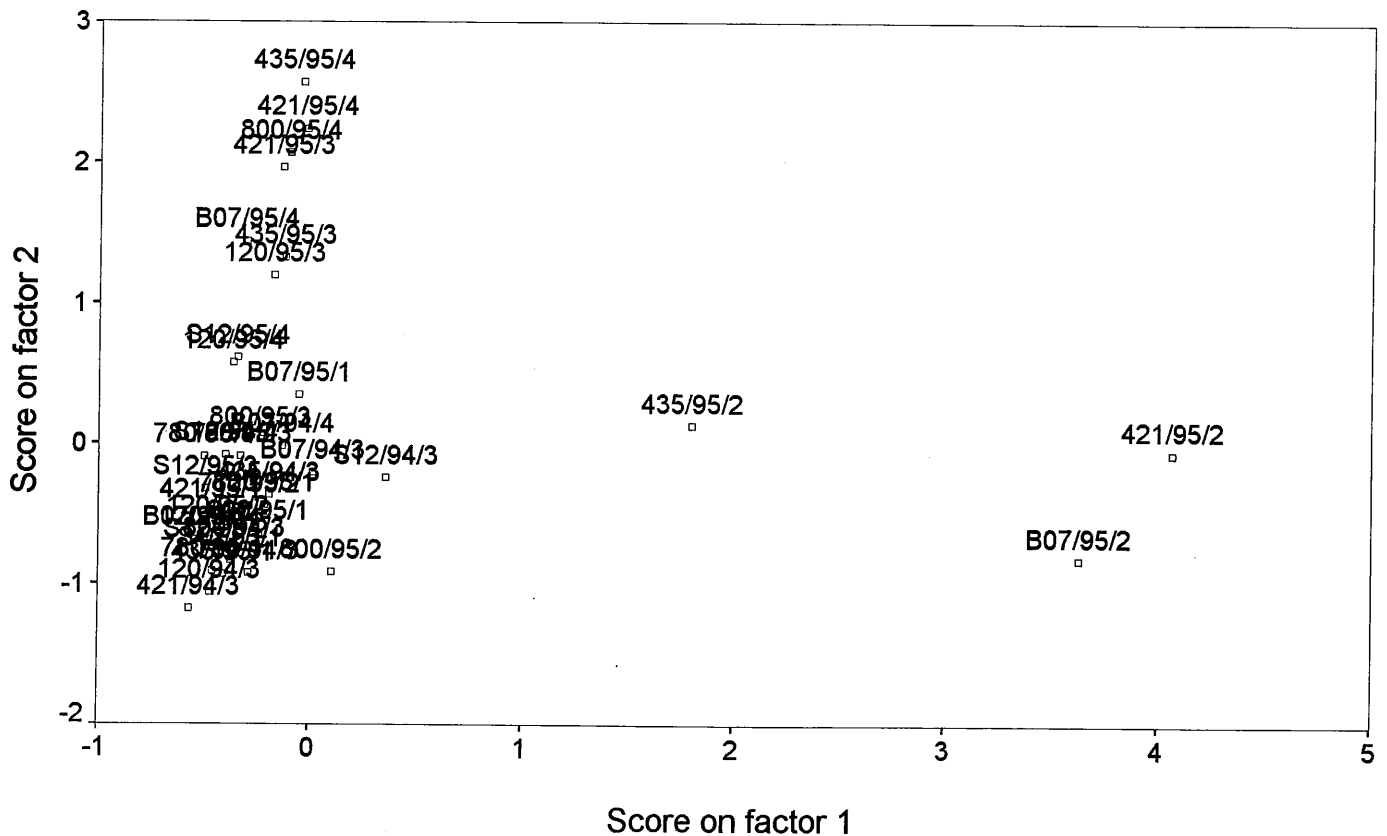
#### IV.3.3.4.1.2.2. MAHs

The PCA on air masses show two main factors (Figure IV.3.10). The first factor is mainly loaded by ethylbenzene (0.92), m/p-xylene (0.98) and o-xylene (0.97), whereas the second factor is mainly loaded by benzene (0.90) and toluene (0.91). The score plot (Figure IV.3.11) shows 3 samples to be distinguished by high scores on factor 1. They are all samples from the second period of 1995: B07/95/2, 421/95/2 and 435/95/2. Their masses of ethylbenzene (9769, 12288, 10575g versus 75 percentile 2914g), m/p-xylene (88529, 83596, 37631g versus 75 percentile 3662g) and o-xylene (51519, 58370, 15751g versus 75 percentile 2617g) are elevated. According to factor 2 a gradient of samples is remarked but no one group of samples can be strictly separated.

The PCA on the water masses of the MAHs only shows one factor so that the interpretation with respect to a limited group of MAHs cannot be done.



**Figure IV.3.10.** Factor loading plot of the PCA on the masses of MAHs in air (etbenz: ethylbenzene, mpxylene: m/p-xylene, oxylene: o-xylene)



**Figure IV.3.11.** Factor score plot of the PCA on the masses of MAHs in air

The PCA on the masses in air and water showed two factors (Figure IV.3.12). The factor 1 is mainly loaded by ethylbenzene (0.92), m/p-xylene (0.99) and o-xylene (0.98) and factor two by benzene (0.91) and toluene (0.90). The same samples as in the PCA on air masses are remarked by a high score on factor 1: B07/95/2, 421/95/2 and 435/95/2 (Figure IV.3.13). Their masses of ethylbenzene (11070, 13330, 12311g versus 75 percentile 3631g), m/p-xylene (92634, 85882, 42343g versus 75 percentile 4382g) and o-xylene (52809, 59092, 17119g versus 75 percentile 3128g) are elevated. According to factor two, a single group cannot be separated from all cases since one recognizes rather a gradient. This is the same conclusion as for the PCA on the air masses.





#### **IV.3.3.4.2. Air/water diffusive exchange**

The water/air diffusive exchange rates for all monitoring campaigns at all sampling locations are presented in Table IV.3.13. The 5, 10, 25, 50, 75, 90 and 95 percentiles for the water/air fluxes of each VOC are presented in Table IV.3.14. The 50 percentiles for the exchange rates of all CHCs are in the 0.5 to 1.2g.km<sup>-2</sup>.day<sup>-1</sup>, except for 1,2-dichloroethane (2.5g.km<sup>-2</sup>.day<sup>-1</sup>), trichloroethylene (6.6g.km<sup>-2</sup>.day<sup>-1</sup>) and chloroform (12.2g.km<sup>-2</sup>.day<sup>-1</sup>). The 50 percentiles of the MAHs are all within the 3.4 to 4.7g.km<sup>-2</sup>.day<sup>-1</sup> range except of toluene (6.3g.km<sup>-2</sup>.day<sup>-1</sup>). So in general more samples with water to air exchange than air to water exchange are observed.

##### **IV.3.3.4.2.1. Cluster analysis**

A cluster analysis on the exchange rates of all individual CHCs and of all individual MAHs was carried out by means of the statistical package SPSS. The obtained agglomeration schedules for both groups of VOCs are presented in Annex IV.3.7.

###### **IV.3.3.4.2.1.1. CHCs**

Two cases are distinguished by the cluster analysis on the diffusive exchange rates of all CHCs: 780/94/3 and B07/95/1. Both cases show high water to air exchange fluxes of chloroform (711, 647g.km<sup>-2</sup>.day<sup>-1</sup> versus 75 percentile 27g.km<sup>-2</sup>.day<sup>-1</sup>), tetrachloromethane (4.6, 1.1 versus 75 percentile 0.7g.km<sup>-2</sup>.day<sup>-1</sup>) and 1,1-dichloroethane (5.7, 2.3 versus 75 percentile 1.5g.km<sup>-2</sup>.day<sup>-1</sup>).

**Table IV.3.13.a.** Air/water exchange rates for all samples of third campaign in 1994 (g.km<sup>-2</sup>.day<sup>-1</sup>)

	B07	S12	120	780	421	435	800
chloroform	58.3	16.4	17.5	711.5	13.3	15.3	20.9
tetrachloromethane	0.6	0.5	0.5	4.6	0.3	0.2	0.3
1,1-dichloroethane	0.7	1.6	0.7	5.7	0.7	0.7	0.7
1,2-dichloroethane	1.4	10.9	1.8	3.8	1.7	17.8	1.1
1,1,1-trichloroethane	0.6	13.8	1.0	4.2	2.1	0.4	1.2
trichloroethylene	-0.2	7.9	2.5	7.8	10.6	8.4	3.3
tetrachloroethylene	-0.1	21.4	0.5	1.5	0.9	0.4	0.3
benzene	4.1	7.7	7.0	9.8	8.3	3.7	7.7
toluene	3.4	6.2	9.3	16.7	11.6	5.5	7.4
ethylbenzene	-0.8	0.3	1.3	2.6	4.0	4.0	0.7
m/p-xylene	6.2	8.5	3.5	4.7	6.5	12.9	3.3
o-xylene	8.1	8.7	4.2	5.8	8.2	10.9	3.8

**Table IV.3.13.b.** Air/water exchange rates for all samples of fourth campaign in 1994 (g.km<sup>-2</sup>.day<sup>-1</sup>)

	B07	S12	120
chloroform	10.2	27.3	11.0
tetrachloromethane	-0.5	0.7	0.2
1,1-dichloroethane	1.1	2.4	1.1
1,2-dichloroethane	3.4	22.0	2.3
1,1,1-trichloroethane	15.0	28.0	1.0
trichloroethylene	-2.0	31.0	-0.4
tetrachloroethylene	1.5	37.3	3.2
benzene	5.8	2.4	7.0
toluene	7.5	-3.6	16.1
ethylbenzene	-1.7	1.1	2.4
m/p-xylene	-5.6	0.9	1.5
o-xylene	-6.9	0.8	0.1

**Table IV.3.13.c.** Air/water exchange rates for all samples of first campaign in 1995 (g.km<sup>-2</sup>.day<sup>-1</sup>)

	B07	S12	120	780	421	435	800
chloroform	646.7	104.5	29.2	19.4	28.1	36.5	27.4
tetrachloromethane	1.1	1.2	0.2	0.4	-1.4	0.6	0.0
1,1-dichloroethane	2.3	4.1	1.6	1.3	1.2	1.5	1.3
1,2-dichloroethane	8.3	23.0	18.9	8.4	0.7	4.5	-0.4
1,1,1-trichloroethane	1.3	50.8	0.3	1.7	-1.2	2.1	11.3
trichloroethylene	8.0	49.3	6.4	14.1	6.7	16.1	22.6
tetrachloroethylene	1.7	57.2	1.1	1.7	1.0	1.8	1.6
benzene	9.4	7.5	7.6	12.5	13.3	21.0	12.9
toluene	-28.5	7.6	0.6	6.7	8.2	17.9	12.4
ethylbenzene	1.3	3.5	26.7	3.3	4.9	27.9	24.8
m/p-xylene	-5.8	2.7	1.6	1.1	3.4	4.7	10.1
o-xylene	-8.2	2.4	2.4	2.4	3.7	5.6	3.5

**Table IV.3.13.d.** Air/water exchange rates for all samples of second campaign in 1995 (g.km<sup>-2</sup>.day<sup>-1</sup>)

	B07	S12	120	780	421	435	800
chloroform	2.5	22.3	4.4	3.6	8.7	5.1	8.2
tetrachloromethane	0.4	0.8	0.4	0.4	0.5	0.2	1.5
1,1-dichloroethane	0.5	1.5	0.6	0.5	0.5	0.5	1.2
1,2-dichloroethane	2.7	44.3	1.7	1.3	0.5	-4.1	3.4
1,1,1-trichloroethane	1.1	21.8	0.5	1.0	2.2	0.2	1.7
trichloroethylene	25.7	19.5	9.6	4.5	7.1	9.4	9.0
tetrachloroethylene	0.7	24.0	0.1	0.0	0.5	0.1	2.4
benzene	8.3	5.7	4.1	6.5	1.3	5.5	4.7
toluene	13.9	8.5	10.5	6.7	3.1	-0.5	5.2
ethylbenzene	36.3	12.2	22.5	18.3	-1.2	12.6	15.3
m/p-xylene	31.6	35.3	62.6	56.9	-81.6	20.3	31.9
o-xylene	-55.9	8.3	18.9	16.2	-104.3	-10.0	7.2

**Table IV.3.13.e.** Air/water exchange rates for all samples of third campaign in 1995 (g.km<sup>-2</sup>.day<sup>-1</sup>)

	B07	S12	120	780	421	435	800
chloroform	5.1	13.5	2.9	5.7	8.5	8.0	73.7
tetrachloromethane	0.5	1.0	0.5	0.6	2.4	0.8	2.1
1,1-dichloroethane	0.5	1.3	0.5	0.5	2.3	0.5	2.2
1,2-dichloroethane	1.8	46.9	1.7	2.0	3.3	0.5	2.0
1,1,1-trichloroethane	1.0	23.0	1.3	0.9	2.3	0.9	2.1
trichloroethylene	1.4	6.9	0.1	-0.2	1.7	1.0	1.3
tetrachloroethylene	1.2	35.0	1.2	0.9	2.1	1.1	8.1
benzene	4.2	3.1	1.4	0.5	4.8	-3.5	3.7
toluene	12.9	11.6	-0.4	0.6	-8.7	-2.8	8.6
ethylbenzene	5.2	6.9	1.1	4.6	11.7	10.9	8.9
m/p-xylene	8.8	15.0	3.1	11.6	27.6	26.4	17.8
o-xylene	6.5	10.9	1.8	8.3	23.7	23.9	16.1

**Table IV.3.13.f.** Air/water exchange rates for all samples of fourth campaign in 1995 (g.km<sup>-2</sup>.day<sup>-1</sup>)

	B07	S12	120	780	421	435	800
chloroform	3.1	16.5	4.0	3.3	2.8	4.5	2.5
tetrachloromethane	0.3	0.3	0.1	0.1	0.0	0.5	-0.1
1,1-dichloroethane	0.5	1.4	0.5	0.5	0.5	0.5	0.5
1,2-dichloroethane	3.4	23.7	0.8	6.3	-0.5	3.8	-1.7
1,1,1-trichloroethane	0.3	10.0	0.2	0.1	-0.1	0.1	-0.3
trichloroethylene	3.6	7.8	1.1	1.6	0.4	0.7	0.4
tetrachloroethylene	1.1	38.1	1.0	1.1	0.6	0.5	0.7
benzene	-6.7	-1.2	-3.8	-2.4	-12.2	-10.0	-12.5
toluene	-2.7	-0.8	6.5	3.0	-0.8	-5.9	-5.3
ethylbenzene	0.9	1.2	1.4	1.3	-1.0	0.1	-0.5
m/p-xylene	1.9	0.6	3.0	2.7	25.6	0.9	-1.1
o-xylene	0.2	1.0	2.0	1.4	-1.5	-0.1	-1.3

**Table IV.3.14.** Percentiles of the air/water exchange rates ( $\text{g.km}^{-2}.\text{day}^{-1}$ )

Compound	5	10	25	50	75	90	95
Chloroform	2.50	2.84	4.43	12.15	27.29	76.81	649.97
Tetrachloromethane	-0.54	-0.05	0.22	0.45	0.72	1.53	2.48
1,1-Dichloroethane	0.49	0.51	0.52	0.73	1.48	2.28	4.22
1,2-Dichloroethane	-1.80	-0.45	1.24	2.49	8.32	23.08	44.40
1,1,1-Trichloroethane	-0.34	0.11	0.40	1.18	2.80	21.96	29.12
Trichloroethylene	-0.47	-0.19	1.08	6.55	9.43	22.89	31.94
Tetrachloroethylene	-0.03	0.14	0.58	1.12	2.15	35.26	39.02
Benzene	-12.23	-7.04	1.10	4.72	7.68	12.52	13.73
Toluene	-9.64	-5.40	-0.56	6.32	9.63	14.07	16.73
Ethylbenzene	-1.27	-0.83	1.03	3.39	11.81	24.95	28.31
m/p-Xylene	-9.55	-1.52	1.57	4.70	18.41	32.27	57.22
o-Xylene	-58.36	-8.41	0.17	3.57	8.34	16.46	23.67

#### IV.3.3.4.2.1.2. MAHs

For the cluster analysis on the exchange of MAHs, two cases are separated from the others: B07/95/2 and 421/95/2. The sample 421/95/2 is separated because of high air to water exchange transfer of ethylbenzene ( $-1.2\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $1.03\text{g.km}^{-2}.\text{day}^{-1}$ ), m/p-xylene ( $-81.6\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $1.6\text{g.km}^{-2}.\text{day}^{-1}$ ) and o-xylene ( $-104\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $0.2\text{g.km}^{-2}.\text{day}^{-1}$ ). Sample B07/95/2 is separated because it shows simultaneously high water to air transfer of ethylbenzene ( $36.3\text{g.km}^{-2}.\text{day}^{-1}$  versus 75 percentile  $11.8\text{g.km}^{-2}.\text{day}^{-1}$ ) and m/p-xylene ( $31.6\text{g.km}^{-2}.\text{day}^{-1}$  versus 75 percentile  $18.4\text{g.km}^{-2}.\text{day}^{-1}$ ) and air to water transfer of o-xylene ( $-55.9\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $0.2\text{g.km}^{-2}.\text{day}^{-1}$ ).

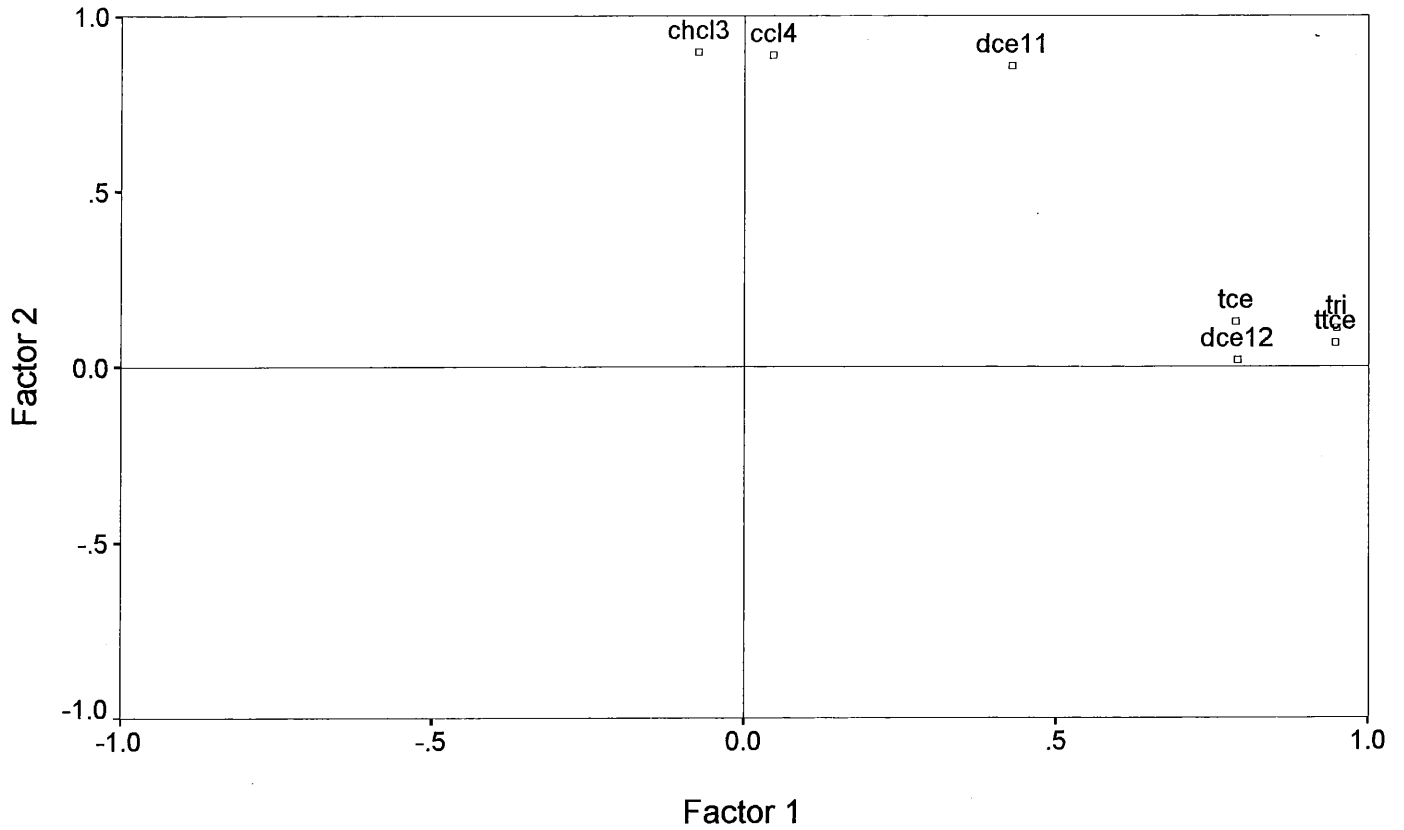
#### IV.3.3.4.2.2. Principal component analysis

A principal component analysis (PCA) was done on the dataset of the exchange rates of CHCs and MAHs. The results are presented in Annex IV.3.8.

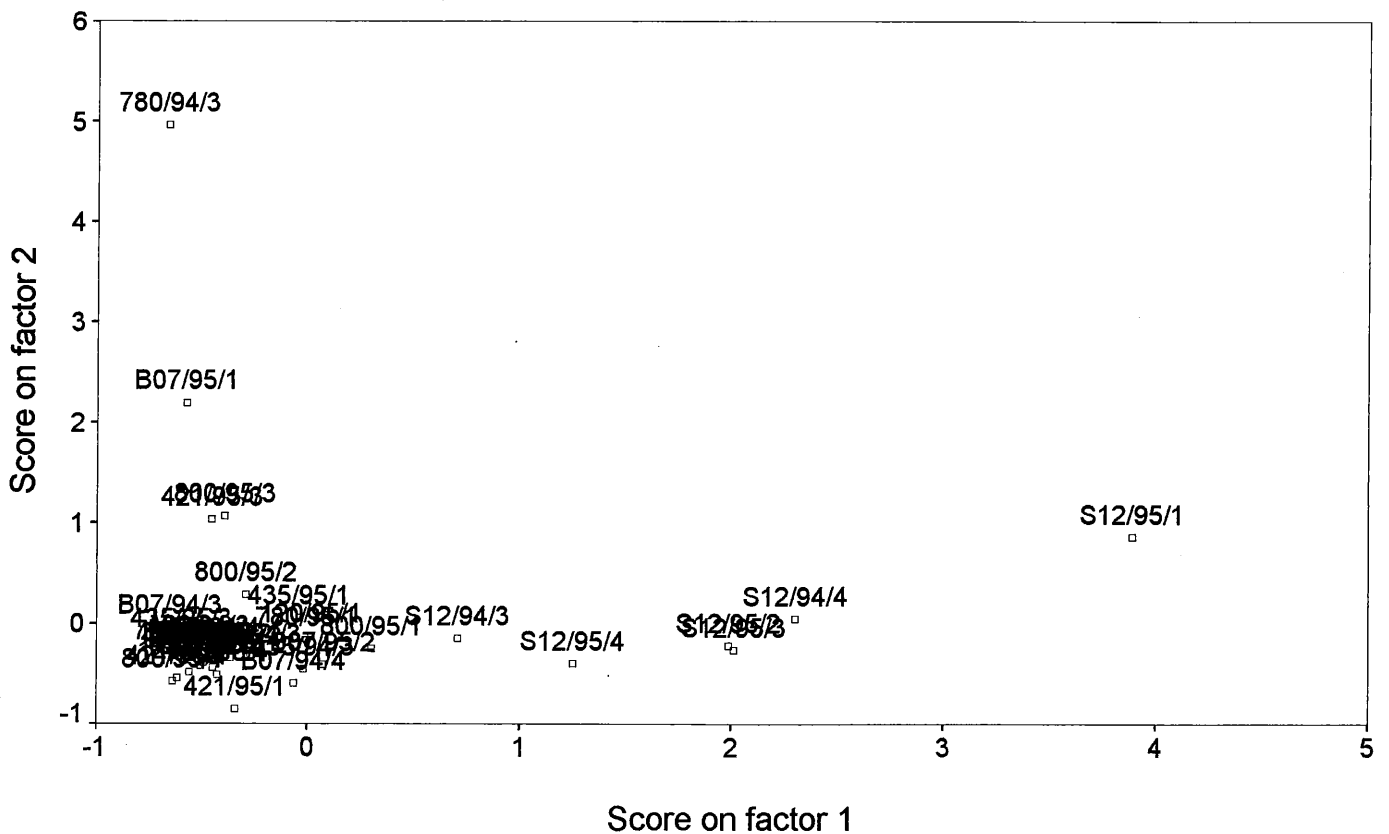
#### IV.3.3.4.2.2.1. CHCs

The PCA on all CHCs shows two factors with eigenvalue above 1. The first factor is loaded by 1,2-dichloroethane (0.79), 1,1,1-trichloroethane (0.95), trichloroethylene (0.79) and tetrachloroethylene (0.95), whereas factor two is mainly loaded by chloroform (0.90), tetrachloromethane (0.89) and 1,1-dichloroethane (0.86) (Figure IV.3.14). The factor score plot (Figure IV.3.15) shows that all samples in the Scheldt estuary taken on location S12 are separated by high scores on factor 1. They all have exchange rates for 1,2-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene above the respective 75 percentiles whereas the exchange rates of trichloroethylene are near or above the 75 percent level.

According to the second factor four samples are remarked by high scores: 780/94/3, B07/95/1, 800/95/3 and 421/95/3. They all have elevated water to air exchange fluxes for chloroform, tetrachloromethane and 1,1-dichloroethane, i.e. above the 75 percentile levels except for chloroform for the case 421/95/3.



**Figure IV.3.14.** Factor loading plot of the PCA on the air/water diffusive exchanges of CHCs (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttoe: tetrachloroethylene)



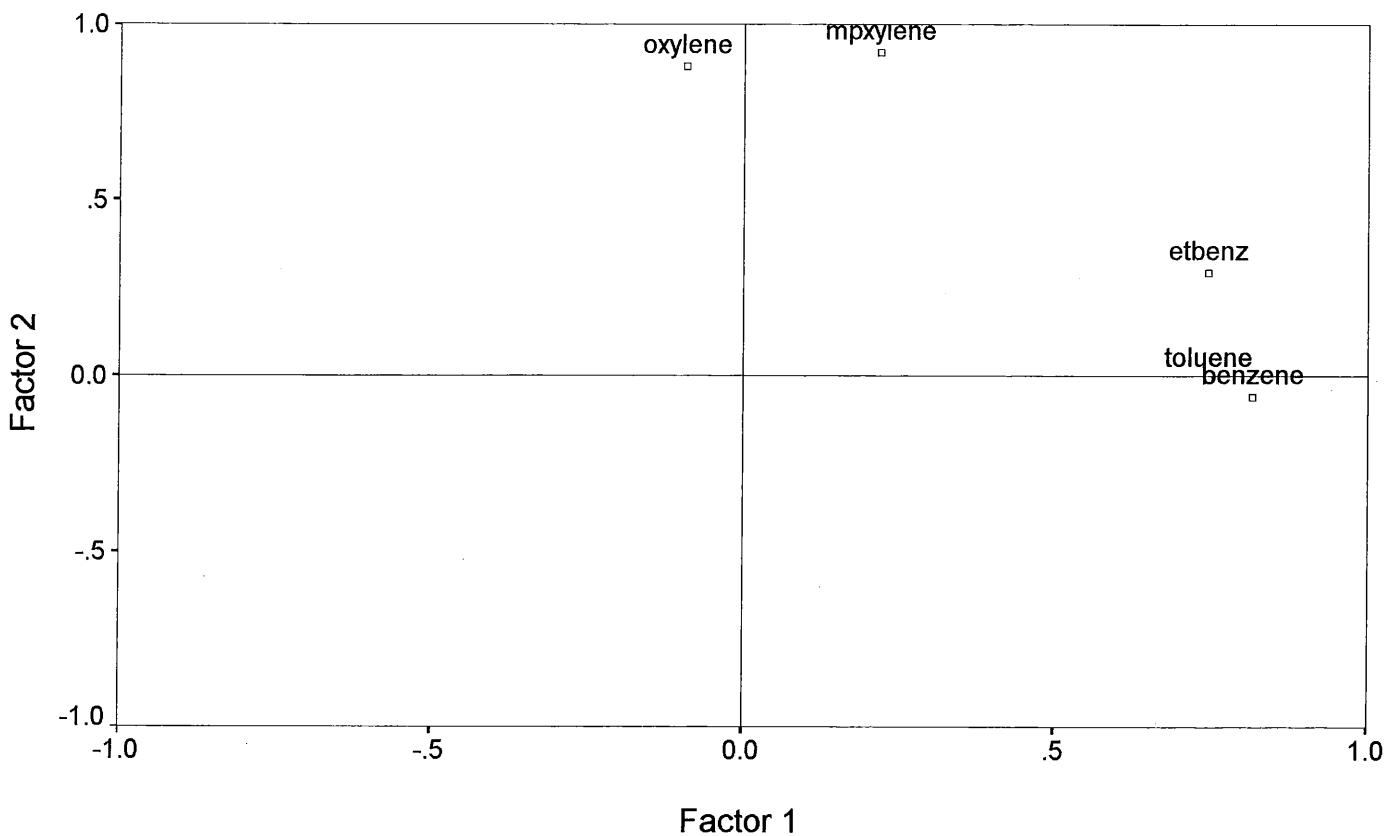
**Figure IV.3.15.** Factor score plot of the PCA on the air/water diffusive exchanges of CHCs



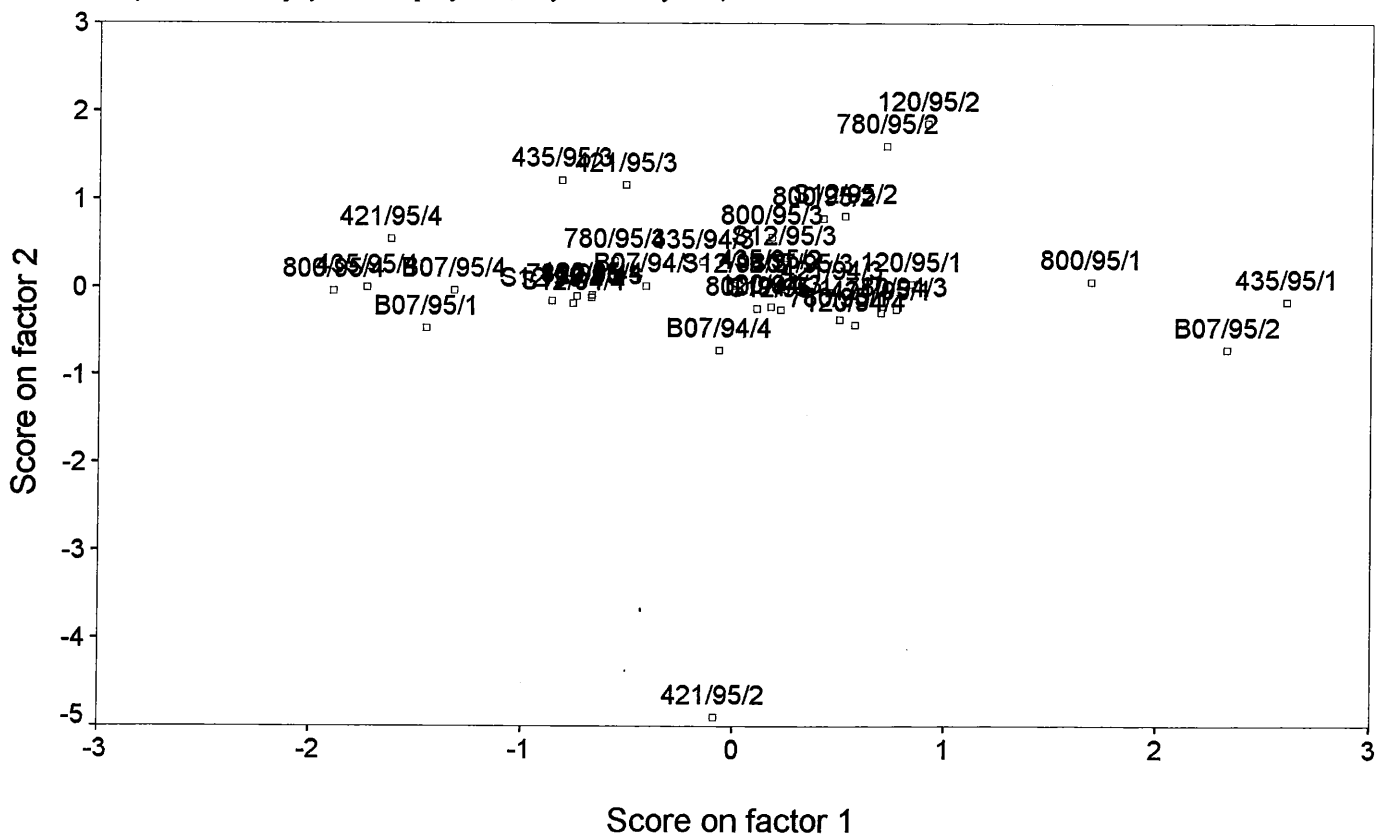
#### IV.3.3.4.2.2.2. MAHs

The PCA on the diffusive exchange rate of all MAHs shows two factors with eigenvalue above 1. The first factor is loaded mainly by benzene (0.82), toluene (0.75) and ethylbenzene (0.75), whereas factor two is governed by m/p-xylene (0.92) and o-xylene (0.88) (Figure IV.3.16).

The factor score plot is presented in Figure IV.3.17. Three set of samples can be remarked. First, three samples show high scores on factor 1: 435/95/1 (2.6), 800/95/1 (1.7) and B07/95/2 (2.3). They all show water to air exchange transfers of benzene, toluene and ethylbenzene above the respective 75 percentiles. Secondly, sample 421/95/2 is remarked by a low score on factor 2 (-4.9) because of high air to water exchange of ethylbenzene ( $-1.25\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $1.03\text{g.km}^{-2}.\text{day}^{-1}$ ) but especially of m/p-xylene ( $-91.6\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $1.6\text{g.km}^{-2}.\text{day}^{-1}$ ) and o-xylene ( $-104.3\text{g.km}^{-2}.\text{day}^{-1}$  versus 25 percentile  $0.2\text{g.km}^{-2}.\text{day}^{-1}$ ). Finally, the two cases of the location near the coast in the second period of 1995 are distinguished by a high score on factor two, i.e. the samples 120/95/2 (1.9) and 780/95/2 (1.6). For ethylbenzene, m/p-xylene and o-xylene, both cases show water to air exchange velocities above the respective 75 percentiles.



**Figure IV.3.16.** Factor loading plot of the PCA on the air/water diffusive exchanges of MAHs (etbenz: ethylbenzene, mpxylene: m/p-xylene, oxylene: o-xylene)



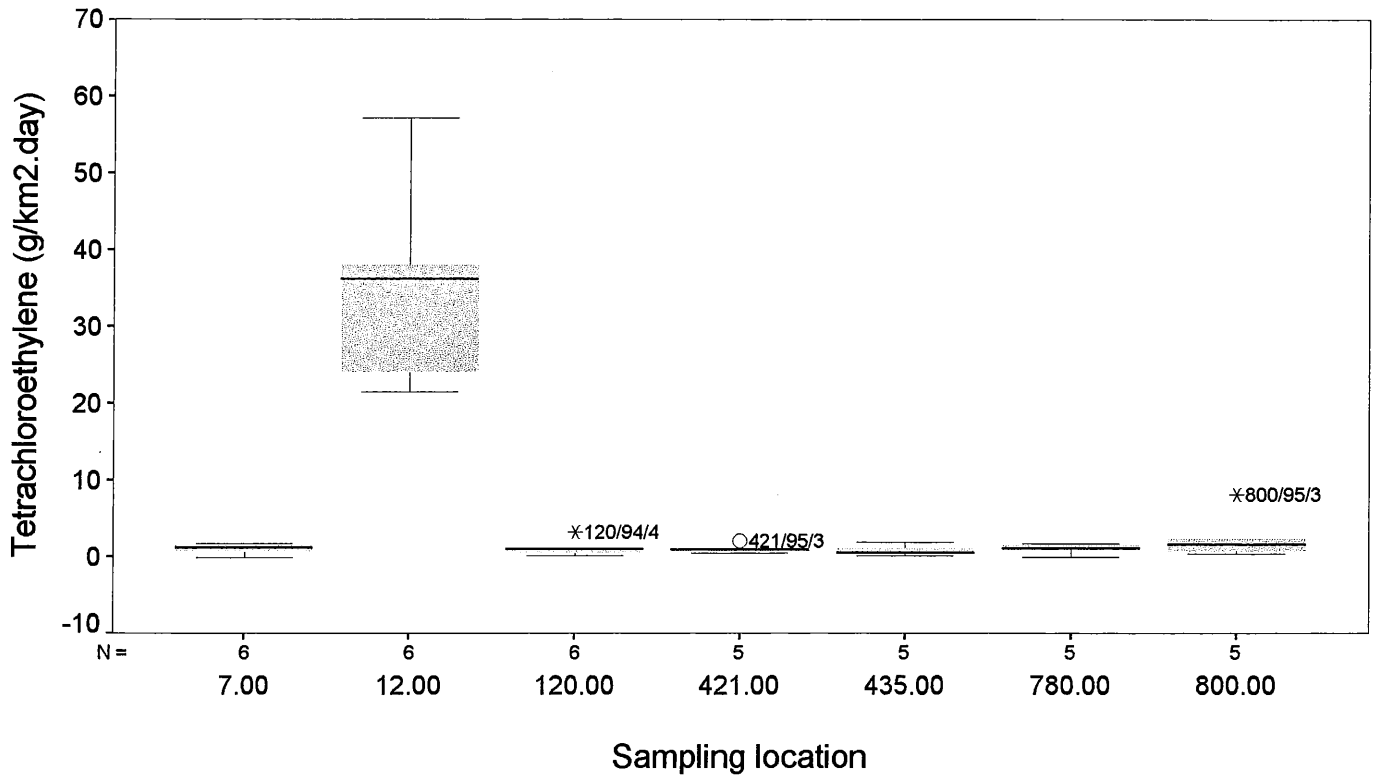
**Figure IV.3.17.** Factor score plot of the PCA on the air/water diffusive exchanges of MAHs

#### IV.3.3.4.2.3. Factor analysis

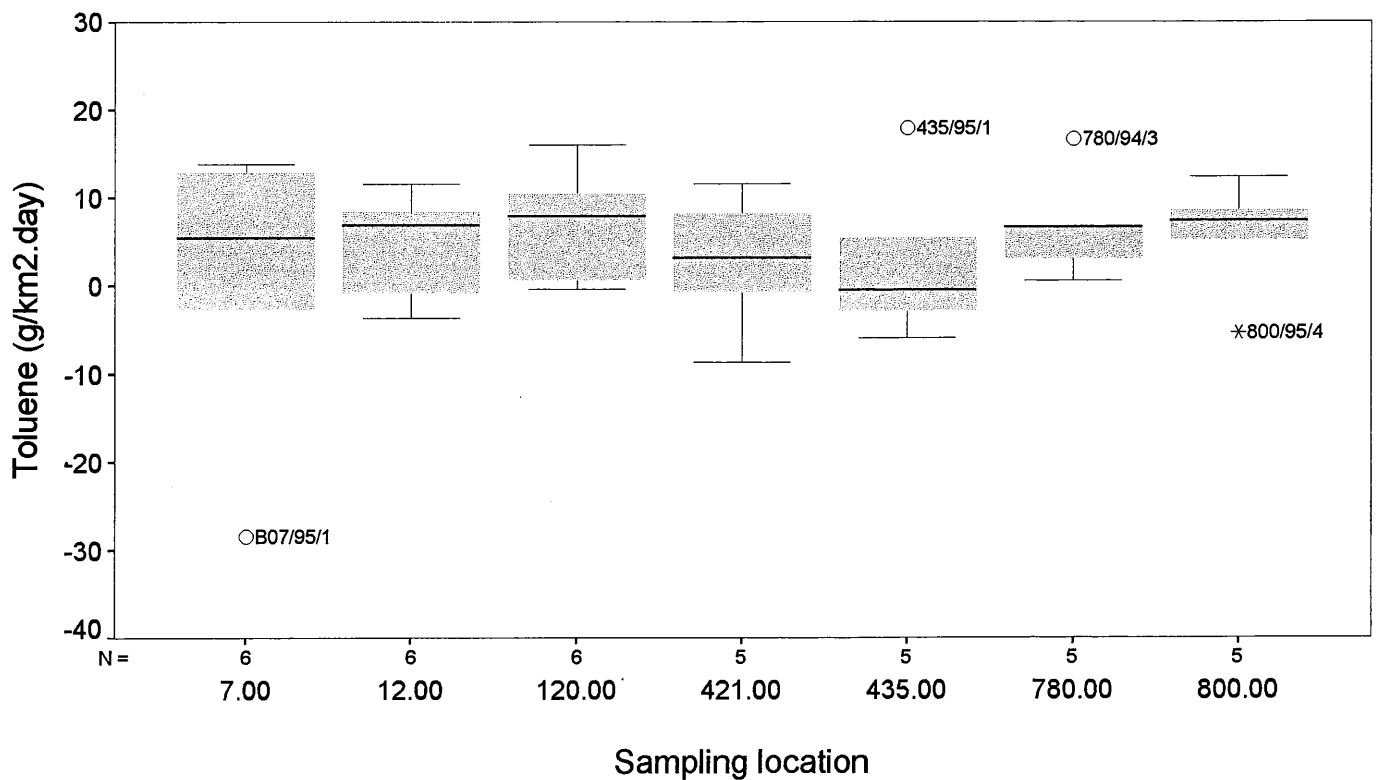
Three factors can be recognized in order to investigate their effect on the water/air exchange fluxes, i.e. sampling location, period of sampling and year of sampling.

Before the statistical approach, the dataset of air/water exchange rates was checked for normal distribution. Only the fluxes of benzene and toluene proved to be normally distributed (K-S test at 0.05 significance level) so that for these two VOCs a one-way analysis of variance can be carried out, whereas for the other VOCs non-parametric tests (Kruskal-Wallis test) is needed.

For the factor sampling location, the flux rates are plotted in boxplots in figure IV.3.18 and IV.3.19 for tetrachloroethylene and toluene respectively. It can be remarked from these plots that for tetrachloroethylene the fluxes at location S12 are enhanced, due to higher water column concentrations. For all VOCs, this representation of the exchange rates is given in Annex IV.3.9. Similar to tetrachloroethylene, higher exchange rates at location S12 are remarked from the plots for 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane and trichloroethylene. From the statistical tests (Annex IV.3.10) no differences for the exchange rates at the different locations are remarked for all MAHs and for the CHCs chloroform, tetrachloromethane, 1,1-dichloroethane and trichloroethylene (significance level 0.05). The CHCs 1,2-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene showed significant elevated exchange rates at location S12. The non-parametric test on 1,1-dichloroethane and trichloroethylene showed significance levels of 0.11 and 0.25 respectively so that the visual interpretation of the boxplots cannot be confirmed statistically by these tests.



**Figure IV.3.18.** Water to air exchange rates of tetrachloroethylene as function of sampling location (Notations: 7.00: location B07, 12.00: location S12)



**Figure IV.3.19.** Water to air exchange rates of toluene as function of sampling location (Notations: 7.00: location B07, 12.00: location S12)

For the factor period of sampling the water to air exchange rates of tetrachloroethylene and toluene are given in Figure IV.3.20 and IV.3.21 respectively. For all VOCs this representation is given in Annex IV.3.11.

The statistical analyses for the factor period of sampling are presented in Annex IV.3.12. The one way analysis of variance for benzene indicates significant differences. The first period shows significant higher water to air exchange rates than all other periods (mean  $12.0\text{g.km}^{-2}.\text{day}^{-1}$ ), whereas period 4 shows significant higher air to water exchange rates (mean  $-3.3\text{g.km}^{-2}.\text{day}^{-1}$ ) than all other periods. For toluene no significant differences are found. For all  $\text{C}_2$ -substituted MAHs, it is remarked that the fourth period of sampling shows lower water to air exchange rates.

The CHCs chloroform and 1,1-dichloroethane shows for the first period of sampling significantly higher water to air exchange rates than for all other periods, whereas tetrachloromethane shows significant lower water to air exchange rates at the fourth period, similar to the  $\text{C}_2$ -substituted MAHs. Trichloroethylene proves to have significantly higher water to air exchange rates at the periods 1 and 2 than at the periods 3 and 4. Finally, no significant differences are observed for 1,2-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene.

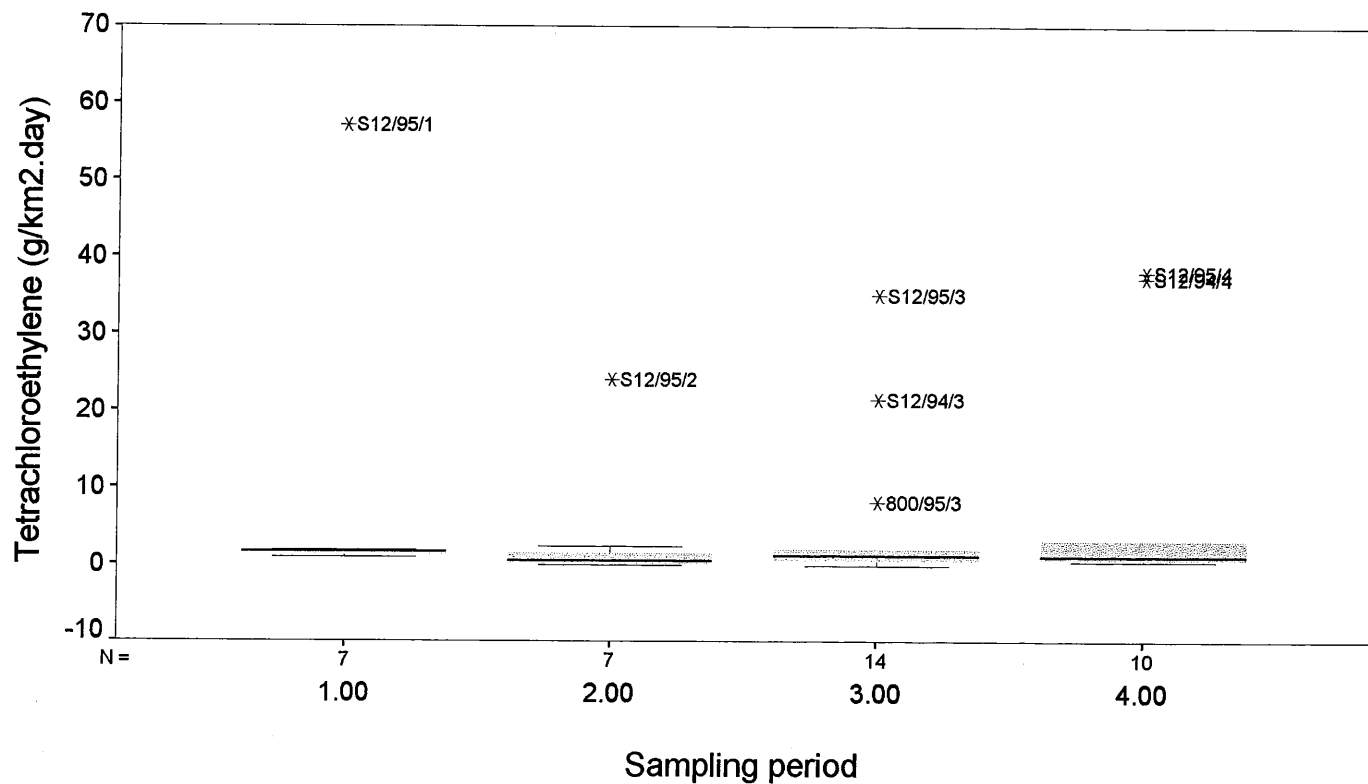


Figure IV.3.20. Water to air exchange rates of tetrachloroethylene as function of period of sampling

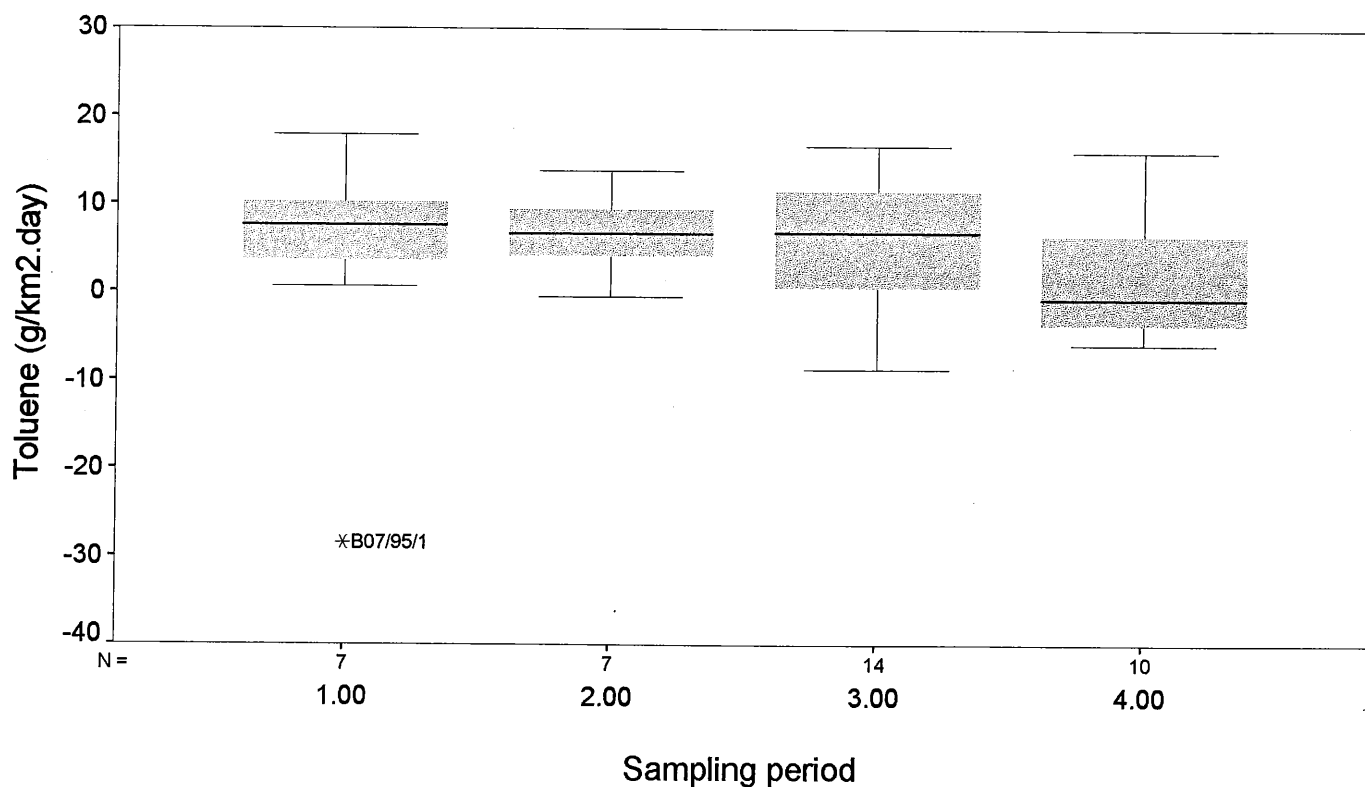


Figure IV.3.21. Water to air exchange rates of toluene as function of period of sampling

For the third factor, year of sampling, the results of the water to air exchange rates are presented by boxplots in Figure IV.3.22 and IV.3.23 for tetrachloroethylene and toluene, respectively. The same figures for all compounds are given in Annex IV.3.13. The results of the statistical analyses (Annex IV.3.14) indicate no significant differences between the exchange rates in 1994 and 1995, except for chloroform and ethylbenzene. Chloroform shows higher water to air exchange rates in 1994 than in 1995, whereas for ethylbenzene the inverse situation is remarked.

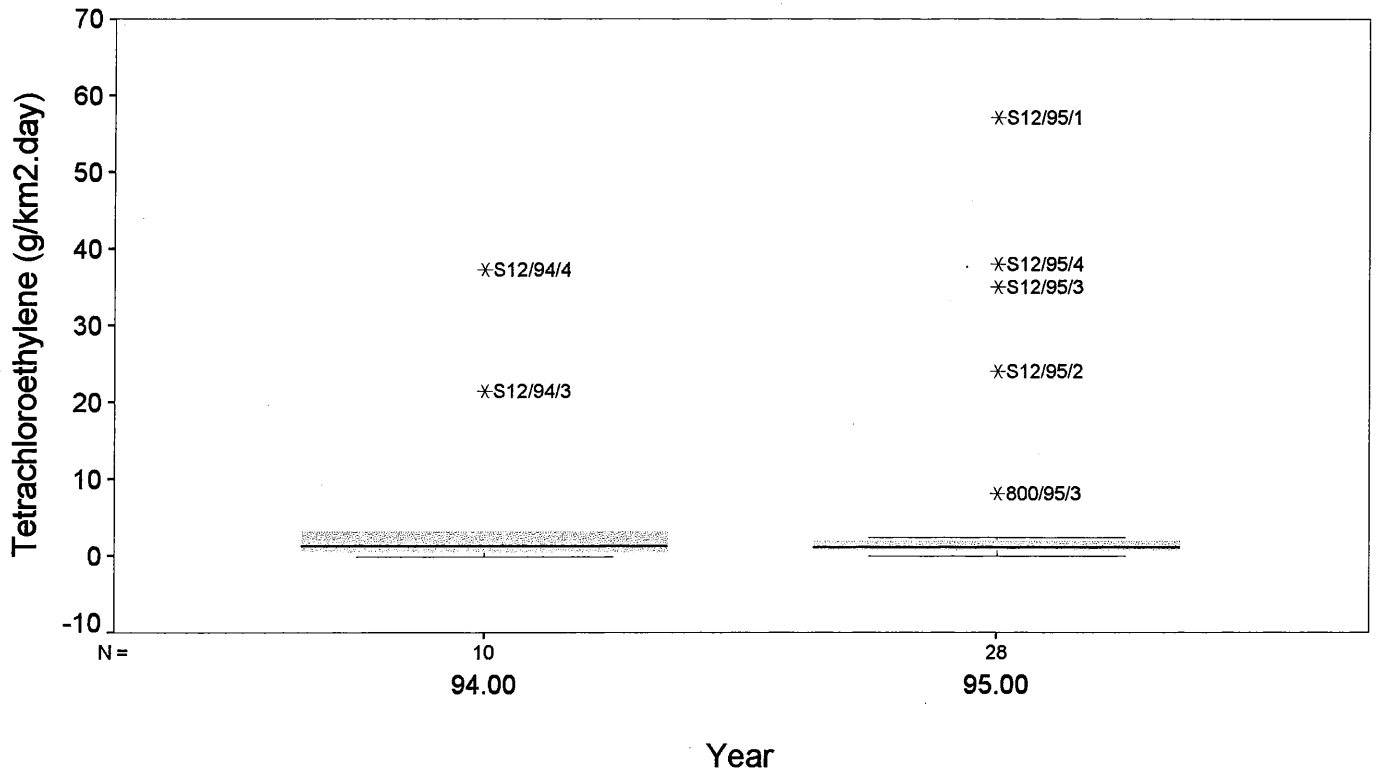


Figure IV.3.22. Water to air exchange rates of tetrachloroethylene as function of year of sampling

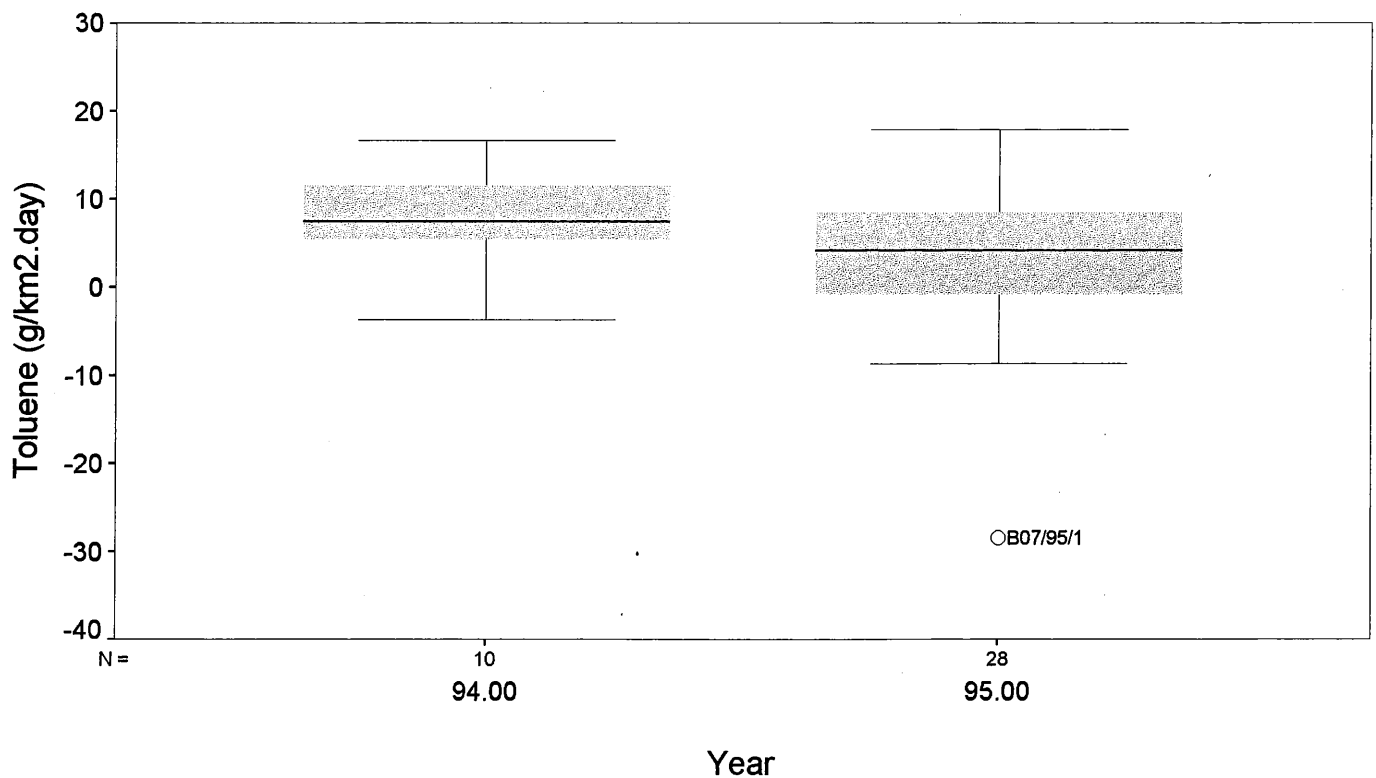


Figure IV.3.23. Water to air exchange rates of toluene as function of year of sampling

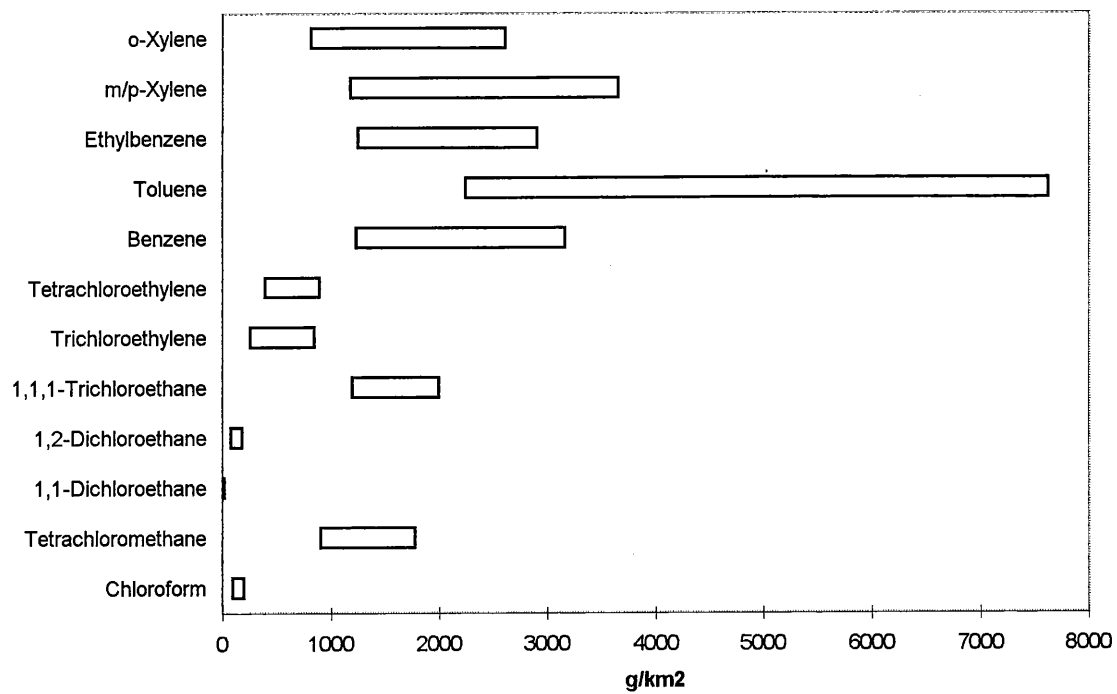


#### IV.3.4. CONCLUSIONS

The fugacity model approach has been worked out in order to determine the masses of the target compounds in the compartments air, water, sediment and biota. Also the exchange rates in the compartments has been modelled.

The model has been applied on the experimental results of the monitoring campaigns. The available data were allowed the application on the simultaneous measurements in the compartments air and water of 6 monitoring campaigns. So for these measurements results the masses in the compartments air and water were calculated, next to diffusive air/water exchange rates and degradation processes. It was shown that the processes such as wet deposition, transfer to higher altitudes and atmospheric degradation are negligible when compared to the diffusive air/water exchange process.

Figures IV.3.24, IV.3.25 and IV.3.26 represent the masses of VOCs in the compartments air, water and the total masses of VOCs in both compartments respectively for an evaluative 1km<sup>2</sup>. The cluster analysis and the Principal Component Analysis (PCA) showed high abundancies of C<sub>2</sub>-MAHs for several sampling locations during the second period of 1995, as well for the compartments air and water as for the sum of masses in both compartments. The PCA on the masses of CHCs in the water compartment showed that all samples taken in the Scheldt estuary (location S12) are grouped because of enhanced masses of 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene (Figure IV.3.7).



**Figure IV.3.24.** 25 to 75 percentile ranges of the masses (g) of VOCs in the air compartment

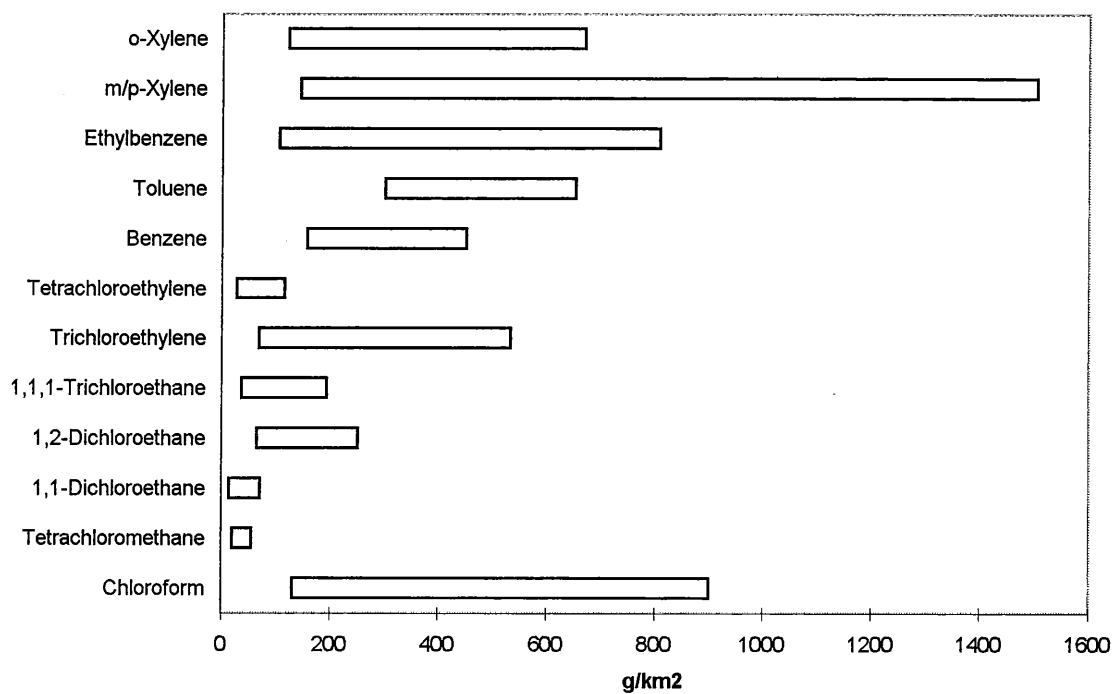


Figure IV.3.25. 25 to 75 percentile ranges of the masses (g) of VOCs in the water compartment

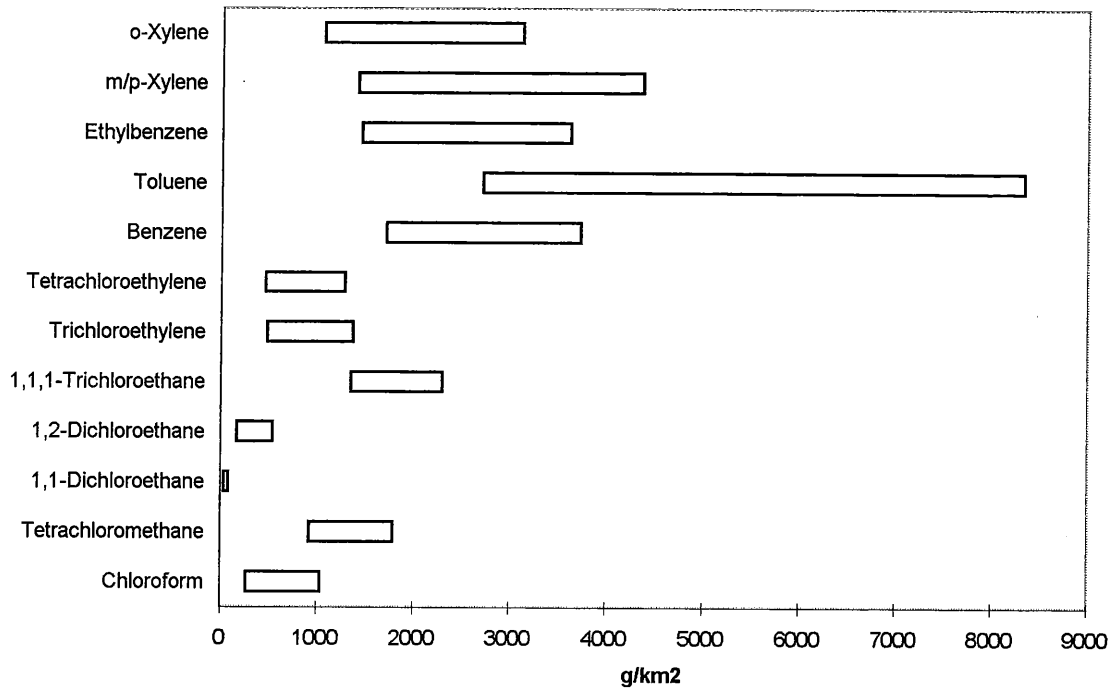
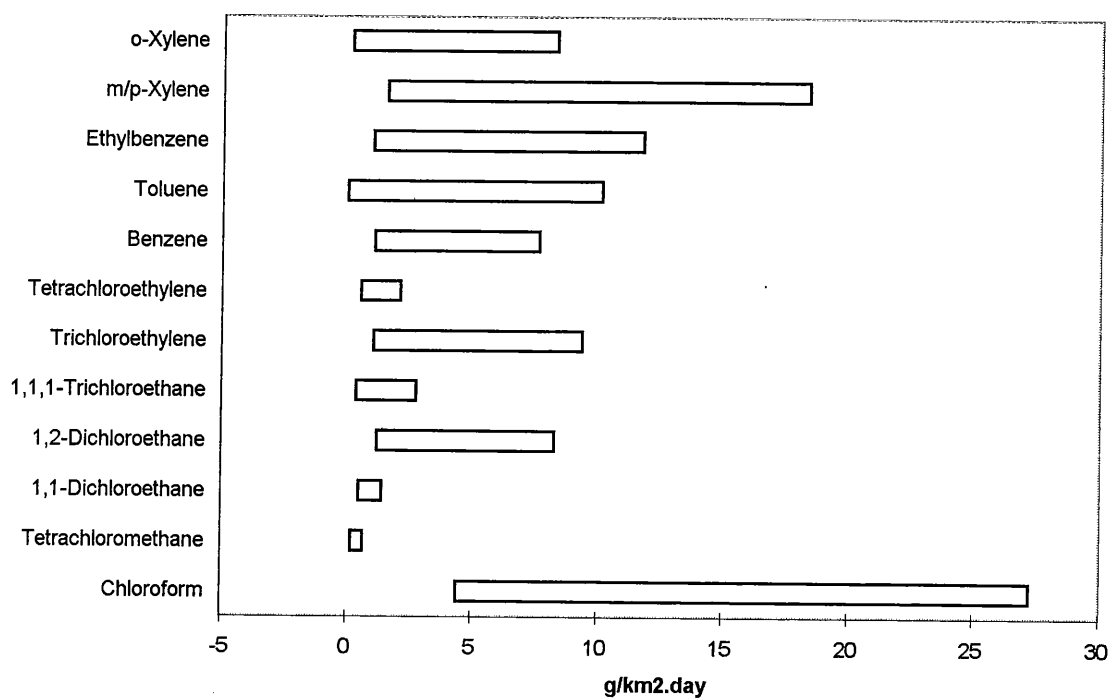


Figure IV.3.26. 25 to 75 percentile ranges of the sum of masses (g) of VOCs in the compartments air and water

By means of the application of the fugacity model, exchange rates between the water and air compartment were calculated. The 25 to 75 percentile ranges are presented in Figure IV.3.27. For all compounds mainly water to air exchange is observed, showing rates in the order of 1 to  $10\text{g}\cdot\text{km}^{-2}\cdot\text{day}^{-1}$ , with higher ranges for chloroform and m/p-xylene. The cluster analysis on this dataset of exchange rates, showed for the CHCs in the samples 780/94/3 and B07/95/1 enhanced water to air exchange rates of chloroform, tetrachloromethane and 1,1-dichloroethane. The PCA on the exchange rate data of CHCs indicated that all samples taken in the Scheldt estuary (at location S12) are remarked by higher water to air transfers, due to higher water column concentrations. For the cluster analysis and PCA on MAHs, samples from the second period of 1995 were remarked because of high air to water and water to air exchange rates of  $\text{C}_2$ -substituted MAHs.

In the factor analysis investigating the factor sampling location, it was shown that significant higher water to air exchange rates are observed at location S12 (Scheldt estuary) for the CHCs 1,2-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene.

In the statistical analysis on the factor period of sampling, it was shown that chloroform, 1,1-dichloroethane and benzene proved to have higher water to air exchange rates in the first period of sampling. On the other hand lower water to air exchange rates were observed for tetrachloromethane, benzene and the  $\text{C}_2$ -substituted MAHs in the fourth period of sampling, when compared to the other periods.



**Figure IV.3.27.** 25 to 75 percentile levels of the water to air exchange rates of VOCs (g.km<sup>-2</sup>.day<sup>-1</sup>)

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