Impulse Programme Marine Sciences 1992-1996

Project n° 4

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

Part III

Monitoring of the target compounds in the marine environment

Department of Organic Chemistry

Faculty of Agricultural & Applied
Biological Sciences

University of Gent

Fisheries Research Station

Centre for Agricultural Research
(Gent)

Impulse Programme Marine Sciences 1992-1996

Project n° 4

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

Part III
Monitoring of the target compounds in the marine environment

Department of Organic Chemistry

Faculty of Agricultural & Applied Biological Sciences

University of Gent

Fisheries Research Station

Centre for Agricultural Research (Gent)

University of Ghent

Faculty of Agricultural &
Applied Biological Sciences

Department of Organic Chemistry

Coupure Links 653
B-9000 Gent

Tel: 09/264 59 53
Fax: 09/264 62 43
e-mail:Herman.vanlangenhove@rug.ac.be

Research Group:

ir. J. Dewulf
ir. B. Heireman
Prof. Dr. ir. H. Van Langenhove

Fisheries Research Station

Centre for Agricultural
Research
(Gent)

Ankerstraat 1
B-8400 Oostende

Tel: 059/32 08 05
Fax: 059/33 06 29
e-mail: Wvyncke@rvz.be

Research Group:

Drs. P. Roose
Dr. K. Cooreman
Dr. ir. W. Vyncke

TABLE OF CONTENTS

III. MONITORING OF THE TARGET COMPOUNDS IN THE MARINE ENVIRONMENT

III.1. AIR

III.1.1. VARIABILITY OF THE CONCENTRATIONS IN AIR SAMPLES AT ONE LOCATION, AT THE SAME TIME

According to the programme the variability of the measured concentrations in multiple sampling on one sampling location was verified. On the location N 51° 21.78, E 3° 08.59 five samples were taken after each other on 31 March 1995. Each sample consisted of two parallel samplings. Each sampling lasted 25 minutes so that the five consecutive samples took approximately 2.5 hours. The measured concentrations for all VOCs for each sample are presented in Table III.1.1.

It can be seen from Table III.1.1 that most compounds show relative standard deviations between 15.8% (benzene) and 33.1% (toluene). Two groups of exceptions are noticed. First, chloroform and 1,1-dichloroethane show relative standard deviations of 41.3 and 40.8%. Both compounds have mean concentrations below $0.1 \mu g.m^{-3}$. Secondly, the C_2-substituted MAHs ethylbenzene, m/p-xylene and o-xylene have relative standard deviations of 44.3, 65.0 and 75.9% respectively. No direct explanation can be found for these higher deviations. It has to be emphasized that the variabilities of the concentrations of all VOCs include sampling, analysis, data treatment and inherent variability of the concentrations in the atmosphere during the sampling time.

Table III.1.1. Results of multiple sampling (sample names A, B, C, D and E) at N 51°21.78, E 3° 08.59 on 31 March 1995 ($\mu g.m^{-3}$), calculated average concentration (X) ($\mu g.m^{-3}$), standard deviation ($\mu g.m^{-3}$) and relative standard deviation in % (%RSD).

	A	B	C	D	E	X	s	%RSD
Chloroform	0.059	0.11	0.038	0.12	0.12	0.086	0.036	41.3
Tetrachloromethane	0.76	0.95	0.87	1.02	0.54	0.83	0.19	22.4
1,1-Dichloroethane	0.006	0.004	0.004	0.011	0.008	0.007	0.003	40.8
1,2-Dichloroethane	0.045	0.060	0.045	0.054	0.065	0.054	0.009	16.4
1,1,1-Trichloroethane	0.81	0.106	0.89	1.03	0.51	0.86	0.22	25.5
Trichloroethylene	0.087	0.097	0.083	0.097	0.056	0.084	0.017	20.2
Tetrachloroethylene	0.22	0.23	0.18	0.19	0.11	0.19	0.048	25.7
Benzene	0.71	0.91	0.88	1.07	0.79	0.87	0.14	15.8
Toluene	1.10	1.20	2.33	1.31	1.55	1.50	0.50	33.1
Ethylbenzene	0.52	0.36	1.01	0.80	1.20	0.78	0.34	44.3
m/p-Xylene	0.27	0.29	0.88	1.44	0.86	0.75	0.49	65.0
o-Xylene	0.27	0.28	0.97	1.29	2.00	0.96	0.73	75.9

III.1.2. MONITORING CONCENTRATIONS OF THE TARGET COMPOUNDS ACCORDING TO THE PROGRAMME

III.1.2.1. SAMPLES: LOCATIONS, TIMES AND ATMOSPHERIC PARAMETERS

Samples were taken at 6 sampling points according to the programme. The sampling locations are indicated on a map of the Belgian Continental Shelf (Figure III.1.1). Two sampling points (120 and 780) are near to the coast (4-15km) and two sampling points (421 and 435) are far from the coast (35-40km). Two sampling points are related to the Scheldt estuary. At the mouth of the Scheldt samples were taken on the sampling point B07 whereas samples in the estuary were taken on station S12, which is close to the border between Belgium and The Netherlands. In addition, a reference point (800), 60km from the coastline, was also sampled in the monitoring campaigns. The positions of all sampling points are given in Table III.1.2.

All dates and locations on which samples were taken, are presented in Table III.1.3. In addition, the parameters wind velocity, wind speed, air temperature and atmospheric pressure are given.

It can be seen from Table III.1.3 that no samples could be taken in 1993 and in the first period of 1994. This was due to a retardation in the development of the analytical technique. Further on, no samples were taken in the second period of 1994 since no campaign time was available. Finally, not all stations could be sampled in the fourth period of 1994 because of bad weather conditions.

Table III.1.2. 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

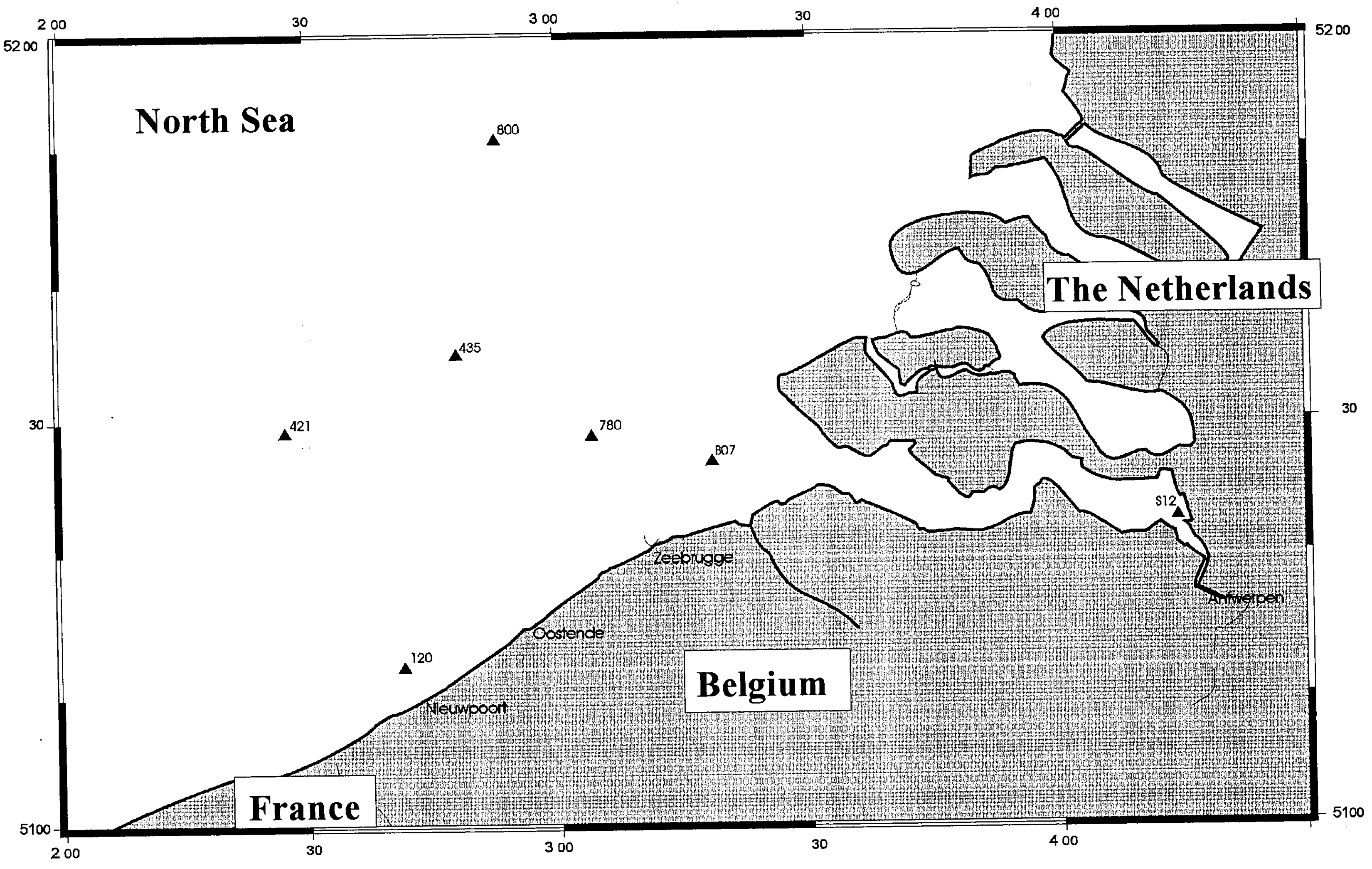


Figure III.1.1. Map of the sampling locations on the Belgian continental shelf and in the Scheldt estuary

Table III.1.3. Overview of samples taken in the monitoring campaigns: date, location, year, period of the year, code, wind velocity (u, in m.s^{-1}), wind direction (u, in°C), air temperature (T, in °C) and atmospheric pressure (P, in mbar)

Date	Location	Year	Period	Code	u (m.s^{-1})	u (°)	T (°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
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

(continued)

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

III.1.2.2. RESULTS

The results for all samples are presented in Table III.1.4 for each sampling period. All samples were classified according to the measured concentrations for each VOC and for the sum of CHCs, MAHs and VOCs. This is illustrated in Figure III.1.2 for 1,1,1-trichloroethane and toluene in a histogram. The number of samples for each class of concentration is presented as a function of the mean concentration value of each class. The same representation for all individual VOCs and for the sum of CHCs, MAHs and VOCs is given in Annex III.1.1.

It can be seen that most distributions show a skewness to the lowest concentrations. A more uniform distribution is remarked for tetrachloromethane and tetrachloroethylene, whereas for the C_2-substituted MAHs ethylbenzene, m/p-xylene and o-xylene a tailed pattern is found. This tailed profile is due to some measurements where high concentrations of these compounds are observed (individual C_2-substituted MAHs concentrations above 5000ng.m^{-3}).

Table III.1.4.a. Measurement results of the campaign in the third period of 1994 for each compound for each sampling station (in $\mu g.m^{-3}$).

	B07	S12	120	780	421	435	800
Chloroform	0.043	0.052	0.072	0.089	0.069	0.046	0.23
Tetrachloromethane	0.24	0.35	0.16	0.24	0.22	0.41	0.29
1,1-Dichloroethane	0.001	0.009	0.011	0.003	0.014	0.016	0.012
1,2-Dichloroethane	0.015	0.033	0.008	0.011	0.007	0.033	0.023
1,1,1-Trichloroethane	0.68	0.43	0.22	0.32	0.22	0.66	0.31
Trichloroethylene	0.24	0.20	0.11	0.080	0.058	0.30	0.079
Tetrachloroethylene	0.61	0.20	0.069	0.10	0.020	0.31	0.078
Benzene	0.52	0.75	0.23	0.26	0.23	0.75	0.60
Toluene	3.47	2.57	0.62	1.05	0.19	2.49	1.15
Ethylbenzene	2.38	3.78	0.63	1.28	0.28	1.60	1.03
m/p-Xylene	1.02	1.01	0.29	0.55	0.11	0.62	0.40
o-Xylene	0.66	0.62	0.17	0.39	0.10	0.53	0.28

Table III.1.4.b. Measurement results of the campaign in the fourth period of 1994 for each compound for each sampling station (in $\mu g.m^{-3}$).

	B07	S12	120
Chloroform	0.053	0.050	0.040
Tetrachloromethane	1.15	0.60	1.05
1,1-Dichloroethane	0.008	0.003	0.007
1,2-Dichloroethane	0.055	0.045	0.043
1,1,1-Trichloroethane	2.80	0.10	0.85
Trichloroethylene	0.63	0.42	0.23
Tetrachloroethylene	0.28	0.53	0.18
Benzene	0.96	1.08	0.83
Toluene	3.72	3.31	1.19
Ethylbenzene	1.32	0.67	0.41
m/p-Xylene	2.16	1.01	0.68
o-Xylene	1.73	0.54	0.68

Table III.1.4.c. Measurement results of the campaign in the first period of 1995 for each compound for each sampling station (in $\mu g.m^{-3}$).

	B07	S12	120	780	421	435	800
Chloroform	0.059	0.13	0.099	0.037	0.082	0.13	0.11
Tetrachloromethane	0.67	0.58	0.91	0.81	1.30	0.51	0.51
1,1-Dichloroethane	0.008	0.005	0.010	0.006	0.011	0.001	0.005
1,2-Dichloroethane	0.045	0.047	0.094	0.047	0.090	0.038	0.15
1,1,1-Trichloroethane	1.01	0.65	1.02	0.76	1.44	0.55	0.61
Trichloroethylene	0.21	0.046	0.12	0.028	0.13	0.042	0.29
Tetrachloroethylene	0.50	0.14	0.22	0.13	0.23	0.16	0.25
Benzene	0.870	0.54	1.12	0.60	1.25	0.52	0.62
Toluene	5.37	1.00	1.56	0.59	1.22	0.66	1.69
Ethylbenzene	1.79	0.93	1.30	0.60	0.56	0.70	1.04
m/p-Xylene	1.83	0.60	1.80	0.57	0.33	1.08	1.89
o-Xylene	1.43	0.28	0.79	0.19	0.15	0.42	1.31

Table III.4.1.d. Measurement results of the campaign in the second period of 1995 for each compound for each sampling station (in $\mu g.m^{-3}$).

	B07	S12	120	780	421	435	800
Chloroform	0.062	0.064	0.041	0.078	0.070	0.27	0.064
Tetrachloromethane	0.61	0.92	0.79	0.47	0.41	1.02	1.06
1,1-Dichloroethane	0.016	0.011	0.009	0.033	0.017	0.026	0.018
1,2-Dichloroethane	0.048	0.093	0.030	0.090	0.13	0.32	0.041
1,1,1-Trichloroethane	0.69	0.88	0.86	0.64	0.62	1.12	1.14
Trichloroethylene	0.37	0.29	0.35	0.63	0.42	0.73	0.30
Tetrachloroethylene	0.25	0.31	0.44	0.53	0.38	0.58	0.29
Benzene	0.73	0.72	0.81	1.09	1.71	1.36	0.69
Toluene	0.59	1.02	1.57	1.67	1.78	3.01	0.37
Ethylbenzene	4.88	0.48	0.51	0.85	6.14	5.29	1.32
m/p-Xylene	44.3	0.89	0.92	1.52	41.8	18.8	7.09
o-Xylene	25.8	0.76	0.72	1.35	29.2	7.88	2.84

Table III.1.4.e. Measurement results of the campaign in the third period of 1995 for each compound for each sampling station (in μg.m^{-3}).

	B07	S12	120	780	421	435	800
Chloroform	0.028	0.043	0.099	0.21	0.048	0.032	0.026
Tetrachloromethane	0.69	0.59	0.50	0.52	0.56	0.38	0.51
1,1-Dichloroethane	0.006	0.007	0.008	0.012	0.010	0.006	0.006
1,2-Dichloroethane	0.036	0.075	0.060	0.042	0.061	0.089	0.045
1,1,1-Trichloroethane	0.71	0.87	0.91	0.48	0.80	0.51	0.57
Trichloroethylene	0.76	0.34	1.23	1.24	0.97	0.38	0.45
Tetrachloroethylene	0.21	0.22	0.81	0.40	0.59	0.41	0.48
Benzene	0.60	1.00	2.00	1.02	1.54	2.93	1.14
Toluene	1.64	2.46	7.02	3.36	11.2	5.80	3.55
Ethylbenzene	0.28	0.38	1.38	0.84	1.54	1.47	1.19
m/p-Xylene	0.44	0.51	1.21	1.11	1.44	1.27	1.28
o-Xylene	0.33	0.43	0.95	0.98	1.13	0.95	0.94

Table III.1.4.f. Measurement results of the campaign in the fourth period of 1995 for each compound for each sampling station (in μg.m^{-3}).

	B07	S12	120	780	421	435	800
Chloroform	0.052	0.092	0.081	0.075	0.34	0.19	0.37
Tetrachloromethane	0.71	0.74	0.88	0.79	1.12	0.81	0.96
1,1-Dichloroethane	0.010	0.011	0.004	0.007	0.006	0.007	0.006
1,2-Dichloroethane	0.090	0.057	0.17	0.058	0.16	0.18	0.19
1,1,1-Trichloroethane	0.80	1.01	0.88	0.92	1.11	1.05	0.99
Trichloroethylene	0.19	0.25	0.13	0.10	0.38	0.43	0.28
Tetrachloroethylene	0.28	0.36	0.21	0.15	0.41	0.60	0.37
Benzene	3.29	2.25	2.66	1.49	5.12	4.87	4.77
Toluene	5.76	4.10	3.17	2.52	5.67	7.59	5.63
Ethylbenzene	0.80	0.76	0.68	0.36	1.45	1.43	1.22
m/p-Xylene	0.91	0.88	0.71	0.39	2.00	1.85	1.85
o-Xylene	0.74	0.63	0.53	0.28	1.31	1.38	1.17

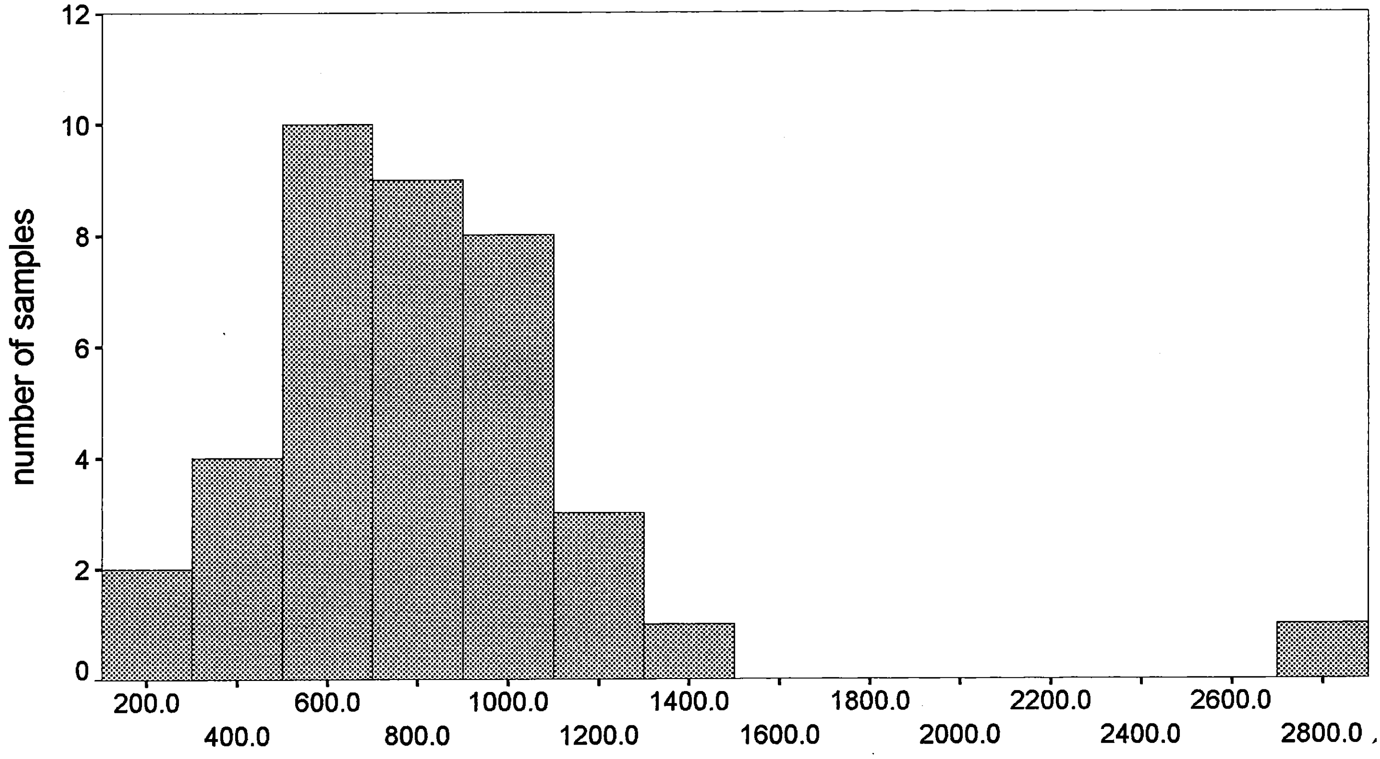


Figure III.1.2.a. Classification of the samples according to the measured concentrations of 1,1,1-trichloroethane (ng.m^{-3}), represented by a histogram

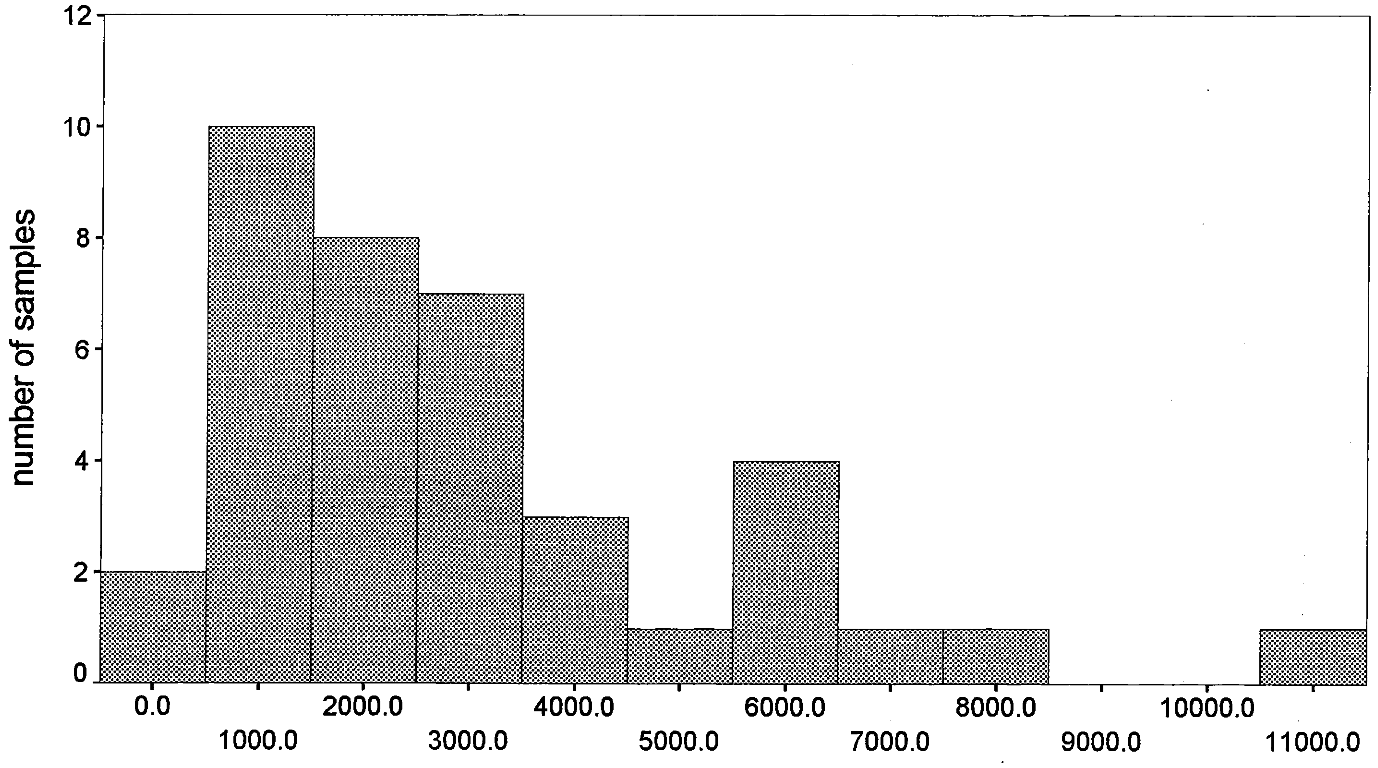


Figure III.1.2.b. Classification of the samples according to the measured concentrations of toluene (ng.m^{-3}), represented by a histogram

III.1.2.3. STATISTICAL TREATMENT OF THE RESULTS

A series of statistical tests was done on the dataset from all monitoring campaigns. The tests were carried out by means of the statistical package SPSS (Statistical Package for Social Sciences, originally developed for social sciences, but now extended for a wide range of applications).

In a first step cluster analyses were done in order to see if some groups of samples were clustering. This was done by means of a hierarchical cluster method with between-groups linkage based on squared Euclidian distances.

Secondly, principal component analysis (PCA) was executed in order to investigate if some underlying relationships between samples could be found. Principal components were extracted when eigenvalues were greater than or equal to one.

Thirdly, bivariate correlations (Pearson coefficients) between the VOCs were checked.

Finally, the parameters period of the sampling and sampling location were considered in order to find out if some periods or locations could be distinguished from each other. Therefore, the normality of the distributions was tested by means of a Kolmogorov-Smirnov test because in the factor analysis normal distribution is assumed. On datasets not showing a normal distribution, a logaritmic transformation was done. Factor analyses, i.e. one way analyses of variance, were done on datasets without and after logaritmic transformation.

III.1.2.3.1. Dataset

In total 38 cases are considered for all 13 individual VOCs, for the sum of CHCs, MAHs and VOCs. In order to do some statistical tests which assume normal distribution, the data were transformed via the natural logaritmic function. The original dataset and the transformed data used in the statistical approach are presented in Annex III.1.2 and III.1.3, respectively. The 5, 10, 25, 50, 75, 90 and 95 percentiles for each individual VOC population and for the populations of the sums of CHCs, MAHs and VOCs are presented in Annex III.1.4.

The datasets after logaritmic transformation can also be presented by means of a histogram as is done for the original datasets in Annex III.1.1. This representation for the data of all individual VOCs, the sum of CHCs, MAHs and VOCs is given in Annex III.1.5.

III.1.2.3.2. Cluster analyses

III.1.2.3.2.1. Cluster analysis on all individual CHCs

A cluster analysis on all individual CHCs was carried out. The obtained agglomeration schedule and dendrogram are presented in Annex III.1.6. From the dendrogram four measurements can be distinguished from the other data. A first case is the sample B07/94/4. It shows a very high concentration of 1,1,1-trichloroethane: 2800ng.m^{-3}, more than twice the 90 percentile (1125ng.m^{-3}). Also the concentrations of tetrachloromethane (1145ng.m^{-3}) and trichloroethylene (632ng.m^{-3}) are high when compared to the 75 percentile of 890 and 424ng.m^{-3}, respectively. The other three samples which can be distinguished are the samples 780/95/3, 421/95/3 and 120/95/3. All these samples are taken in the third period of 1995. These samples have trichloroethylene concentrations above the 90 percentile level (=784ng.m^{-3}): 1235, 967 and 1227ng.m^{-3}. Within this cluster, a subgroup can be found. The samples 421/95/3 and 120/95/3 have tetrachloroethylene concentrations equal to and above the 90 percentile: 592 and 814ng.m^{-3}, respectively.

In conclusion, three samples from the third period of 1995 are isolated. No direct explanation can be given for this observation.

III.1.2.3.2.2. Cluster analysis on all individual MAHs

The agglomeration schedule and the dendrogram of the cluster analysis on all samples for all individual MAHs are presented in Annex III.1.7. It is clear from the dendrogram that 35 samples from the complete dataset are clustered. Three samples from the second period in 1995 are separated. They are separated because of high concentrations of C_2-substituted MAHs. The ethylbenzene concentrations for the samples 421/95/2, B07/95/2 and 435/95/2 are 6.14µg.m^{-3}, 4.88µg.m^{-3} and 5.29µg.m^{-3} whereas the 90 percentile is 3.89µg.m^{-3}. Also the concentrations of m/p-xylene are higher than the 90 percentile (=8.26µg.m^{-3}): 41.8, 44.3 and 18.8µg.m^{-3}, respectively. Finally, the same observation is made for o-xylene with concentrations of 29.2, 25.8 and 7.9µg.m^{-3} respectively, whereas the 90 percentile value is 3.3µg.m^{-3}.

The elevated concentrations of C_2-substituted MAHs can not directly contributed to any reason. However, also in the water analyses higher concentrations were observed at that time.

It can be hypothesized that the water body acts as a source for these higher atmospheric concentrations via a water/air transfer.

III.1.2.3.2.3. Cluster analysis on all individual VOCs

The results of the cluster analysis on all individual VOCs are presented in Annex III.1.8. From the dendrogram three samples are separated from the other data which are all clustered together. The three samples are 421/95/2, B07/95/2 and 435/95/2. This is the same result as in the cluster analysis on all individual MAHs where it was shown that these samples have high concentrations of C_2-substituted MAHs.

From this cluster analysis it is concluded that the most remarkable difference within the whole dataset of all VOCs is due to some samples with elevated concentrations of C_2-substituted MAHs. Moreover, it proves that no clusters are separated because of simultaneously high concentrations of (some) CHCs and of high concentrations of (some) MAHs.

III.1.2.3.3. Principal component analysis

III.1.2.3.3.1. Principal component analysis on all individual CHCs

A principal component analysis on all measured concentrations of all individual CHCs was carried out. The results are presented in annex III.1.9. Three factors with eigenvalues greater than one are found. They contribute 36.1, 22.3 and 17.3% respectively to the total variance of the dataset. For the factor matrix and the factor loading plot after rotation (Figure III.1.3) it appears that the highest contributions to the first factor are from 1,1,1-trichloroethane (0.94) and tetrachloromethane (0.89). Factor two is mainly determined by trichloroethylene (0.90) and tetrachloroethylene (0.87) whereas chloroform (0.88) and 1,2-dichloroethane (0.83) contribute most of all CHCs to factor 3. This means that all individual CHCs are well related to only one factor, except 1,1-dichloroethane, which is weakly related to factor 2 (loading 0.43) and factor 3 (loading 0.32).

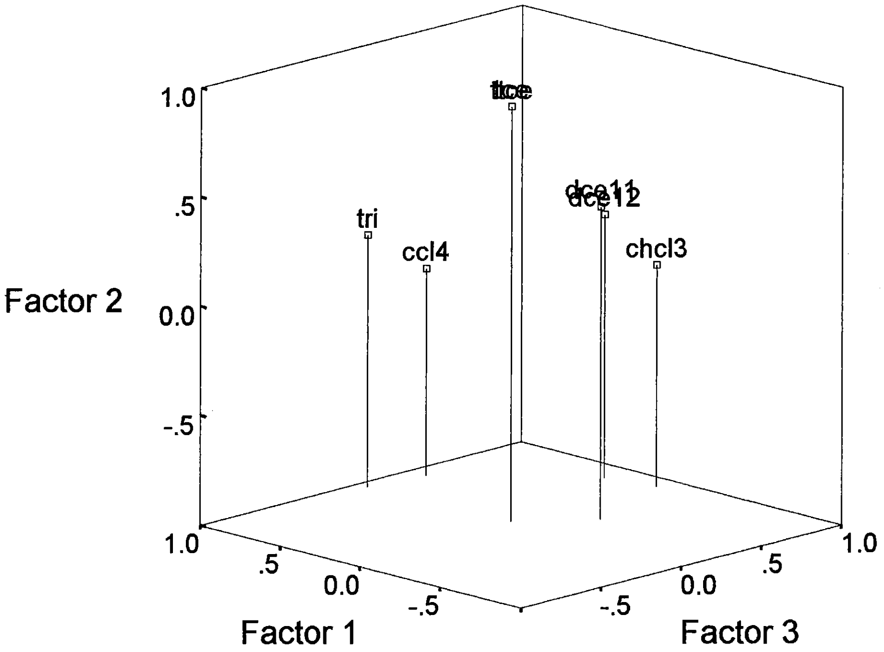


Figure III.1.3. Factor loading plot of the PCA on all individual CHCs (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttce: tetrachloroethylene)

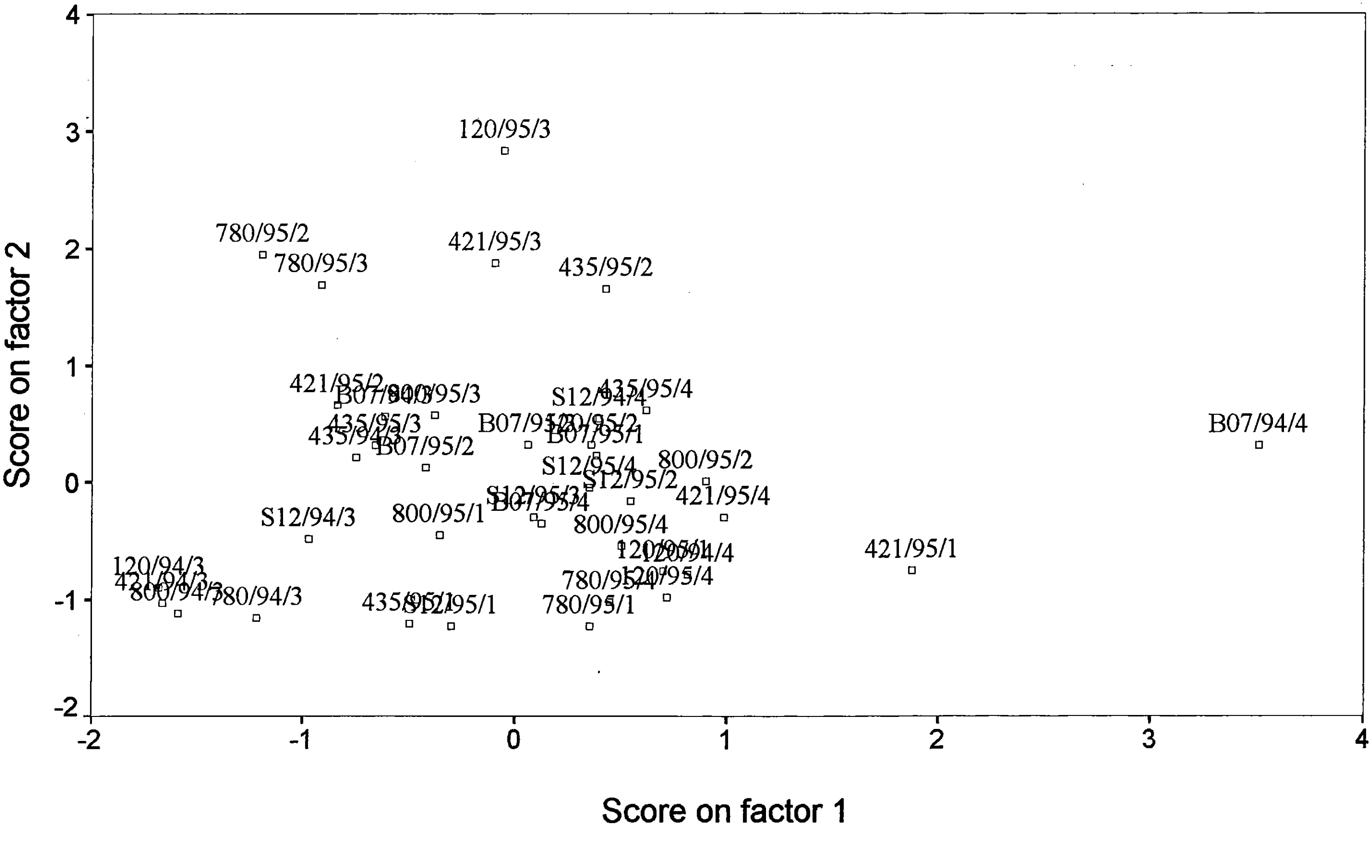


Figure III.1.4.a. Factor score plot of the PCA on all individual CHCs (factor 1 and 2)

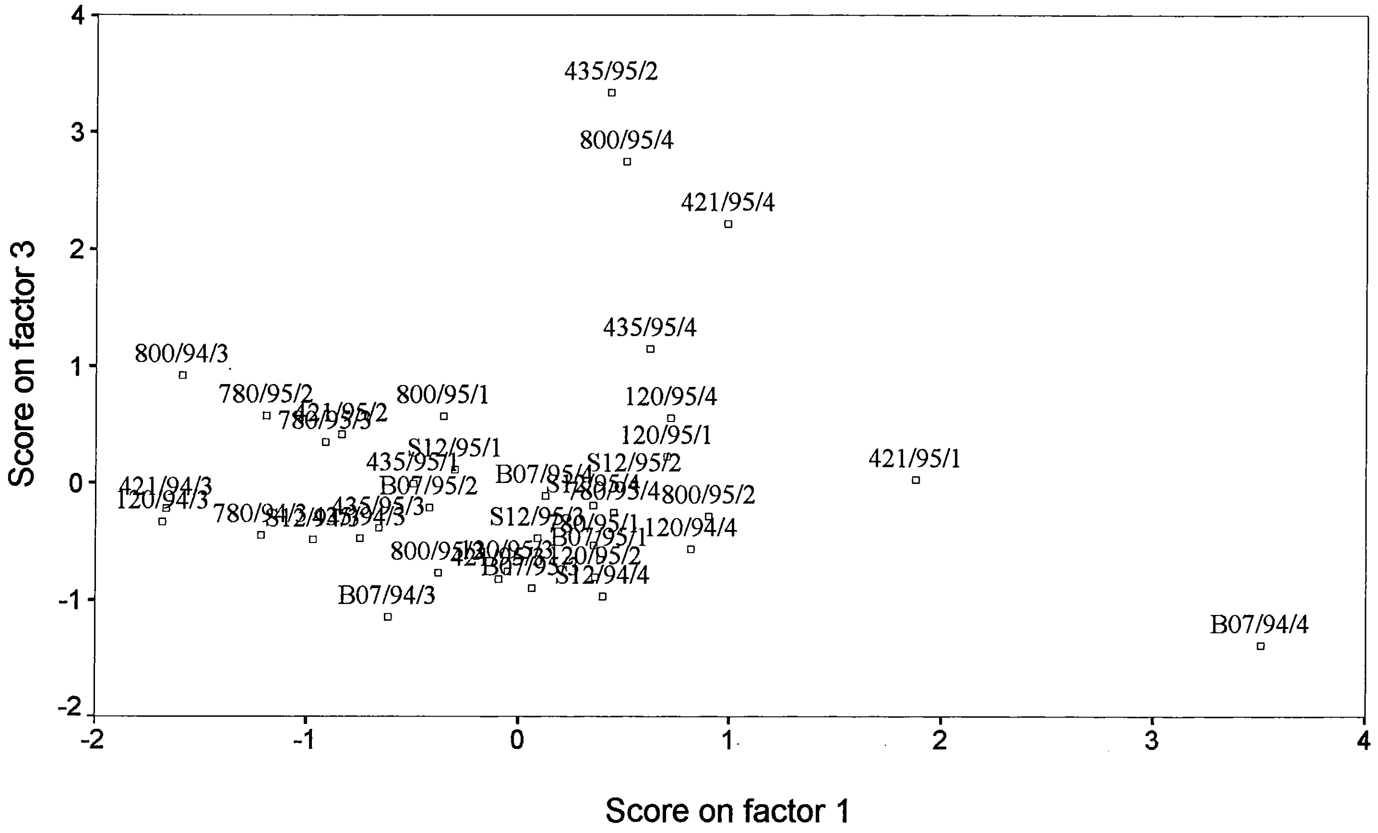


Figure III.1.4.b. Factor score plot of the PCA on all individual CHCs (factor 1 and 3)

When the factor scores of all samples are considered (*see* the factor score table and the factor score plot), it can be seen that 29 of the 38 measurements for all CHCs are clustered in an array determined by a score on factor 1 below 1, by a score on factor 2 below 0.7 and by a score on factor 3 below 1.15 (*see* Figure III.1.4). According to the first factor two samples are separated: B07/94/4 (score 3.51) and 421/95/1 (score 1.88). The concentration in these samples of tetrachloromethane (1145ng.m^{-3} and 1303ng.m^{-3} respectively) and of 1,1,1-trichloroethane (2800 and 1436ng.m^{-3} respectively) are high concentrations, higher than the 90 percentile (1070 and 1125ng.m^{-3} respectively). A second group of samples to be distinguished consists of five samples: 120/95/3 (2.83), 780/95/2 (1.95), 780/95/3 (1.69), 421/95/3 (1.87) and 435/95/2 (1.65). They have high scores on factor 2, due to higher concentrations of trichloroethylene and tetrachloroethylene. The concentrations of trichloroethylene for these samples are 1227, 625, 1235, 967 and 735ng.m^{-3} respectively, higher than the 75 percentile, 425ng.m^{-3}. Also the concentrations of tetrachloroethylene (814, 526, 396, 592 and 580ng.m^{-3} respectively) are above the 75 percentile (452ng.m^{-3}). Finally, three samples are distinguished by a high score on factor 3, i.e. 435/95/2 (3.34), 800/95/4 (2.75) and 421/95/4 (2.22). They show elevated concentrations of chloroform (269, 370 and 340ng.m^{-3} respectively) and of 1,2-dichloroethane (321, 194 and 163ng.m^{-3} respectively), whereas the 75 percentiles for these compounds are 100.8 and 91.2ng.m^{-3}.

Within the three groups of samples isolated, only for the third group a common factor can be found. The three samples with high concentrations of chloroform and 1,2-dichloroethane, are taken at locations far from the coast. Finally, it has to be noted that the samples from the sampling location in the Scheldt estuary (S12) do not have any elevated concentration of the CHCs.

III.1.2.3.3.2. Principal component analysis on all individual MAHs

A principal component analysis on all results of all individual MAHs was carried out. The results are given in Annex III.1.10. Two factors show eigenvalues above 1. They contribute 55.5 and 33.0% to the total variance of the dataset. From the factor matrix and the factor loading plot after rotation (Figure III.1.5) it can be seen that both factors are determined by different MAHs. The first factor is dominated by the C_2-substituted MAHs ethylbenzene (loading 0.92), m/p-xylene (loading 0.98) and o-xylene (loading 0.97). Factor two in mainly loaded by benzene (0.90) and toluene (0.91).

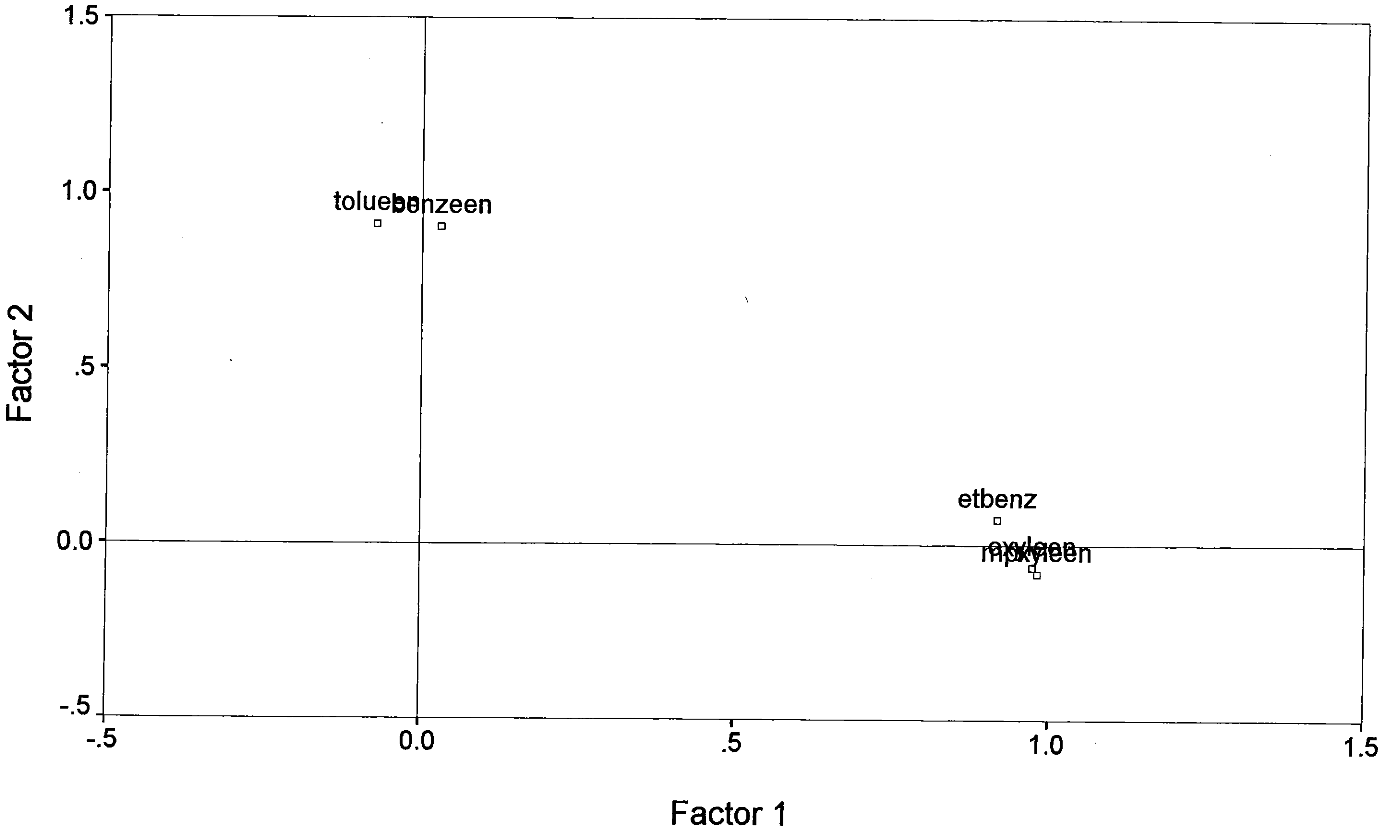


Figure III.1.5. Factor loading plot of the PCA on all individual MAHs (benzeen: benzene, tolueen: toluene, etbenz: ethylbenzene, oxyleen: o-xylene, mpxyleen: m/p-xylene)

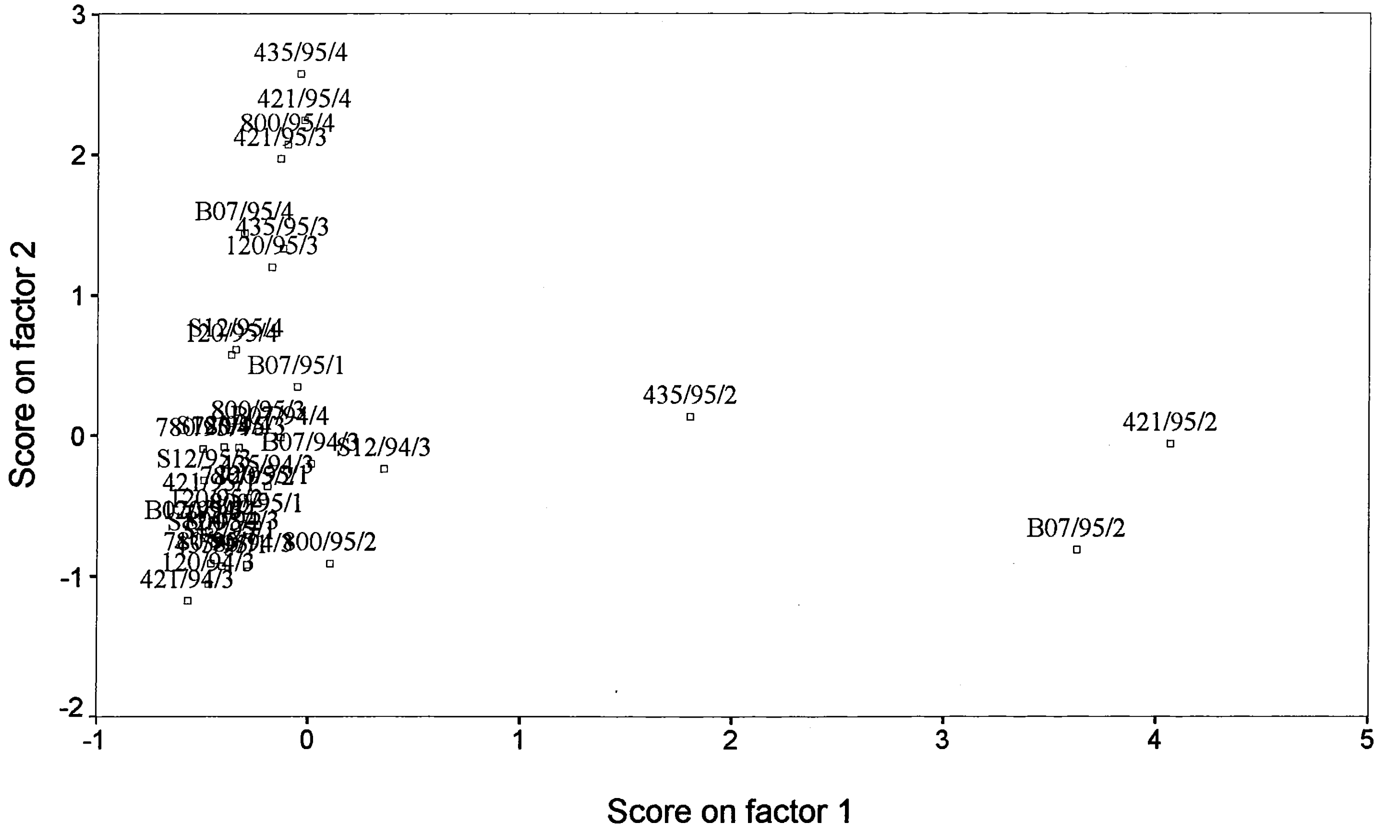


Figure III.1.6. Factor score plot of the PCA on all individual MAHs

The largest part (28 samples) of the total dataset fall within an area with scores on factor 1 below 0.40 and on factor 2 below 0.65 (Figure III.1.6). Three samples are isolated because of high scores on factor 1: 421/95/2 (4.07), 435/95/2 (1.80) and B07/95/2 (3.63). They show high concentrations of ethylbenzene (6.14, 5.29 and 4.88$\mu g.m^{-3}$ respectively), m/p-xylene (41.8, 18.8 and 44.3$\mu g.m^{-3}$ respectively) and o-xylene (29.2, 7.88 and 25.8 respectively) if their concentrations are compared to the 90% percentiles of 3.89, 8.26 and 3.35$\mu g.m^{-3}$ respectively. A second set of samples is separated from the main group because of high scores on factor 2. It consists of seven samples which have scores above 1 on factor 2: 435/95/4 (2.57), 421/95/4 (2.24), 800/95/4 (2.07), 421/95/3 (1.97), B07/95/4 (1.44), 435/95/3 (1.33) and 120/95/3 (1.20). Their concentrations on benzene and toluene are elevated. They vary from 1.54 to 5.12$\mu g.m^{-3}$ and from 5.62 to 11.20$\mu g.m^{-3}$ respectively, whereas the 75 percentile for benzene is 1.58 and for toluene 3.81$\mu g.m^{-3}$.

Also in this principal component analysis, no samples from the sampling location in the Scheldt estuary (S12) are remarked by higher concentrations. Some samples are separated because of high concentrations of C_2-substituted MAHs. They are taken during the second period in 1995. This is the same results as in the cluster analyses on all MAHs and on all VOCs. As already suggested, the water body can be supposed to act as a source for these compounds via a water to air mass transfer.

The samples isolated by their higher benzene and toluene concentrations are samples from the third and fourth period in 1995. All samples were taken at a situation where the wind direction was between 80 and 184°. This means that the air mass sampled at that time was of a continental origin. In conclusion, it can be suggested that the higher concentrations of benzene and toluene are from anthropogenic continental sources and that this can be observed independently of the sampling location on the Belgian Continental Shelf.

III.1.2.3.3.3. Principal component analysis on all individual VOCs

A principal component analysis on all data of all individual VOCs was carried out. The results are presented in Annex III.1.11. Four factors with eigenvalues greater than one were identified. They contribute respectively 29.8, 24.8, 14.3 and 11.0% to the total variance of the dataset. From the factor matrix and the factor loading plot after rotation (Figure III.1.7), it is clear that the first factor is mainly loaded by the C_2-substituted MAHs ethylbenzene (0.89), m/p-xylene (0.96) and o-xylene (0.94). The second factor is mostly determined by trichloroethylene (0.84), tetrachloroethylene (0.89) and toluene (0.80). The third factor is principally related to chloroform (0.85), 1,2-dichloroethane (0.76) and benzene (0.84). Finally factor four is loaded mainly by tetrachloromethane (0.91) and 1,1,1-trichloroethane (0.92). In conclusion, all VOCs are obvious related to one single factor except 1,1-dichloroethane, which is mostly related to factor 1 (0.60).

The loadings for all factors in the current analysis can be compared to the loadings of the factors in the principal component analysis on all CHCs and to those from the principal component analysis on all MAHs. The three factors in the CHCs analysis can be recognized in the factor two, three and four in the current analysis. The first factor from the CHCs analysis is now found in the fourth factor (dominated by tetrachloromethane and 1,1,1-trichloroethane), the second in the second factor (dominated by trichloroethylene and tetrachloroethylene) and the third factor of the previous analysis can be recognized in the third factor (mainly determined by chloroform and 1,2-dichloroethane). In both analyses, 1,1-dichloroethane is not well related to one single factor.

The first factor in the principal component analysis on all MAHs, dominated by the C_2-substituted MAHs ethylbenzene, m/p-xylene and o-xylene, is found in the first factor of the present analysis. But, the compounds in the second factor of the previous analysis, i.e. benzene and toluene, are now spread over two factors. Toluene is now part of the second factor which includes also trichloroethylene and tetrachloroethylene, whereas benzene is involved in the third factor, which is also related to chloroform and 1,2-dichloroethane.

This means that the group of 13 VOCs are splitted into four groups with related concentration behaviour. Whereas in the analyses of water concentrations no relations between individual CHCs and individual MAHs were observed, now the MAHs benzene and toluene proved to be related separately to some individual CHCs.

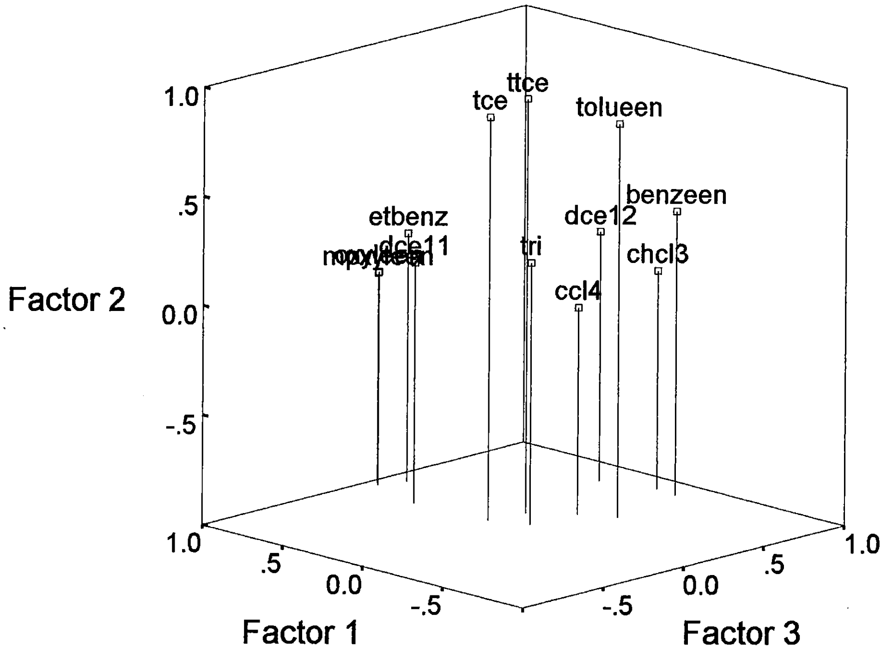


Figure III.1.7. Factor loading plot of the PCA on all individual VOCs (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttce: tetrachloroethylene, benzeen: benzene, tolueen: toluene, etbenz: ethylbenzene, oxyleen: o-xylene, mpxyleen: m/p-xylene)

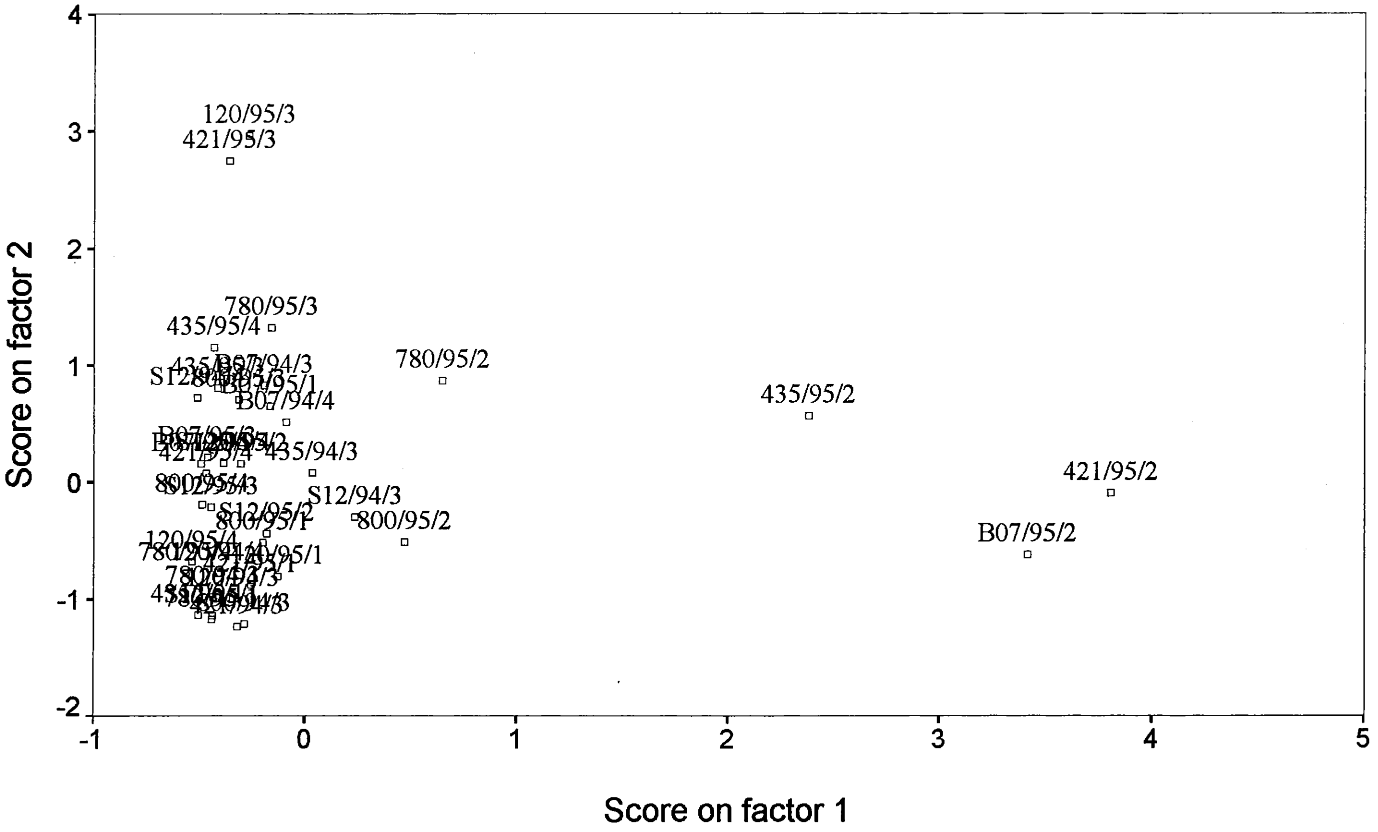


Figure III.1.8.a. Factor score plot of the PCA on all individual VOCs (factor 1 and 2)

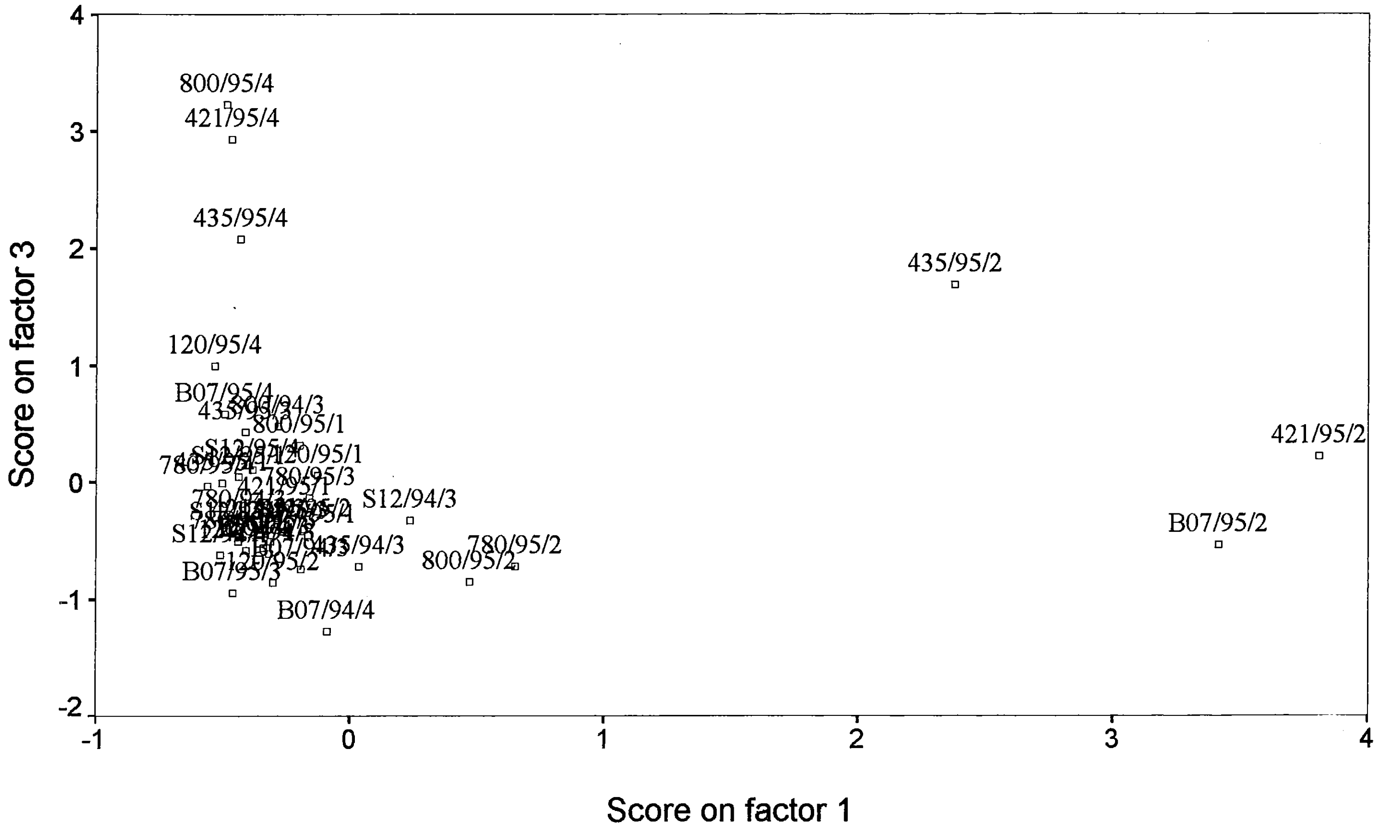


Figure III.1.8.b. Factor score plot of the PCA on all individual VOCs (factor 1 and 3)

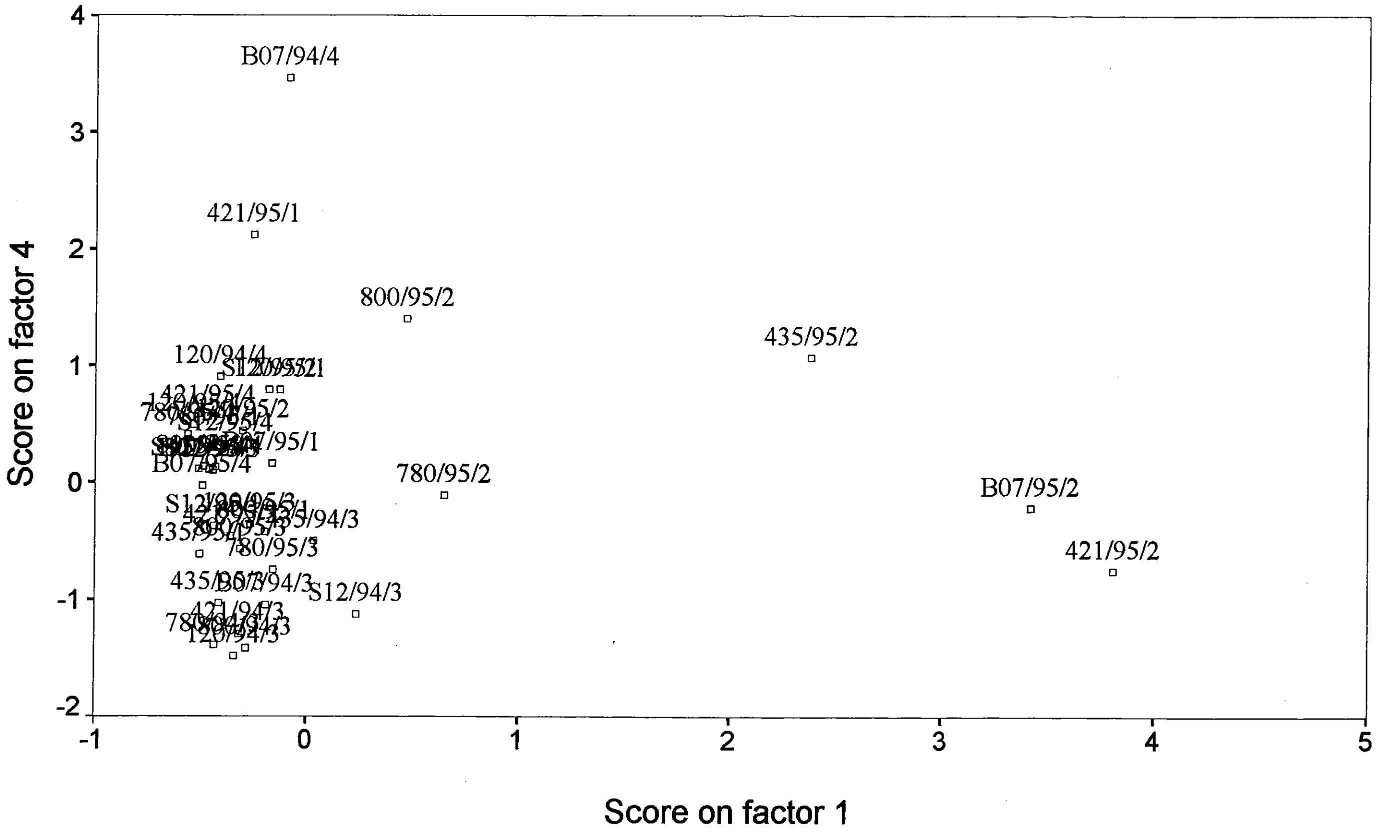


Figure III.1.8.c. Factor score plot of the PCA on all individual VOCs (factor 1 and 4)

When now the factor scores of the samples are discussed (Figure III.1.8), 27 measurements of VOCs are clustered in the factor score plots within a space, limited by a score on factor 1 below 0.65, by a score on factor 2 below 1.35, a score on factor 3 below 1 and a score on factor 4 below 0.9. When now the separated samples are considered in the 4-dimensional space, a first group is isolated by their high scores on factor 1: B07/95/2 (3.42), 421/95/2 (3.81) and 435/95/2 (2.38), which are three samples taken in the second period of 1995. Their concentrations for ethylbenzene are 4.88, 6.14 and 5.29μg.m^{-3} respectively (90 percentile: 3.89μg.m^{-3}), for m/p-xylene 44.27, 41.80 and 18.82μg.m^{-3} respectively (90 percentile 8.26μg.m^{-3}) and for o-xylene 25.76, 29.19 and 7.88μg.m^{-3} respectively (90 percentile 3.35μg.m^{-3}). The second factor isolate two samples from the third period in 1995: 120/95/3 (score 2.96) and 421/95/3 (score 2.75). Both samples simultaneously have high scores for the CHCs trichloroethylene (1227 and 967ng.m^{-3} respectively, whereas the 90 percentile is 784ng.m^{-3}) and tetrachloroethylene (814 and 592ng.m^{-3} respectively, whereas the 90 percentile is 593ng.m^{-3}), and for the MAH toluene (7.0 and 11.2μg.m^{-3}respectively, whereas the 90 percentile is 5.9μg.m^{-3}). In a third place three samples from the fourth period in 1995, i.e. 421/95/4, 435/95/4 and 800/95/4, are separated because of high scores on factor 3: 2.93, 2.08 and 3.23 respectively. They simultaneously have elevated concentrations of chloroform (340, 187 and 370ng.m^{-3} respectively, whereas the 90 percentile is 231ng.m^{-3}), of 1,2-dichloroethane (163, 181 and 194ng.m^{-3} respectively, whereas the 90 percentile is 172ng.m^{-3}) and of the MAH benzene (5.12, 4.87 and 4.77ng.m^{-3} respectively, whereas the 90 percentile is 3.44μg.m^{-3}). Also the concentrations of toluene are enhanced (5.67, 7.59 and 5.63μg.m^{-3} whereas the 75 percentile is 3.81μg.m^{-3}). Finally the factor four isolates the samples B07/94/4 (score 3.47), 421/95/1 (score 2.12) and 800/95/2 (score 1.40) because of higher concentrations of tetrachloromethane (1145, 1303 and 1064ng.m^{-3} respectively whereas the 90 percentile is 1070ng.m^{-3}) and of 1,1,1-trichloroethane (2800, 1436 and 1139ng.m^{-3} respectively whereas the 90 percentile is 1125ng.m^{-3}).

III.1.2.3.4. Correlations between individual VOCs

Correlations between all individual VOCs were investigated considering all samples. The correlation coefficient matrix is presented in Annex III.1.12.

The best correlations are found between the C_2-substituted MAHs ethylbenzene, m/p-xylene and o-xylene with correlation coefficients of 0.84 (ethylbenzene - m/p-xylene), 0.81 (ethylbenzene - o-xylene) and 0.99 (m/p-xylene - o-xylene). A significant correlation between tetrachloromethane and 1,1,1-trichloroethane (0.75) is remarked. All other correlations show correlation coefficients below 0.70.

The correlation coefficient matrix indicates that the VOCs are in general poorly related (except the C_2-substituted MAHs), when they are compared to those from the analysis of the water samples.

III.1.2.3.5. Factor analysis

For the factor analysis three parameters, i.e. the factor sampling location, year of sampling and sampling period of the year can be considered. The results of all individual VOCs measurements and of the sum of CHCs, MAHs and VOCs can be represented as a function of these parameters by means of boxplots. This is illustrated for 1,1,1-trichloroethane and toluene in Figure III.1.9 for the factor year, in Figure III.1.10 for the factor period of the year and for the factor sampling location in Figure III.1.11. The same representation is given in the Annexes III.1.13, III.1.14 and III.1.15 for all individual VOCs, the sum of CHCs, MAHs and VOCs.

Since the dataset is limited, the dataset is not suited to do a factor analysis for the parameter year. No air samples were taken in 1993, 10 samples in 1994 and 28 samples were taken in 1995. This means that only samples from 1994 and 1995 can be compared. However, the datasets for both years are not equal. No samples for the first and second period of 1994 are available so that these periods are unequally presented in this type of analysis.

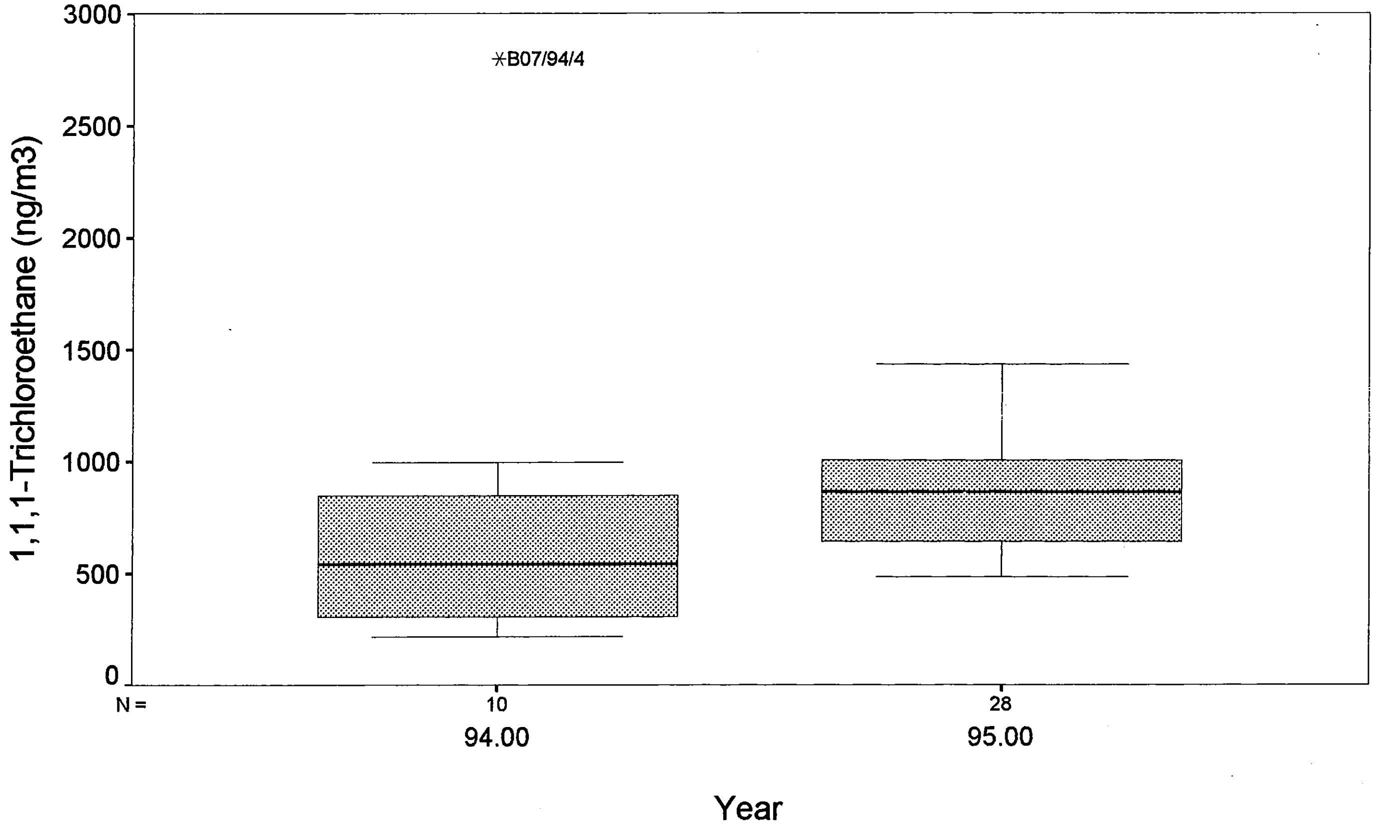


Figure III.1.9.a. Measurement results of 1,1,1-trichloroethane as a function of the year of sampling, represented by boxplots

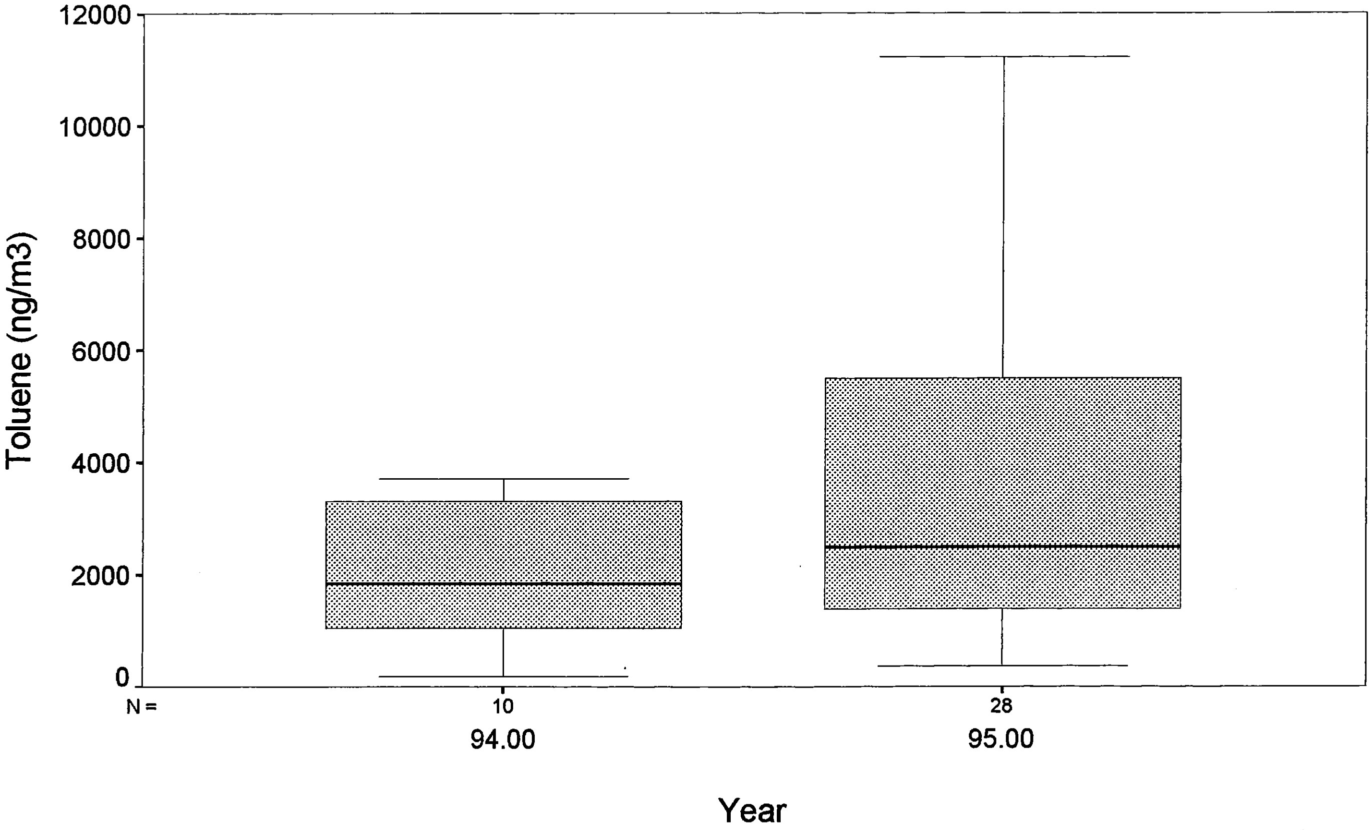


Figure III.1.9.b. Measurement results of toluene as a function of the year of sampling, represented by boxplots

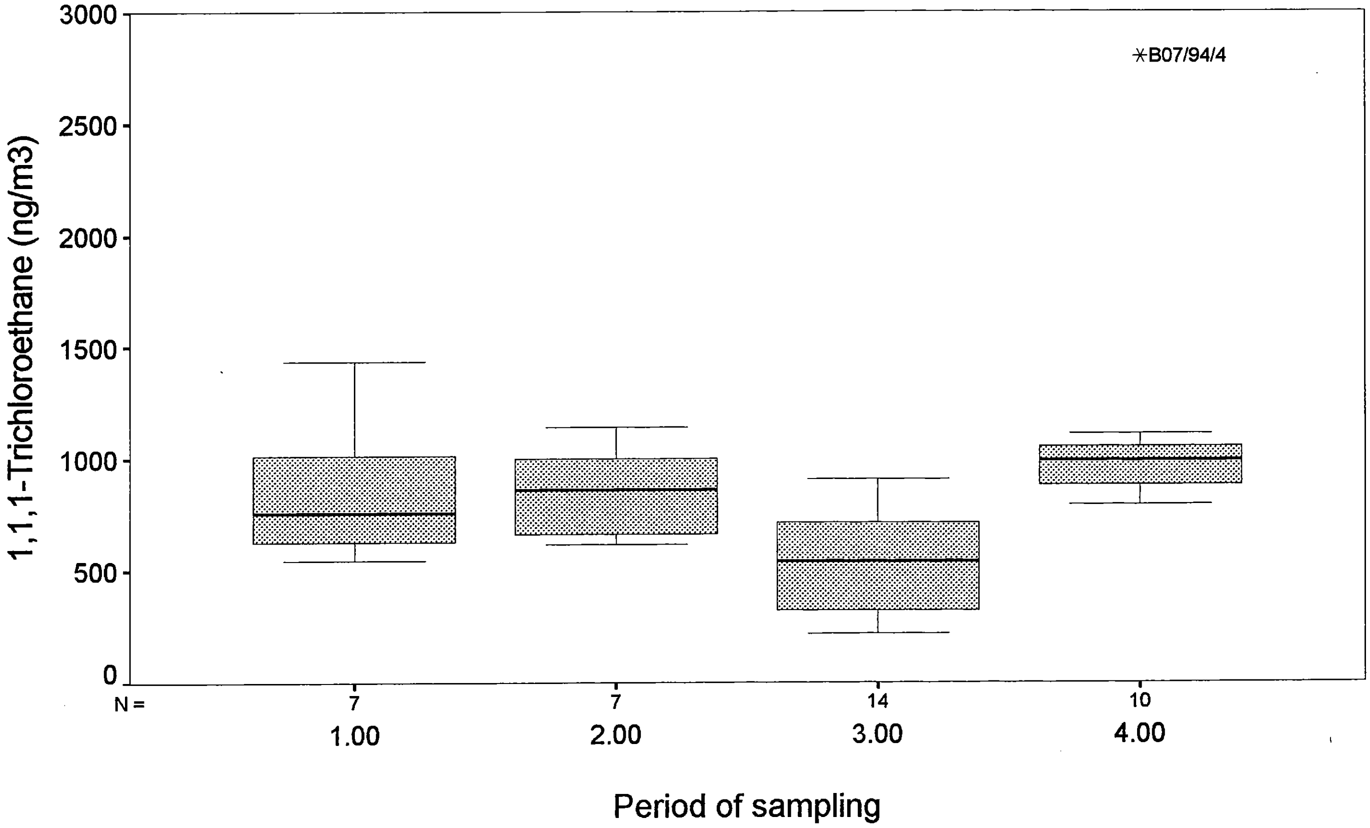


Figure III.1.10.a. Measurement results of 1,1,1-trichloroethane as a function of the period of sampling during the year, represented by boxplots

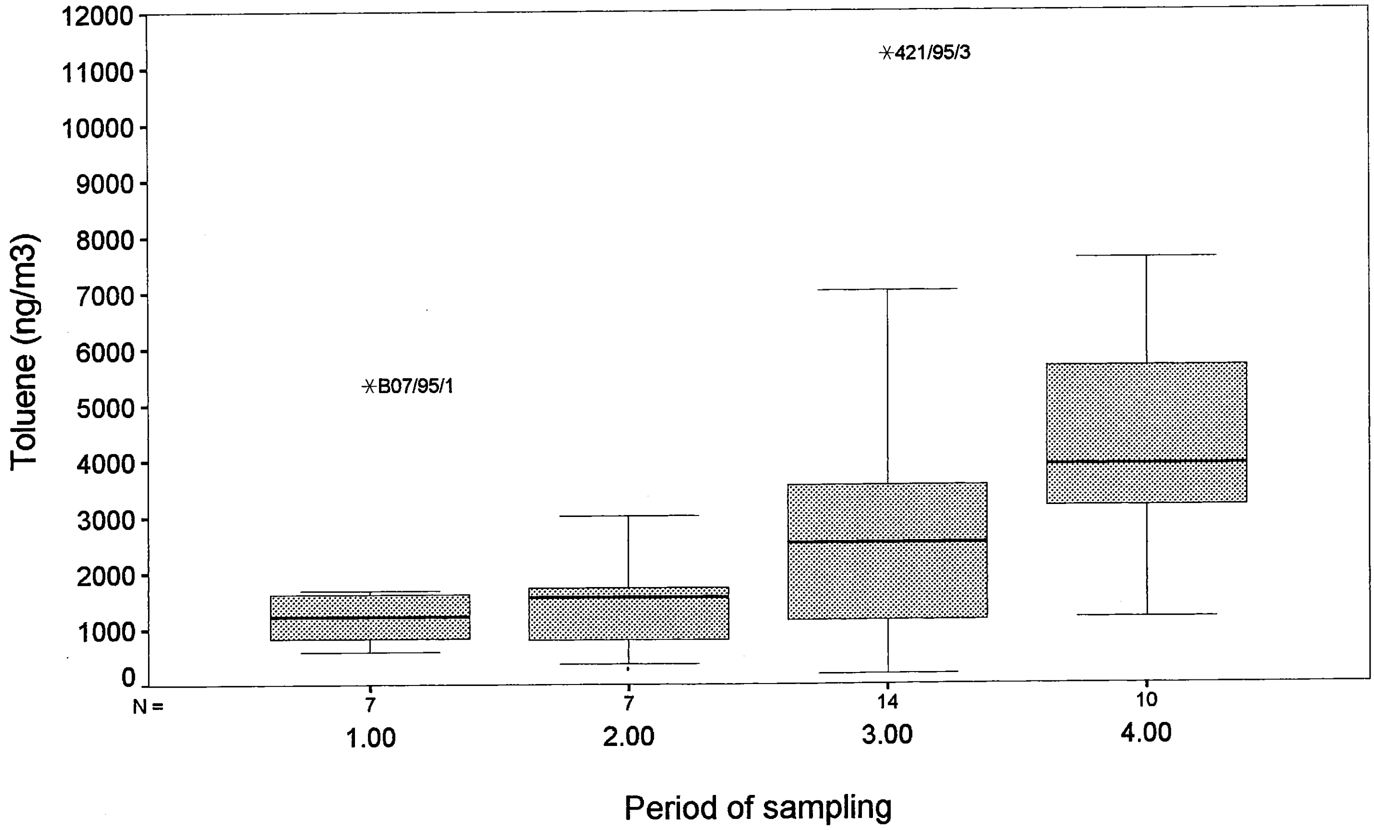


Figure III.1.10.b. Measurement results of toluene as a function of the period of sampling during the year, represented by boxplots

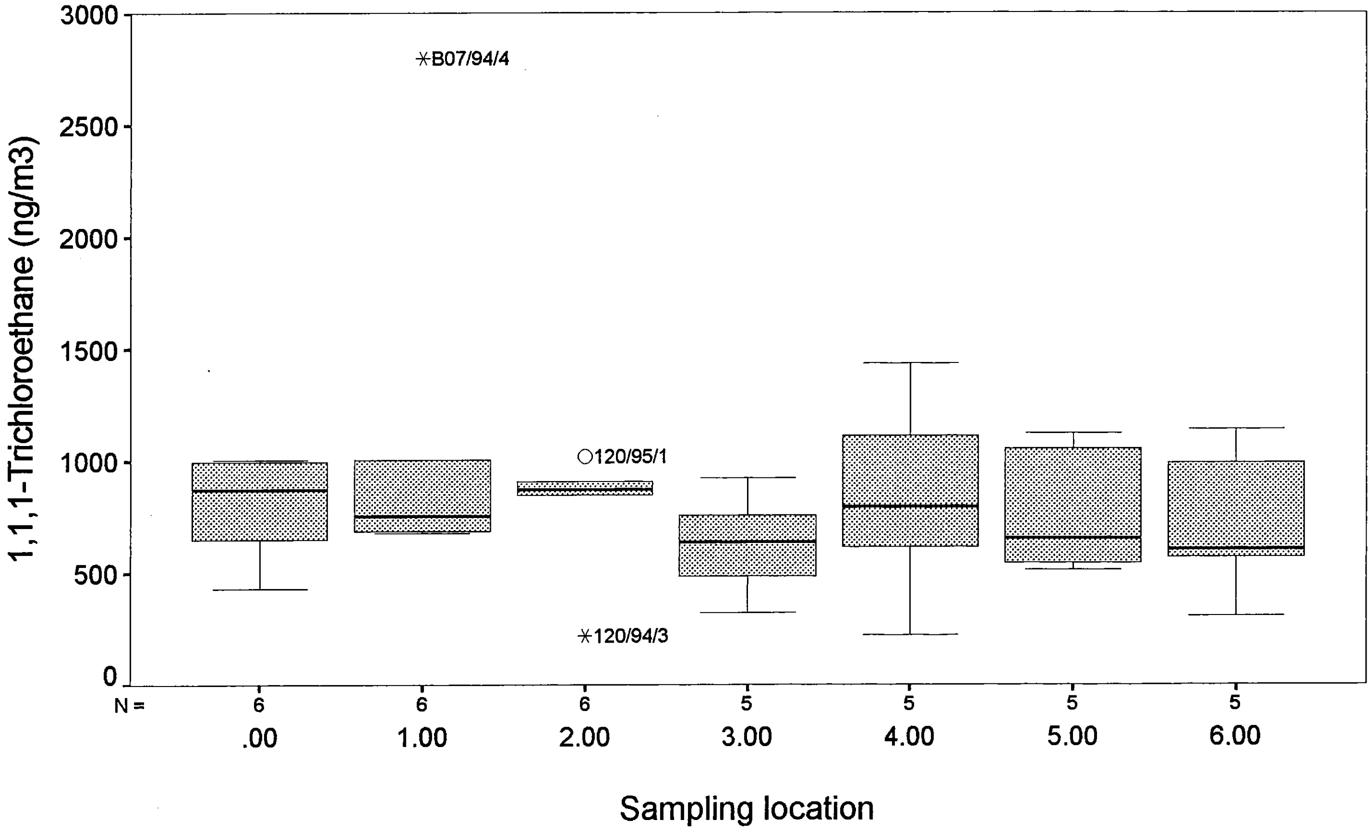


Figure III.1.11.a. Measurement results of 1,1,1-trichloroethane as a function of sampling location, represented by boxplots (.00: location S12, 1.00: location B07, 2.00: location 120, 3.00: location 780: 4.00: location 421, 5.00: location 435, 6.00: location 800)

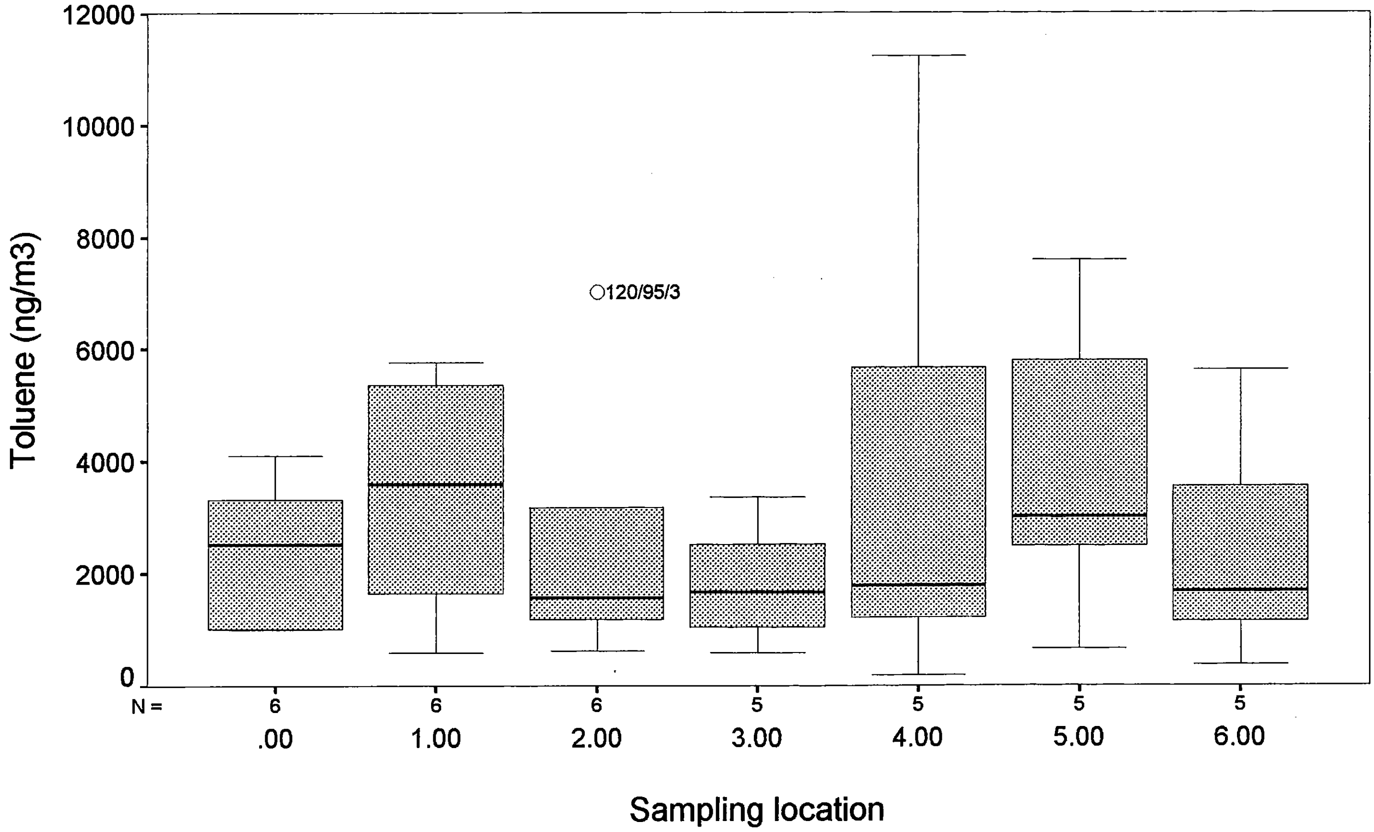


Figure III.1.11.b. Measurement results of toluene as a function of sampling location, represented by boxplots

In order to do an analysis for the factors period and sampling location, it is suitable to consider only the samples of 1995 so that for every period and location exactly 7 and 4 samples respectively are available. When the datasets of the samples taken in 1995 for all individual VOCs and for the sum of CHCs, MAHs and VOCs are considered (28 measurements), a test on normality for each dataset has to be done prior to factor analysis. By means of the Kolmogorov-Smirnov test it was shown that all individual VOCs and the sum of CHCs are normally distributed at a 0.05 significance level, except chloroform and the C_2-substituted MAHs ethylbenzene, m/p-xylene and o-xylene. However also chloroform can be assumed to be normally distributed (p value 0.046). This means that only for the C_2-substituted MAHs and the sum of MAHs and VOCs a natural logaritmic transformation is needed. These latter populations showed a normal distribution at a 0.05 significance level after the transformation, except m/p-xylene, which can be considered normally distributed as well at a 0.01 significance level (p value 0.027).

III.1.2.3.5.1. Factor period

A one way analysis of variance on all data of 1995 for all individual VOCs and for the sum of CHCs, MAHs and VOCs was carried out, together with a least significance difference test, for the factor period of the year. The results for the populations for which no transformation was needed (individual CHCs, benzene, toluene, sum of CHCs), are presented in Annex III.1.16. The results for the populations for which a transformation was needed (C_2-substituted MAHs, sum of MAHs, sum of VOCs), are given in Annex III.1.17.

For the CHCs chloroform, tetrachloromethane, 1,2-dichloroethane and 1,1,1-trichloroethane, it can be seen that the results of the fourth period are significantly higher than those for the third period. For 1,1-dichloroethane, the measurements in the second period are significantly higher than those from all other periods, whereas the results of trichloroethylene of the third period are higher than for all other periods. In addition the second period shows higher concentrations of trichloroethylene than the first period. Finally tetrachloroethylene concentrations are significantly higher in the third period than in the first period.

For the MAHs benzene and toluene, high concentrations are observed in the fourth period. For benzene, these concentrations are higher than all other periods whereas for toluene the fourth period together with the third period showed significantly higher concentrations than the first and second period. Whereas for ethylbenzene no significant differences were noticed, the xylenes showed significantly higher concentrations in the second period than in all other periods.

Since the dataset is limited it is unsuitable to make some conclusions with respect to the dependancy of the concentration levels on the time of sampling during the year.

III.1.2.3.5.2. Factor sampling location

A one way analysis of variance on all data of 1995 for all individual VOCs and for the sum of CHCs, MAHs and VOCs was carried out, together with a least significance difference test, for the factor sampling location. The results for the populations for which no transformation was needed (individual CHCs, benzene, toluene, sum of CHCs), are presented in Annex III.1.18. The results for the populations for which a transformation was needed (C_2-substituted MAHs, sum of MAHs, sum of VOCs), are given in Annex III.1.19.

No one sampling location proved to have significantly higher concentrations of one individual VOC than another except 1,2-dichloroethane. This compound had significantly higher concentrations at location 435 than at the locations B07 and 780. However, this difference is based on a small dataset.

In these analyses, it was proven that for the VOCs the location of sampling on the Belgian Continental Shelf or at the mouth of the Scheldt estuary of in the Scheldt estuary does not make any difference in the concentration levels of the VOCs.

III.1.2.4. CONCLUSIONS

III.1.2.4.1. Conclusions with respect to concentration levels

The concentration levels of the individual VOCs are different among the VOCs. This can be seen from the 25 and 75 percentiles. A schematic representation is given in Figure III.1.12.

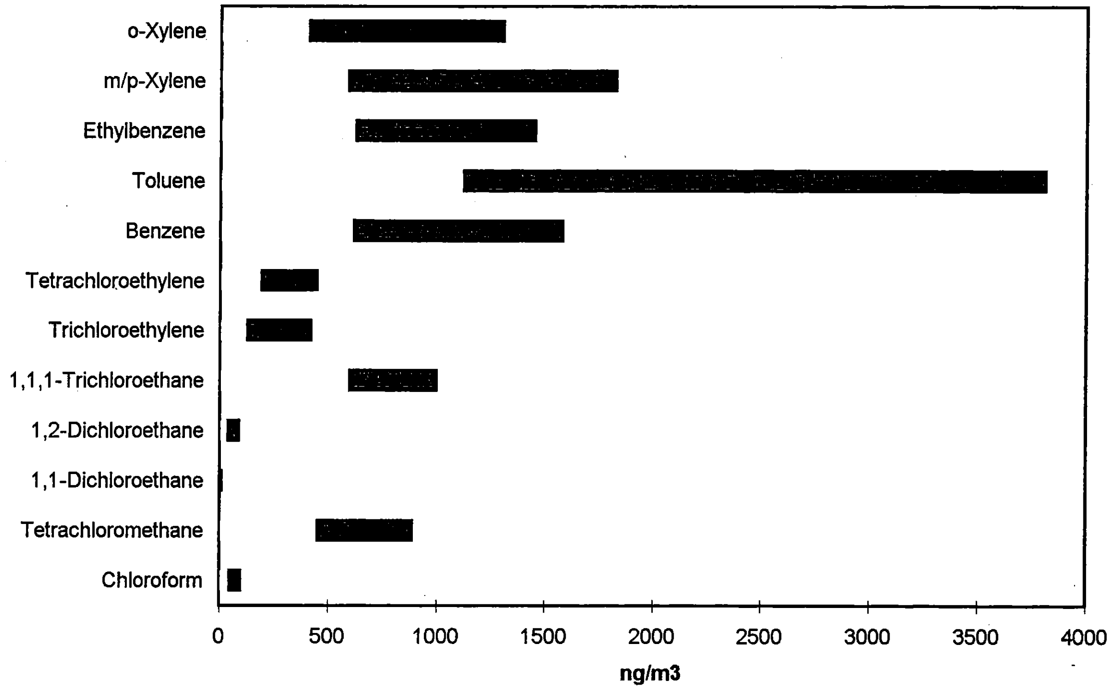


Figure III.1.12. Representation of the 25- to 75- percentile range of all individual VOCs of all samples

Within the CHCs, four groups can be recognized. The first group only consists of 1,1-dichloroethane with concentrations generally below 10ng.m^{-3} (25 and 75 percentiles 5.9 and 11.5ng.m^{-3}). A second group shows concentration in the 10 to 100ng.m^{-3} range and contains chloroform (25-75 percentile range: 48-101ng.m^{-3}) and 1,2-dichloroethane (25-75 percentile range: 38-91ng.m^{-3}). Next, trichloroethylene and tetrachloroethylene are grouped by their concentrations in the 100 to 500ng.m^{-3}. Their 25- to 75-percentile ranges are 128-425ng.m^{-3} and 194-452ng.m^{-3} respectively. Finally, the group with the highest concentrations, i.e. in the 500 to 1000ng.m^{-3} range, contains tetrachloromethane (25- to 75-percentile range: 454-890ng.m^{-3}) and 1,1,1-trichloroethane (25- to 75-percentile range: 597-999ng.m^{-3}).

All MAHs are in general in the 500 to 1500ng.m^{-3} concentration range, except toluene (Figure III.1.12). The 25- and 75-percentiles for benzene are 615 and 1583ng.m^{-3}, for ethylbenzene 625 and 1457ng.m^{-3}, for m/p-xylene 589 and 1831ng.m^{-3} and for o-xylene 407 and 1308ng.m^{-3}. Toluene shows higher concentrations with the 25- and 75-percentile as 1123 and 3814ng.m^{-3}.

III.1.2.4.2. Conclusions with respect to relationships between individual VOCs

From the principal component analysis on the VOCs and from the correlation coefficients between all individual VOCs, some conclusions with respect to relationships between the

VOCs can be made.

Within the group of CHCs, the compounds most correlated are 1,1,1-trichloroethane and tetrachloromethane. In the correlation coefficient matrix they showed a correlation coefficient of 0.75. The correlation is also found in the principal component analysis on all individual CHCs where they are the main compounds of the first factor. Also in the principal component analysis on all individual VOCs they are grouped together (4th factor). Other groups revealed by the principal component analysis are a group of trichloroethylene and tetrachloroethylene and a group of chloroform and 1,2-dichloroethane.

The best correlations among the MAHs are those between C_2-substituted MAHs. The correlation coefficients between ethylbenzene and m/p-xylene is 0.84, between ethylbenzene and o-xylene 0.81 and between m/p-xylene and o-xylene 0.99. This relationship was also found in the principal component analysis on all individual MAHs and on all individual VOCs, where these compounds were in both cases mainly contributing to the first factor. The relationship between benzene and toluene was not so high as it was for the C_2-substituted MAHs. Their correlation coefficient was lower (0.65). In the principal component analysis on all individual MAHs they were grouped together in a second factor but in the principal component analysis on all individual VOCs they were separated and contributed to different factors.

Correlations between individual CHCs and MAHs are poor. No one of all correlation coefficients between an individual CHC and an individual MAH was above 0.60 (1,2-dichloroethane and benzene), except between tetrachloroethylene and toluene, showing a correlation coefficient of 0.68. In the principal component analysis on all individual VOCs, relationships between trichloroethylene, tetrachloroethylene and toluene were shown, next to relationships between chloroform, 1,2-dichloroethane and benzene.

The relationships are schematically represented in Figure III.1.13.

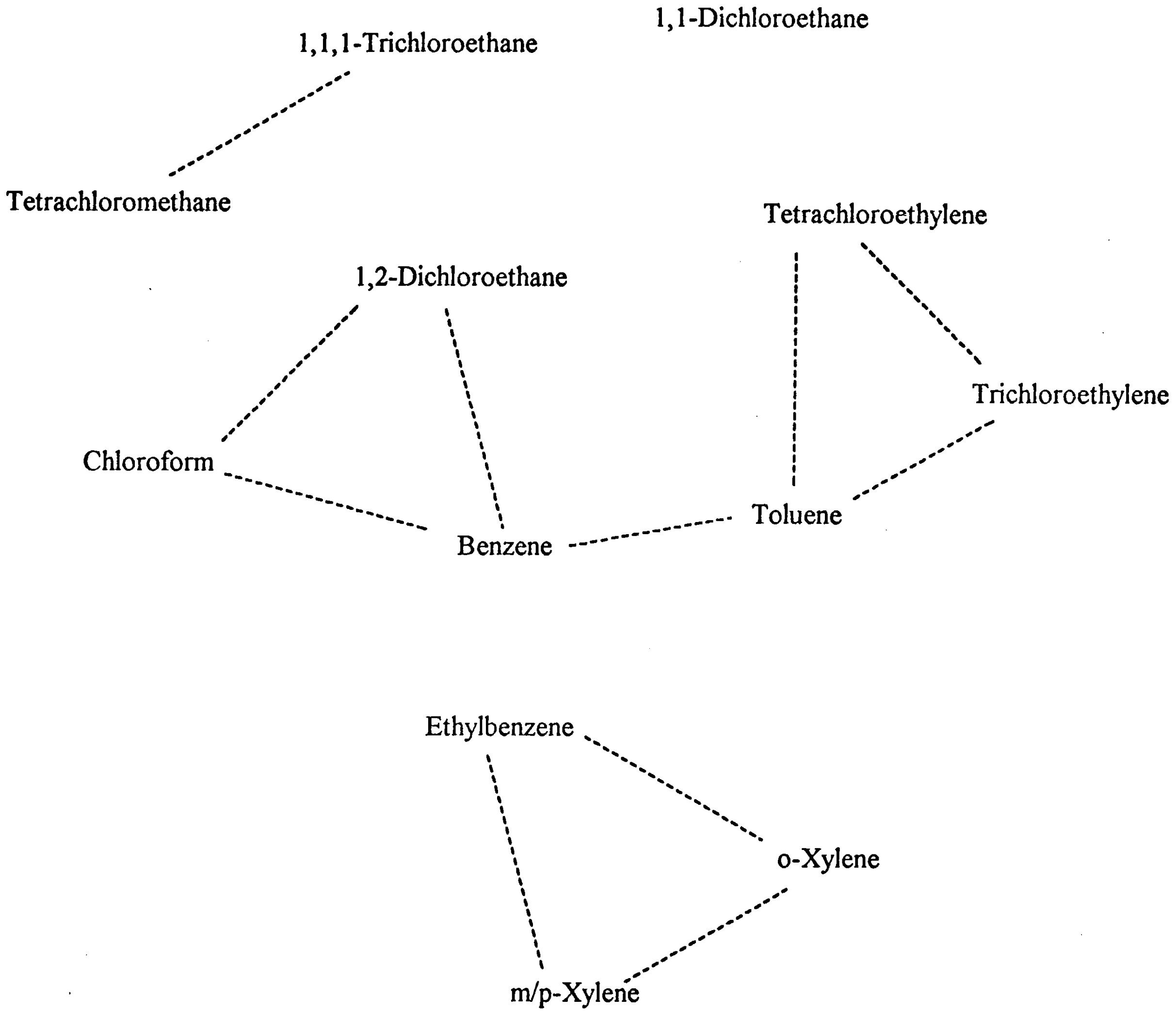


Figure III.1.13. Relationships between VOCs, observed in the correlation analysis and PCA

III.1.2.4.3. Conclusions with respect to sampling location

From the factor analysis evaluating the factor sampling location, no one single or one group of sampling locations proved to have higher concentrations of one compound than another single sampling location or group of sampling locations, except for 1,2-dichloroethane. 1,2-Dichloroethane showed higher concentrations at location 435 (location far from the coast line) than at the locations B07 and 780, which are locations near to the mouth of the Scheldt estuary and near to the coast.

In conclusion it is clear that nor the location in the Scheldt estuary (near Doel), nor the location at the mouth of the Scheldt estuary, nor the group of sampling locations near the coast, nor the group of sampling locations far from the coast could be distinguished by higher or lower concentrations from another group.

III.1.2.4.4. Conclusions with respect to the time of sampling

With respect to the time of sampling, two groups of samples can be remarked. A first group of samples which is separated consists of three samples taken in the second period of 1995. They show higher concentrations of C_2-substituted MAHs. This was illustrated by the cluster analysis on all individual MAHs, by the cluster analysis on all individual VOCs, by the principal component analysis on all individual MAHs and by the principal component analysis on all individual VOCs. At the same time also water samples with elevated water concentrations were found. No clear explanation can be found in the literature for these higher concentrations. However, it can be suggested that the water body act as a (biogenic) source at that time so that the concentrations in the atmosphere were elevated by an input from the water body.

A second group of samples to be distinguished contains three samples taken during the third period of 1995 and showed higher concentrations of trichloroethylene and tetrachloroethylene. This was proven in the cluster analysis on CHCs. The samples were taken at the locations 780 and 120 (near to the coast) and at location 421 (far from the coast). No direct explanation can be given for the elevated concentrations of trichloroethylene and tetrachloroethylene in the third period of the year.

III.2. WATER

III.2.1. VARIABILITY OF THE CONCENTRATIONS IN WATER SAMPLES AT ONE LOCATION, AT THE SAME TIME

According to the programme the variability of the measured concentrations in multiple sampling on one sampling location was verified. On sampling location 780 (N 51° 28.27, E 3° 03.48) five samples were taken after each other on 27 May 1993. All samples were taken within a 30 minutes period. The measured concentrations for all VOCs for each sample are presented in Table III.2.1. The relative standard deviation varies from 6.3% for toluene to 44.3% for 1,2-dichloroethane. The mean value of the deviation is 22.1%. Data presented are overall variabilities including sampling, analysis, data treatment and inherent variability of concentrations in the water samples.

Table III.2.1. Results of multiple sampling (sample names A, B, C, D and E) on location 780 (N 51°28.27, E 3° 03.48) on 27 May 1993 ($ng.L^{-1}$), calculated average concentration (X) ($ng.L^{-1}$), standard deviation ($ng.L^{-1}$) and relative standard deviation in % (%RSD).

	A	B	C	D	E	X	s	%RSD
Chloroform	11.34	11.77	13.44	14.61	4.84	11.2	3.79	33.8
Tetrachloromethane	0.58	0.88	1.00	1.32	1.01	0.96	0.27	27.8
1,1-Dichloroethane	<1.14	<1.14	<1.14	<1.14	<1.14	-	-	-
1,2-Dichloroethane	4.89	8.44	10.36	10.34	17.39	10.28	4.56	44.3
1,1,1-Trichloroethane	2.11	2.68	1.95	2.27	2.32	2.27	0.27	12.1
Trichloroethylene	4.87	5.05	5.25	4.08	4.28	4.71	0.50	10.7
Tetrachloroethylene	1.50	1.52	1.11	1.02	1.12	1.25	0.24	18.9
Benzene	26.51	45.28	37.35	31.94	31.63	34.54	7.12	20.6
Toluene	35.16	39.00	39.40	38.75	34.41	37.34	2.36	6.3
Ethylbenzene	9.44	46.74	7.28	6.11	6.05	7.22	1.58	22.0
m/p-Xylene	11.02	90.36	10.25	7.76	7.49	9.13	1.77	19.4
o-Xylene	9.76	196.56	13.48	7.26	8.52	9.76	2.68	27.5

III.2.2. MONITORING OF CONCENTRATIONS OF THE TARGET COMPOUNDS IN WATER SAMPLES DURING THREE YEARS, ACCORDING TO THE PROGRAMME

III.2.2.1. SAMPLES: LOCATIONS AND TIMES

Samples were taken at 6 sampling points according to the programme. The sampling points are indicated on a map of the Belgian Continental Shelf (Figure III.2.1). Two sampling points (120 and 780) are near to the coast (4-15km) and two sampling points (421 and 435) are far from the coast (35-40km). Two sampling points are related to the Scheldt estuary. At the mouth of the Scheldt samples were taken on the sampling point B07 whereas samples in the estuary were taken at station S12, which is close to the border between Belgium and The Netherlands. In addition, a reference point (800), 60km from the coastline, was also sampled in the monitoring campaigns. The positions of all sampling points are given in Table III.2.2.

All dates and locations on which samples were taken, are presented in Table III.2.3. It was planned to take samples in four periods each year. Therefore each sample can be coded by means of *sampling point/year/period*. Periods are defined as period 1 for samples taken in February and March, as period 2 for samples taken at the end of April and in May, as period 3 for samples taken at the end of September and in October and as period 4 for samples taken during the second half of November and the first half of December. The codes are also given in Table III.2.3 and will be used further on.

It can be seen from Table III.2.3 that for the first and fourth period in 1994 not all stations could be sampled because of bad weather conditions. Moreover, no samples were taken in the second period of 1994 since no campaign time was available.

Table III.2.2. 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

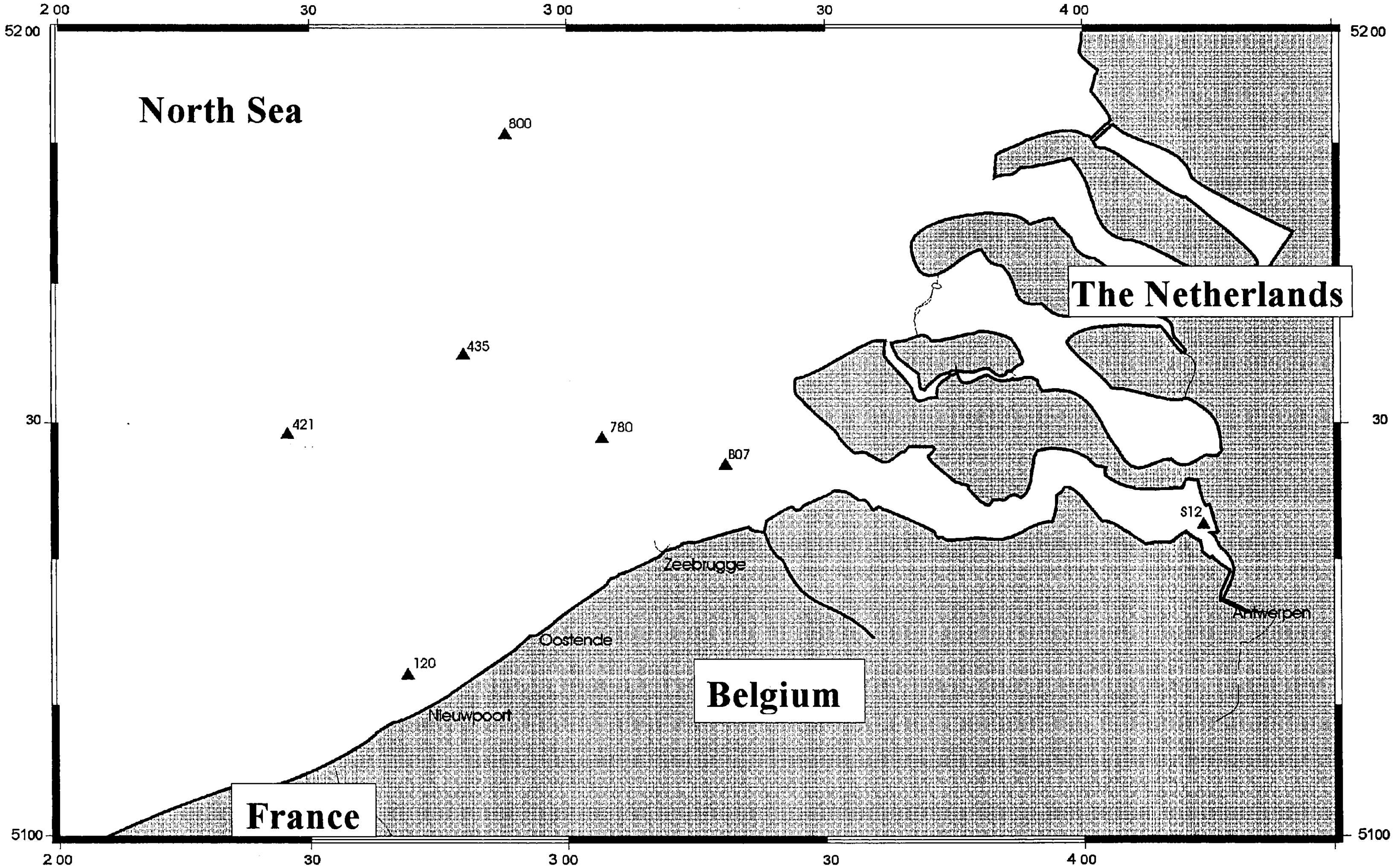


Figure III.2.1. Map of the sampling locations on the Belgian continental shelf and in the Scheldt estuary

Table III.2.3. Overview of samples taken in the monitoring campaigns: date, location, year, period of the year and code.

Date	Location	Year	Period	Code
16/03/93	B07	1993	1	B07/93/1
16/03/93	S12	1993	1	S12/93/1
8/03/93	120	1993	1	120/93/1
10/03/93	780	1993	1	780/93/1
9/03/93	421	1993	1	421/93/1
9/03/93	435	1993	1	435/93/1
11/03/93	800	1993	1	800/93/1
27/05/93	B07	1993	2	B07/93/2
26/05/93	S12	1993	2	S12/93/2
24/05/93	120	1993	2	120/93/2
27/05/93	780	1993	2	780/93/2
25/05/93	421	1993	2	421/93/2
25/05/93	435	1993	2	435/93/2
25/05/93	800	1993	2	800/93/2
11/10/93	B07	1993	3	B07/93/3
11/10/93	S12	1993	3	S12/93/3
19/10/93	120	1993	3	120/93/3
19/10/93	780	1993	3	780/93/3
18/10/93	421	1993	3	421/93/3
18/10/93	435	1993	3	435/93/3
13/10/93	800	1993	3	800/93/3
30/11/93	B07	1993	4	B07/93/4
29/11/93	S12	1993	4	S12/93/4
2/12/93	120	1993	4	120/93/4
29/11/93	780	1993	4	780/93/4
1/12/93	421	1993	4	421/93/4
1/12/93	435	1993	4	435/93/4
1/12/93	800	1993	4	800/93/4
14/03/94	B07	1994	1	B07/94/1
1/02/94	S12	1994	1	S12/94/1
20/09/94	B07	1994	3	B07/94/3
20/09/94	S12	1994	3	S12/94/3
15/09/94	120	1994	3	120/94/3

Date	Location	Year	Period	Code
14/09/94	780	1994	3	780/94/3
15/09/94	421	1994	3	421/94/3
19/09/94	435	1994	3	435/94/3
22/09/94	800	1994	3	800/94/3
5/12/94	B07	1994	4	B07/94/4
5/12/94	S12	1994	4	S12/94/4
7/12/94	120	1994	4	120/94/4
28/03/95	B07	1995	1	B07/95/1
27/03/95	S12	1995	1	S12/95/1
30/03/95	120	1995	1	120/95/1
30/03/95	780	1995	1	780/95/1
31/03/95	421	1995	1	421/95/1
30/03/95	435	1995	1	435/95/1
4/04/95	800	1995	1	800/95/1
15/05/95	B07	1995	2	B07/95/2
18/05/95	S12	1995	2	S12/95/2
17/05/95	120	1995	2	120/95/2
17/05/95	780	1995	2	780/95/2
16/05/95	421	1995	2	421/95/2
16/05/95	435	1995	2	435/95/2
15/05/95	800	1995	2	800/95/2
18/10/95	B07	1995	3	B07/95/3
18/10/95	S12	1995	3	S12/95/3
17/10/95	120	1995	3	120/95/3
16/10/95	780	1995	3	780/95/3
16/10/95	421	1995	3	421/95/3
16/10/95	435	1995	3	435/95/3
16/10/95	800	1995	3	800/95/3
4/12/95	B07	1995	4	B07/95/4
4/12/95	S12	1995	4	S12/95/4
6/12/95	120	1995	4	120/95/4
5/12/95	780	1995	4	780/95/4
6/12/95	421	1995	4	421/95/4
7/12/95	435	1995	4	435/95/4
7/12/95	435	1995	4	800/95/4

III.2.2.2. RESULTS

The results for all samples are presented in Table III.2.4 for each sampling period. All samples were classified according to the measured concentrations for each VOC and for the sum of CHCs, MAHs and VOCs. This is illustrated in Figure III.2.2 for 1,1,1-trichloroethane and toluene in a histogram. The number of samples for each class of concentration is presented as a function of the mean concentration value of each class. The same representation for all individual VOCs and for the sum of CHCs, MAHs and VOCs is given in Annex III.2.1.

Table III.2.4.a. Measurement results of the campaign in the first period of 1993 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	154.1	175.5	33.4	100.4	124.2	57.8	160.7
Tetrachloromethane	8.6	21.0	4.5	3.9	5.4	5.3	7.0
1,1-Dichloroethane	<1.1	14.8	<1.1	<1.1	<1.1	<1.1	<1.1
1,2-Dichloroethane	21.9	108.3	5.8	30.5	8.3	7.6	23.8
1,1,1-Trichloroethane	12.9	198.7	5.0	10.6	4.6	6.6	8.3
Trichloroethylene	28.3	135.5	11.8	15.0	13.4	11.1	18.5
Tetrachloroethylene	4.2	215.8	2.6	1.8	1.5	2.4	5.9
Benzene	26.6	34.5	16.3	21.0	23.6	23.4	85.0
Toluene	41.0	64.7	22.2	30.8	31.9	25.0	43.7
Ethylbenzene	16.6	20.1	11.1	7.7	9.4	13.3	14.6
m/p-Xylene	17.1	180.8	15.0	7.5	13.4	22.2	10.2
o-Xylene	19.6	28.1	12.7	7.0	15.1	19.2	10.5

Table III.2.4.b. Measurement results of the campaign in the second period of 1993 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	17.4	42.6	31.3	11.3	11.1	12.8	11.3
Tetrachloromethane	2.4	3.0	<0.8	<0.8	1.0	1.4	1.5
1,1-Dichloroethane	<1.1	6.9	<1.1	<1.1	<1.1	<1.1	<1.1
1,2-Dichloroethane	8.7	48.0	41.8	4.9	23.3	9.8	10.5
1,1,1-Trichloroethane	3.6	101.5	3.1	2.1	3.7	3.1	3.1
Trichloroethylene	7.3	54.7	9.5	4.9	6.4	6.0	6.0
Tetrachloroethylene	1.4	52.9	1.7	1.5	1.5	1.0	1.0
Benzene	34.7	21.0	22.3	26.5	18.4	26.8	96.9
Toluene	52.0	46.4	48.5	35.2	34.1	49.7	96.2
Ethylbenzene	18.7	36.9	7.2	9.4	8.2	11.4	7.2
m/p-Xylene	15.1	22.9	11.4	11.0	7.9	12.8	9.5
o-Xylene	11.9	21.0	10.7	9.8	12.4	10.9	8.0

Table III.2.4.c. Measurement results of the campaign in the third period of 1993 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	373.8	349.9	11926.4	9718.4	96.5	180.3	206.2
Tetrachloromethane	1.2	2.4	14.7	13.5	<0.8	1.3	1.0
1,1-Dichloroethane	<1.1	5.7	17.5	1.1	<1.1	<1.1	<1.1
1,2-Dichlooroethane	6.4	401.9	18.7	4.4	0.9	3.0	<1.1
1,1,1-Trichloroethane	6.6	55.7	12.4	7.4	3.9	6.9	2.5
Trichloroethylene	7.0	88.2	10.9	7.2	3.9	4.2	5.2
Tetrachloroethylene	1.8	104.4	6.7	4.9	1.0	4.0	1.7
Benzene	25.1	22.7	29.5	26.1	22.7	25.1	15.5
Toluene	38.4	30.4	76.2	57.8	63.6	32.1	17.6
Ethylbenzene	134.1	15.4	16.2	12.5	9.4	5.5	4.9
m/p-Xylene	177.7	13.9	24.2	16.2	14.4	7.5	5.7
o-Xylene	129.7	21.7	31.7	16.5	12.1	6.9	7.3

Table III.2.4.d. Measurement results of the campaign in the fourth period of 1993 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	72.3	113.9	125.4	122.4	53.7	71.8	66.0
Tetrachloromethane	2.2	8.1	1.5	5.2	0.9	1.0	1.2
1,1-Dichloroethane	1.2	6.8	<1.1	<1.1	<1.1	<1.1	<1.1
1,2-Dichloorethane	23.3	159.0	20.1	8.9	17.3	16.8	<1.1
1,1,1-Trichloroethane	14.3	80.5	7.0	6.1	2.3	6.6	6.0
Trichloroethylene	11.6	201.0	13.7	8.1	5.0	10.5	9.0
Tetrachloroethylene	3.2	130.2	3.1	2.6	1.9	3.1	3.2
Benzene	28.0	29.1	32.0	27.4	19.5	32.4	21.2
Toluene	39.5	59.0	70.8	114.5	26.9	66.4	36.8
Ethylbenzene	10.5	22.7	83.9	35.2	8.4	14.5	7.7
m/p-Xylene	15.5	15.3	53.2	23.9	8.7	19.8	9.9
o-Xylene	15.0	21.7	39.4	24.2	8.9	18.5	9.3

Table III.2.4.e. Measurement results of the campaign in the first period of 1994 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12
Chloroform	11.0	146.7
Tetrachloromethane	<0.8	6.0
1,1-Dichloroethane	1.2	16.5
1,2-Dichloorethane	33.7	54.1
1,1,1-Trichloroethane	10.7	246.2
Trichloroethylene	1030.6	272.2
Tetrachloroethylene	6.3	372.4
Benzene	21.9	20.0
Toluene	35.2	112.5
Ethylbenzene	12.2	18.4
m/p-Xylene	15.4	33.6
o-Xylene	9.0	13.9

Table III.2.4.f. Measurement results of the campaign in the third period of 1994 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	87.1	44.4	26.7	1060.3	20.3	23.2	32.9
Tetrachloromethane	1.3	1.8	0.9	7.5	<0.8	<0.8	0.8
1,1-Dichloroethane	<1.1	4.3	<1.1	8.6	<1.1	<1.1	<1.1
1,2-Dichloroethane	2.5	30.2	2.9	5.9	2.7	27.5	2.4
1,1,1-Trichloroethane	2.2	40.9	2.1	7.4	3.8	1.9	2.5
Trichloroethylene	<0.5	23.9	4.4	12.9	17.5	14.6	5.6
Tetrachloroethylene	1.0	62.6	1.0	2.7	1.5	1.2	0.7
Benzene	9.3	26.3	12.1	16.7	14.1	10.0	15.3
Toluene	23.5	33.9	18.4	32.6	19.9	21.4	17.9
Ethylbenzene	8.9	21.3	4.9	10.0	8.0	13.5	5.5
m/p-Xylene	15.3	31.7	7.2	10.5	11.7	25.0	7.4
o-Xylene	18.2	31.9	8.2	12.4	14.6	21.9	8.2

Table III.2.4.g. Measurement results of the campaign in the fourth period of 1994 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120
Chloroform	10.4	48.2	11.1
Tetrachloromethane	1.0	2.2	1.6
1,1-Dichloroethane	<1.1	4.2	<1.1
1,2-Dichloroethane	5.4	40.1	3.8
1,1,1-Trichloroethane	22.1	55.6	3.0
Trichloroethylene	<0.5	61.1	<0.5
Tetrachloroethylene	2.3	72.3	3.8
Benzene	12.4	13.2	12.7
Toluene	31.3	17.9	24.4
Ethylbenzene	5.3	6.7	4.9
m/p-Xylene	6.0	8.6	5.4
o-Xylene	6.3	7.2	5.4

Table III.2.4.h. Measurement results of the campaign in the first period of 1995 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	551.1	184.4	26.1	17.0	24.9	32.7	24.6
Tetrachloromethane	2.2	3.3	1.7	1.7	0.8	1.3	0.8
1,1-Dichloroethane	2.0	7.4	1.5	<1.1	1.1	1.3	1.2
1,2-Dichlooroethane	9.2	42.4	20.5	9.4	4.9	5.6	6.7
1,1,1-Trichloroethane	4.0	98.3	3.0	3.6	2.7	3.3	12.0
Trichloroethylene	8.5	94.1	6.5	13.3	6.8	15.1	22.4
Tetrachloroethylene	3.1	108.8	1.6	1.9	1.6	2.2	2.2
Benzene	15.6	18.8	15.9	16.0	21.9	22.7	16.3
Toluene	14.9	23.9	12.4	10.8	16.8	21.7	24.2
Ethylbenzene	13.4	14.8	34.3	7.3	8.5	31.9	31.1
m/p-Xylene	7.0	10.4	13.7	4.9	5.6	11.9	22.6
o-Xylene	6.3	8.4	10.1	4.2	5.0	9.5	15.9

Table III.2.4.i. Measurement results of the campaign in the second period of 1995 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	5.4	78.1	8.8	7.7	17.3	12.6	16.2
Tetrachloromethane	1.7	4.7	2.0	1.5	1.5	1.9	4.5
1,1-Dichloroethane	1.1	5.4	<1.1	<1.1	<1.1	<1.1	2.4
1,2-Dichloroethane	7.1	157.3	4.5	6.2	6.2	5.7	8.2
1,1,1-Trichloroethane	4.0	84.7	3.1	3.6	5.9	3.1	6.1
Trichloroethylene	54.7	75.3	21.5	12.2	16.5	22.5	20.0
Tetrachloroethylene	2.1	91.6	1.4	1.3	2.0	1.7	5.6
Benzene	21.7	27.1	14.1	20.9	15.1	20.8	14.2
Toluene	32.9	40.7	32.4	25.2	18.5	19.1	13.2
Ethylbenzene	108.5	52.5	52.0	44.9	32.6	57.9	41.0
m/p-Xylene	342.1	147.9	142.4	133.7	71.5	157.1	112.1
o-Xylene	107.5	41.8	'47.3	46.9	22.6	45.6	39.8

Table III.2.4.j. Measurement results of the campaign in the third period of 1995 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	10.9	51.5	6.7	13.5	17.8	16.8	152.3
Tetrachloromethane	1.9	4.8	1.7	1.8	5.8	2.2	5.2
1,1-Dichloroethane	<1.1	5.2	<1.1	<1.1	4.8	1.1	4.7
1,2-Dichloroethane	4.9	178.8	5.2	5.4	8.6	3.8	5.5
1,1,1-Trichloroethane	3.5	96.1	4.5	3.0	6.6	3.0	5.7
Trichloroethylene	5.8	29.9	4.3	3.7	7.0	3.6	4.4
Tetrachloroethylene	3.2	144.0	4.2	2.7	5.7	3.3	19.0
Benzene	12.5	19.1	14.2	6.8	18.8	8.9	14.2
Toluene	37.6	63.0	34.2	18.3	35.9	22.3	37.0
Ethylbenzene	13.4	32.2	8.4	14.5	34.0	32.0	26.1
m/p-Xylene	22.8	68.3	12.8	32.6	71.9	68.5	48.0
o-Xylene	17.5	50.7	10.3	26.0	62.9	62.4	43.8

Table II.2.4.k. Measurement results of the campaign in the fourth period of 1995 for each compound for each sampling station (in ng.L^{-1}).

Compound	B07	S12	120	780	421	435	800
Chloroform	7.0	73.9	9.1	7.6	9.5	11.3	9.3
Tetrachloromethane	1.7	2.8	1.5	1.5	1.6	2.2	1.1
1,1-Dichloroethane	1.1	6.2	<1.1	<1.1	<1.1	<1.1	<1.1
1,2-Dichlooroethane	11.0	106.7	9.1	15.5	6.0	15.6	4.9
1,1,1-Trichloroethane	2.8	51.0	2.7	2.6	2.4	2.9	1.8
Trichloroethylene	9.1	39.0	3.1	4.1	2.6	3.4	2.2
Tetrachloroethylene	3.2	183.5	2.8	2.9	2.4	2.7	2.6
Benzene	11.1	14.7	12.1	6.3	12.4	15.3	9.0
Toluene	34.9	30.6	36.8	24.6	37.3	39.0	26.6
Ethylbenzene	7.1	12.1	7.4	5.4	6.4	8.8	6.2
m/p-Xylene	10.2	9.7	11.6	8.9	73.2	13.4	8.8
o-Xylene	7.3	12.4	9.6	5.9	8.0	11.9	7.1

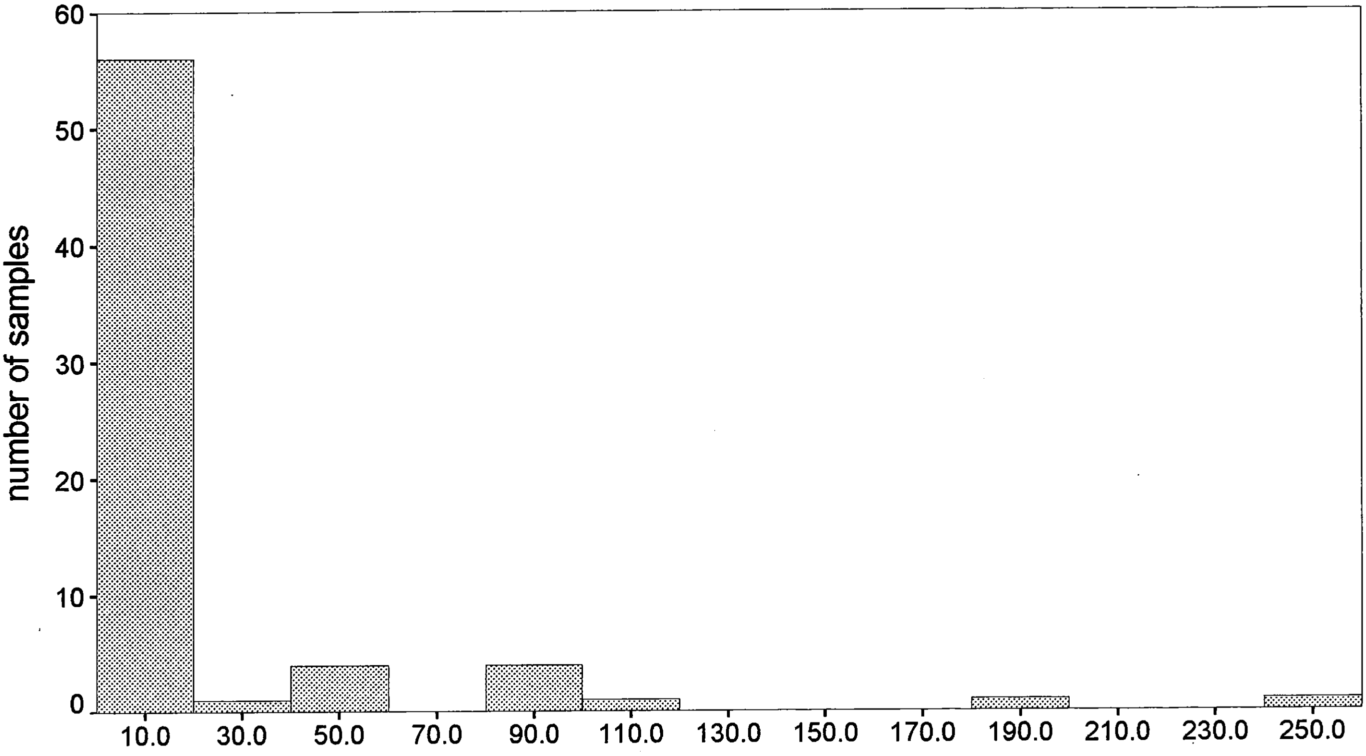


Figure III.2.2.a. Classification of the samples according to the measured concentration of 1,1,1-trichloroethane (ng.L^{-1}), represented by a histogram

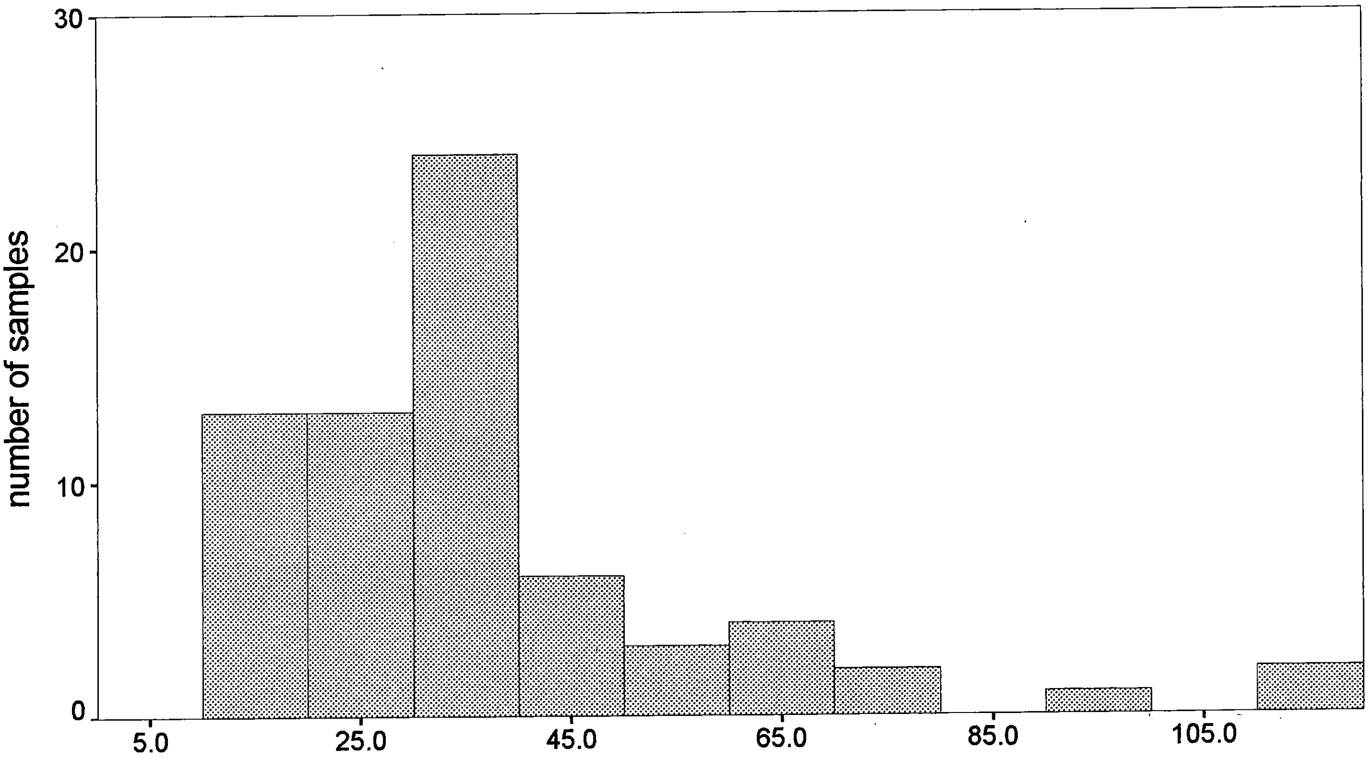


Figure III.2.2.b. Classification of the samples according to the measured concentration of toluene (ng.L^{-1}), represented by a histogram

It can be seen that the distribution of the concentration classes is very skewed to the lowest concentrations for chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, ethylbenzene and the xylenes. A similar skewness is found for the sum of CHCs, MAHs and VOCs. It has to be remarked that for these distributions individual compounds with the largest concentrations determine the group profile. The skewness is less pronounced for benzene and toluene.

III.2.2.3. STATISTICAL APPROACH OF THE RESULTS

A series of statistical tests was done on the dataset from all monitoring campaigns. The tests were carried out by means of the statistical package SPSS (Statistical Package for Social Sciences, originally developed for social sciences, but now extended for a wide range of applications).

In a first step cluster analyses were done in order to see if some groups of samples were clustering. This was done by means of a hierarchical cluster method with between-groups linkage based on squared Euclidian distances.

Secondly, principal component analysis (PCA) was executed in order to investigate if some underlying relationships between samples could be found. Principal components were extracted when eigenvalues were greater than or equal to one.

Thirdly, bivariate correlations (Pearson coefficients) between the VOCs were checked.

Finally, some parameters like year, period and location were considered in order to find out if some years, periods or locations could be distinguished from other years, periods or locations respectively. Therefore, the normality of the distributions was tested by means of a Kolmogorov-Smirnov test because in the factor analysis normal distribution is assumed. Since the datasets showed no normal distribution, a logaritmic transformation was done and proved to be normally distributed in almost all cases. So factor analyses, i.e. one way analyses of variance and independent-sample t-tests, were done on datasets after logaritmic transformation.

III.2.2.3.1. Dataset

In total 68 cases are considered for all 13 individual VOCs, for the sum of CHCs, MAHs and VOCs. In order to do some statistical tests which assume normal distribution, the data were transformed via the natural logaritmic function. The original dataset and transformed datasets used in the statistical approach are presented in Annex III.2.2 and III.2.3, respectively. The 5, 10, 25, 50, 75, 90 an 95 percentiles for each individual VOC population and for the populations of the sums of CHCs, MAHs and VOCs are presented in Annex III.2.4.

Since some statistical tests assume normal distribution, normality of the datasets with and without transformation was verified. No populations of the original data showed normal distribution with the Kolmogorov-Smirnov test at a 0.05 significance level. This is also clear from the histograms presented in Annex III.2.1. After a logaritmic transformation all populations showed a normal distribution except 1,1-dichloroethane, 1,1,1-trichloroethane, tetrachloroethylene and m/p-xylene. However, m/p-xylene showed normal distribution at 0.01 significance level whereas 1,1,1-trichloroethane and tetrachloroethylene showed normal distributions when samples from the location in the Scheldt estuary (S12) were not considered. 1,1-Dichloroethane was obviously not normally distributed, due to the large number of data below the limit of detection (45 cases out of 68 cases). The distributions after logaritmic transformation are presented in Annex III.2.5.

III.2.2.3.2. Cluster analyses

III.2.2.3.2.1. Cluster analysis on all individual CHCs

A cluster analysis on all individual CHCs was carried out. The obtained agglomeration schedule and dendrogram are presented in Annex III.2.6.

From the dendrogram it is clear that two samples can be distinguised out of the 68 cases, i.e. samples 120/93/3 and 780/93/3. This is due to higher chloroform concentrations, 11.9 and 9.7$\mu g.L^{-1}$ respectively. They are more than 10 times higher than the 95 percentile, being 0.83$\mu g.L^{-1}$. For these higher chloroform concentrations biogenic sources can be suggested (*see* Literature Study).

A second cluster analysis on all individual CHCs was executed, without the samples 120/93/3 and 780/93/3. The results are presented in Annex III.2.7. From the dendrogram it can be seen that 54 samples out of 66 cases are clustered. 12 Samples are separated from the main group because of three reasons. A first group shows high chloroform concentrations: 780/94/3 (1060ng.L^{-1}), B07/93/3 (373.4ng.L^{-1}) and B07/95/1 (551ng.L^{-1}). This is the same reason as in the case of 120/93/3 and 780/93/3, but chloroform concentrations are lower. The second group is a number of samples taken in the Scheldt estuary: S12/93/3, S12/94/1, S12/93/1, S12/95/1, S12/95/2, S12/95/3, S12/95/4 and S12/93/4. This cluster can be attributed to increased concentrations of all CHCs. The sum of CHCs is 1008, 1114, 870, 539, 497, 510, 463 and 700ng.L^{-1} respectively, whereas the 75 percentile is 230ng.L^{-1}. Finally, sample B07/94/1 is separated because of a high trichloroethylene concentration: 1031ng.L^{-1} where the 95 percentile is 172ng.L^{-1}. These higher concentrations of CHCs can be due to anthropogenic activities near the Scheldt estuary whereas for the high trichloroethylene concentrations at the mouth at the Scheldt estuary both biogenic and anthropogenic sources can be suggested.

III.2.2.3.2.2. Cluster analysis on all individual MAHs

The agglomeration schedule and dendrogram of the cluster analysis on all samples for all individual MAHs are presented in Annex III.2.8. A first cluster which is separated is the sample B07/95/2 because of high concentrations of C_2-substituted MAHs. For ethylbenzene, m/p-xylene and o-xylene, concentrations of 108.5, 342.1 and 107.6ng.L^{-1} are observed whereas the 95 percentiles are 72.2, 168.4 and 62.7ng.L^{-1} respectively. On a second level a cluster containing 7 samples with elevated MAHs concentrations is observed. It are the samples B07/93/3, S12/93/1 and five samples from the second period in 1995: 800/95/2, 435/95/2, S12/95/2, 780/95/2 and 120/95/2. The concentrations of ethylbenzene, m/p-xylene and o-xylene in these samples are 134.1, 177.7 and 129.7ng.L^{-1}; 20.1, 180.8 and 28.1ng.L^{-1}; 41.0, 112.1 and 39.8ng.L^{-1}; 57.9, 157.1 and 45.6ng.L^{-1}; 52.5, 148.0 and 41.8ng.L^{-1}; 44.9, 133.8 and 46.9ng.L^{-1}; and 52.0, 142.4 and 47.3ng.L^{-1}, respectively. All these data show high concentrations (75 percentiles are respectively 29.8, 32.4 and 23.8ng.L^{-1}), except for the sample S12/95/1 with only a high m/p-xylene concentration. For these higher concentrations of C_2-substituted MAHs in the second period of 1995, no direct explanation can be found. Since this observation was made at all sampling locations, direct local (anthropogenic) input can be rejected. Biogenic sources could be suggested. However, this hypothesis is poorly supported by the literature (*see* Part I, Literature study).

III.2.2.3.2.3. Cluster analysis on all individual VOCs

The results of a cluster analysis on all individual VOCs are presented in Annex III.2.9. From this analysis it can be seen that two samples can be distinguished from the whole dataset: sample 120/93/3 and sample 780/93/3. The reason for this cluster to be distinguished is the elevated chloroform concentration as already found out in the cluster analysis on all individual CHCs.

III.2.2.3.3. Principal component analysis

III.2.2.3.3.1. Principal component analysis on all individual CHCs

A principal component analysis on all measured concentrations of all individual CHCs was carried out. The results are presented in Annex III.2.10. Two factors with eigenvalues greater than one are found. They contribute for 49.3 and 21.8% respectively to the total variance of the dataset. From the factor matrix and the factor loading plot after rotation (Figure III.2.3) it appears that the highest contributions to the first factor are from 1,1,1-trichloroethane (0.91) and tetrachloroethylene (0.92). 1,2-Dichloroethane (0.68), 1,1-dichloroethane (0.65) and trichloroethylene (0.45) contribute to this same factor. Factor two is mainly determined by chloroform (0.88) and tetrachloromethane (0.85). Also 1,1-dichloroethane contributes to this factor (0.67).

When the factor scores of all samples are considered (see the factor score table and the factor score plot), it can be seen that all data are clustering in an array with a score on factor 1 lower than zero and a factor score on factor 2 lower than one, except two groups (Figure III.2.4). A first group which can be identified is the group containing all samples taken on location S12 in the Scheldt estuary and one sample at the mouth of the Scheldt estuary: B07/94/1 (Figure III.2.4). They all showed scores on factor 1 higher than 0.45. Considering the factor loadings, it is clear that these group is distinguished by higher concentrations of C_2-CHCs. Anthropogenic emissions from industrial and private activities can be suggested as an input for these compounds so that higher concentrations are found at this location in the Scheldt estuary.

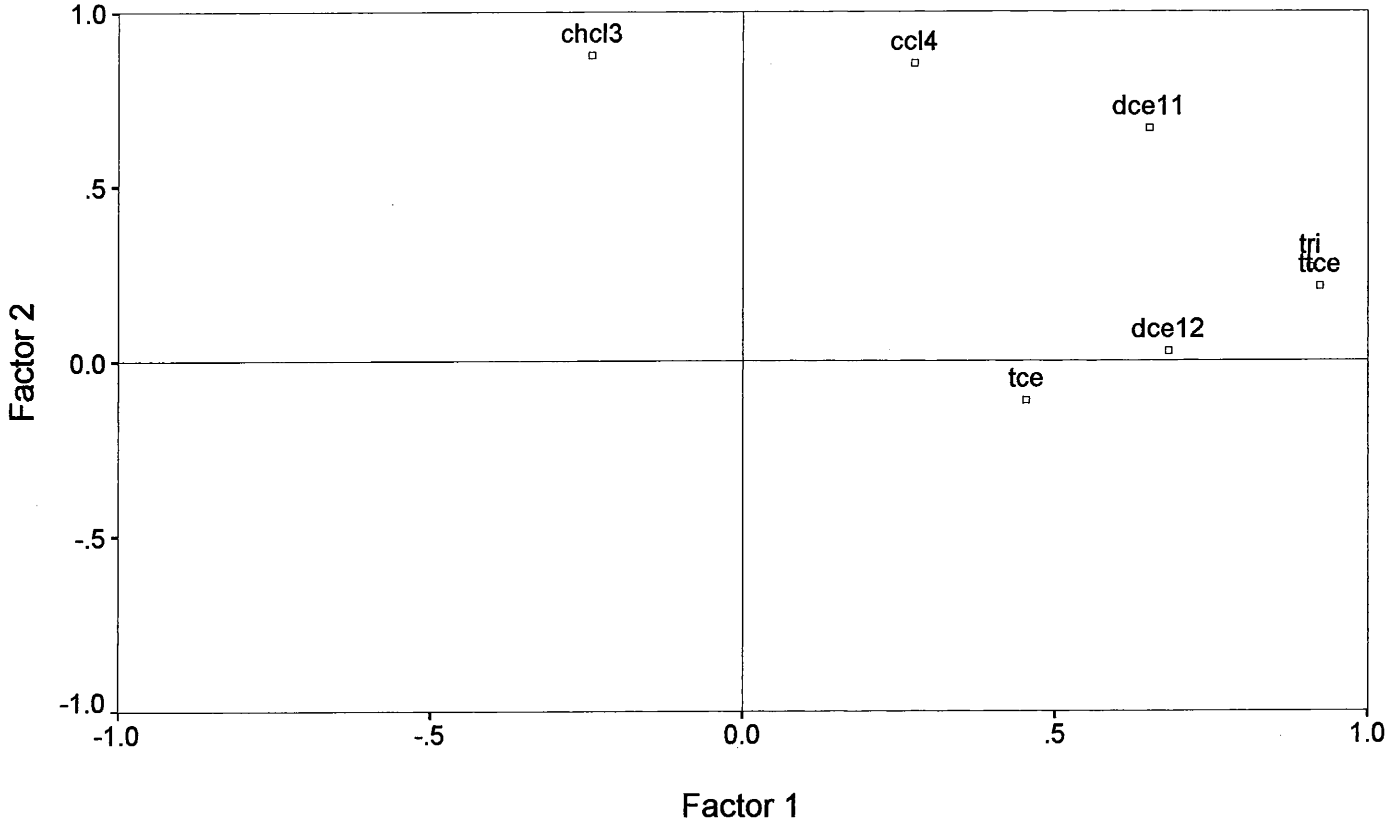


Figure III.2.3. Factor loading plot of the PCA on all individual CHCs (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttce: tetrachloroethylene)

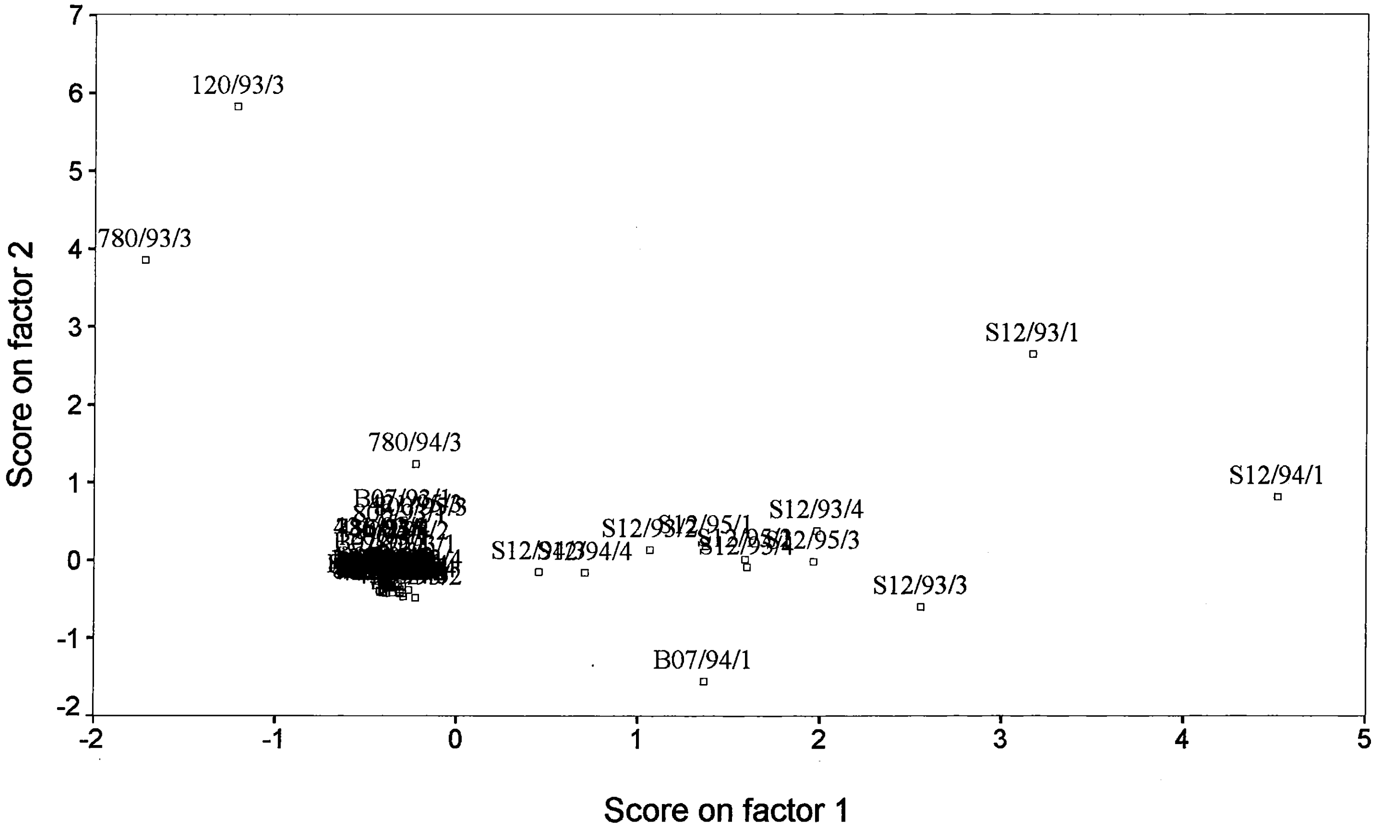


Figure III.2.4. Factor score plot of the PCA on all individual CHCs

A second group which can be identified shows high scores on factor 2 (Figure III.2.4). Two of them have a score higher than 3.85, i.e. 780/93/3 and 120/93/3. When the loading of this factor is considered, it is obvious that these samples are separated because of their high concentrations of chloroform (9718 and 11926ng.L^{-1} whereas the 95 percentile is 831ng.L^{-1}) and of tetrachloromethane (14.72 and 13.46ng.L^{-1} whereas the 95 percentile is 11.29ng.L^{-1}). Further on sample 780/94/3 (score 1.24) is separated from the cluster because of the same reason: the concentration of chloroform and tetrachloromethane are 1060 and 7.54ng.L^{-1} respectively. Both for chloroform and tetrachloromethane biogenic marine sources are suggested in the literature (*see* Part I, Literature study). Also in our observations, this type of input for these compounds can be suggested.

III.2.2.3.3.2. Principal component analysis on all individual MAHs

A principal component analysis on all results of all individual MAHs was carried out. The results are presented in Annex III.2.11. Two factors show eigenvalues greater than one. They contribute respectively 53.5 and 30.0% to the total variance of the dataset. From the factor matrix and the factor loading plot after rotation (Figure III.2.5) the two considered factors are determined by different MAHs. The first factor is dominated by C_2-substituted MAHs. The loadings for ethylbenzene, m/p-xylene and o-xylene are respectively 0.95, 0.92 and 0.96. The second factor is mainly determined by benzene (0.87) and toluene (0.87).

The largest part of the samples (52 cases) shows factor scores lower than 0.51 on factor 1 and lower than 1.31 on factor 2 (Figure III.2.6). When the samples with scores greater than 0.15 on factor one are considered, two groups can be distinguished (Figure III.2.6). A first group contains two samples from the Scheldt mouth: B07/93/3 (score 4.72) and B07/95/2 (score 4.54). They prove to have elevated concentrations of ethylbenzene (134.1 and 108.5ng.L^{-1} respectively), of m/p-xylene (177.7 and 342.1ng.L^{-1} respectively) and of o-xylene (129.7 and 107.6ng.L^{-1} respectively), whereas the 95 percentiles are 72.2, 168.4 and 62.7ng.L^{-1} respectively. A second group showing a high score on factor one (between 0.82 and 1.67) are the samples S12/93/1, S12/95/3, S12/95/2, 421/95/3, 780/95/2, 120/95/2, 435/95/2, 421/95/2, 800/95/2 and 435/95/3. Also this group shows higher concentrations of C_2-substituted MAHs.

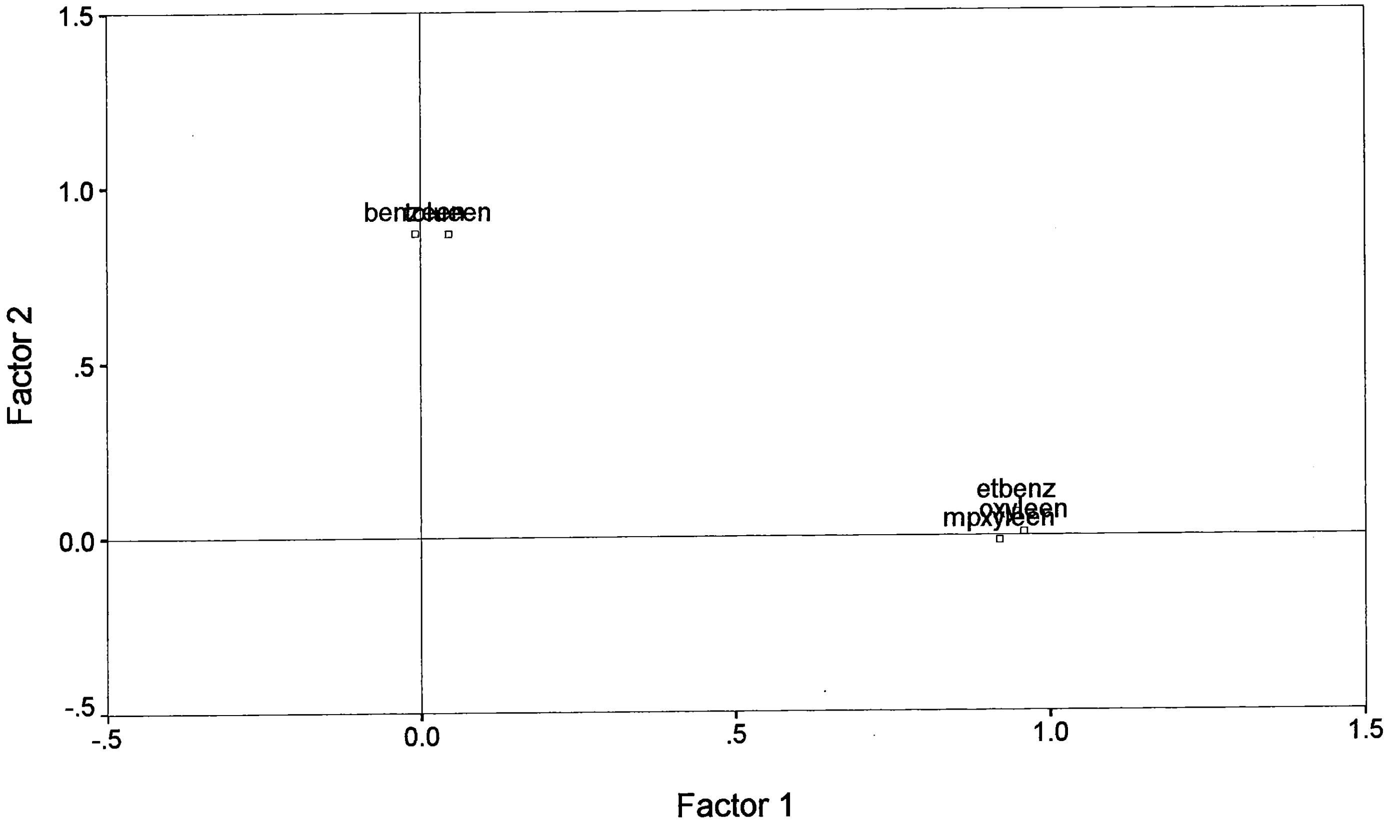


Figure III.2.5. Factor loading plot of the PCA on all individual MAHs (benzeen: benzene, tolueen: toluene, etbenz: ethylbenzene, oxyleen: o-xylene, mpxyleen: m/p-xylene)

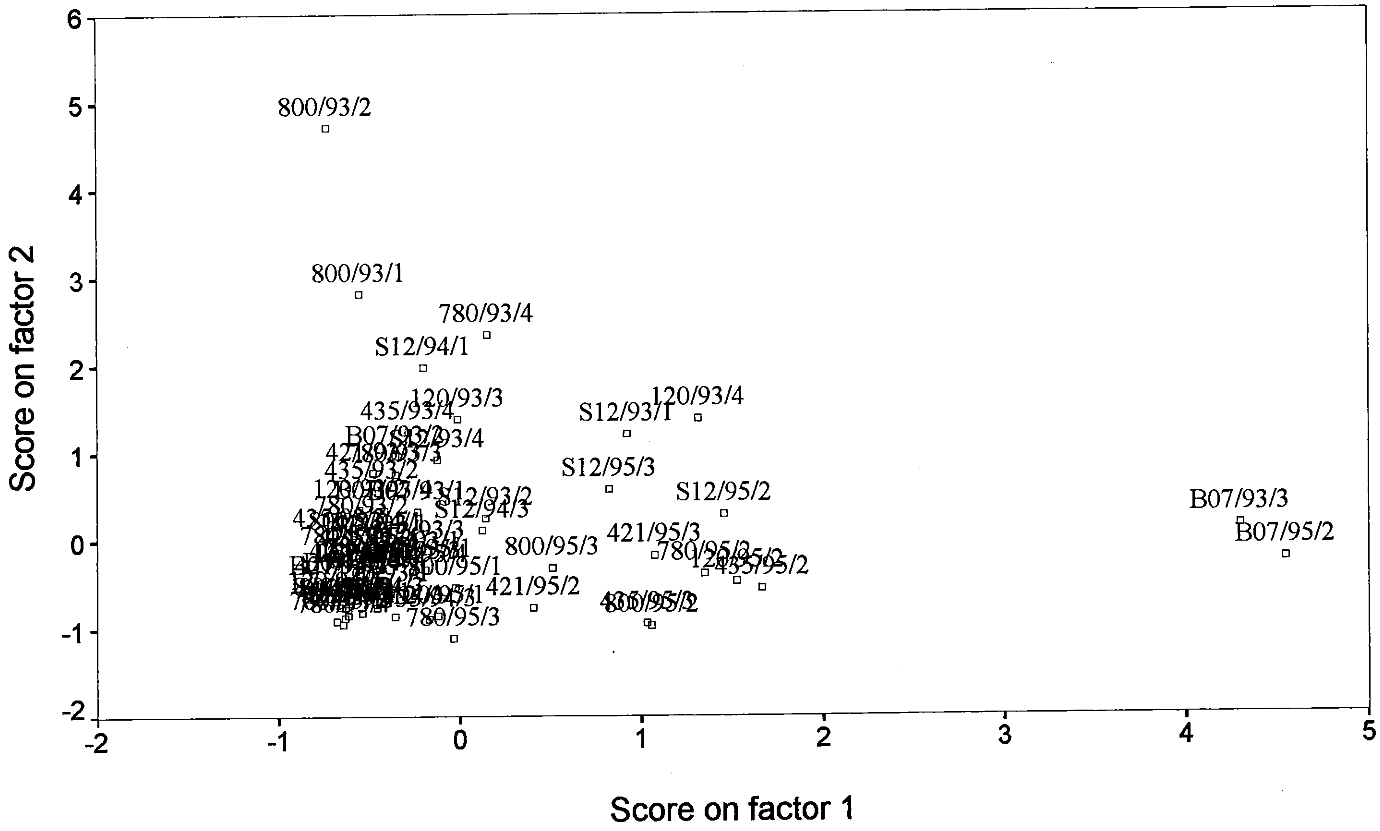


Figure III.2.6. Factor score plot of the PCA on all individual MAHs

The relationship within this group of samples can be found in two elements. First, six of these ten samples are taken during the second period in 1995 and secondly, three of them are taken in the Scheldt estuary (sampling station S12). For the samples from the Scheldt estuary, the application of these compounds in industrial activities near the Scheldt can be suggested. For the higher concentrations in the second period of 1995, it is referred to the cluster analysis where biogenic sources could be hypothesized.

When the samples with high scores on factor two are considered, two groups of data can be identified (Figure III.2.6). A first group contains two samples taken on sampling station 800 in 1993: 800/93/2 and 800/93/1. They show higher concentrations of benzene (96.9 and 85.0ng.L^{-1} respectively) and of toluene (96.2 and 43.7ng.L^{-1}), whereas the 75 percentiles are respectively 25.1 and 41.0ng.L^{-1}. A second group contains the samples 780/93/4 (score 2.35) and S12/94/1 (score 1.98), due to high toluene concentrations (114.5 and 112.5ng.L^{-1}, respectively). No direct explanation for these observations can be given.

III.2.2.3.3.3. Principal component analysis on all individual VOCs

A principal component analysis on all data of all individual VOCs was carried out. The results are presented in Annex III.2.12. Four factors with eigenvalues greater than one were identified. They contribute for 31.9, 21.9, 13.7 and 9.9% respectively to the total variance of all samples. From the factor matrix and the factor loading plot after rotation (Figure III.2.7), it is clear that factor one is mainly determined by 1,1,1-trichloroethane (loading 0.92) and tetrachloroethylene (loading 0.93). Factor two is dominated by C_2-substituted MAHs: the loadings of ethylbenzene, m/p-xylene and o-xylene are respectively 0.95, 0.92 and 0.96. Factor three is mainly determined by chloroform (loading 0.88) and tetrachloromethane (0.81). Finally factor four is mainly related to benzene (loading 0.92) and toluene (loading 0.74). This means that all individual VOCs are closely related to only one factor, except 1,1-dichloroethane and 1,2-dichloroethane. They are mostly related to factor 1/factor 3 (loadings 0.68/0.64) and to factor 1 (loading 0.67), respectively.

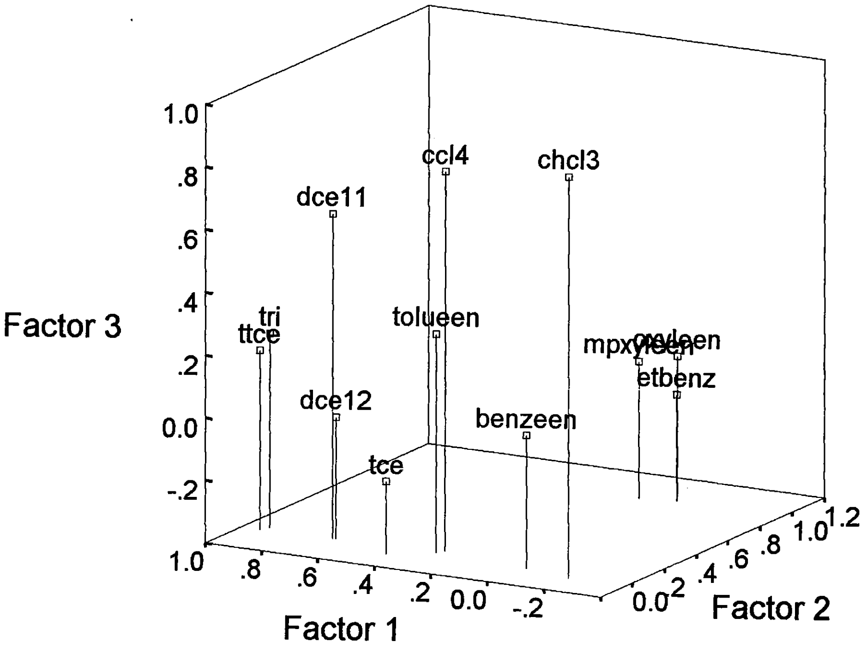


Figure III.2.7.a. Factor loading plot of the PCA on all individual VOCs (factors 1, 2 and 3) (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttce: tetrachloroethylene, benzeen: benzene, tolueen: toluene, etbenz: ethylbenzene, oxyleen: o-xylene, mpxyleen: m/p-xylene)

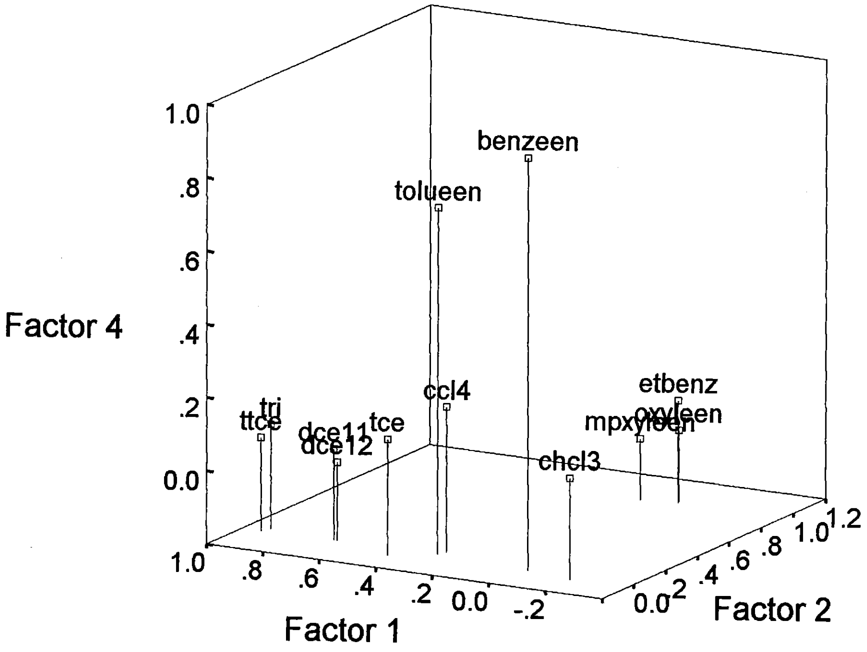


Figure III.2.7.b. Factor loading plot of the PCA on all individual VOCs (factors 1, 2 and 4) (chcl3: chloroform, ccl4: tetrachloromethane, dce11: 1,1-dichloroethane, dce12: 1,2-dichloroethane, tri: 1,1,1-trichloroethane, tce: trichloroethylene, ttce: tetrachloroethylene, benzeen: benzene, tolueen: toluene, etbenz: ethylbenzene, oxyleen: o-xylene, mpxyleen: m/p-xylene)

The first factor in this analysis is related to the first factor in the principal component analysis on all individual CHCs which was also dominated by 1,1,1-trichloroethane and tetrachloroethylene. Factor two in the current analysis, dominated by C_2-substituted MAHs, is similar to the first factor in the principal component analysis on all individual MAHs. The third factor in the current analysis, dominated by chloroform and tetrachloromethane, is similar to the second factor in the principal component analysis on all individual CHCs, whereas the fourth factor, mainly determined by benzene and toluene, is related to the second factor in the principal component analysis on all individual MAHs.

From the total dataset of 13 individual VOCs in 68 cases, four groups can be distinguished from the main group (Figure III.2.8). First, all samples taken in the Scheldt estuary (location S12) together with one sample at the mouth of the Scheldt estuary (B07/94/1) show scores on factor one higher than 0.40 whereas all other samples show scores below zero (Figure III.2.8). This is due to higher concentrations of mainly 1,1,1-trichloroethane, tetrachloroethylene, 1,1-dichloroethane, 1,2-dichloroethane and trichloroethylene for the S12-samples whereas B07/94/1 has a high trichloroethylene concentration (1031ng.L^{-1}).

Secondly, a group of nine samples shows higher concentrations of C_2-substituted MAHs (factor two) in comparison with all other samples having scores below 0.51 (excluding samples from location S12) (Figure III.2.8). The samples B07/95/2 and B07/93/3 show the highest scores (4.54 and 4.31 respectively). A second group of samples with higher scores, i.e. between 1.04 and 1.67, consists of seven samples. It concerns the samples 120/93/4, 120/95/2, 780/95/2, 435/95/2, 800/95/2, 421/95/3 and 435/95/3. Four of these seven samples are samples taken in the second period of 1995.

In a third place, the samples 120/93/3, 780/93/3 and 780/94/3 are grouped because of high concentrations of chloroform and tetrachloromethane (Samples from S12 are no longer considered) (Figure III.2.8). These cases are samples from stations near to the coast and from the third period of the year. The scores on factor three are 5.88, 3.87 and 1.30 respectively, whereas all other samples show score all below 0.51. The chloroform and tetrachloromethane concentrations for these three samples are respectively 11926 and 13.46ng.L^{-1}; 9718 and 14.72ng.L^{-1} and 1060 and 7.54ng.L^{-1}, whereas the 95 percentiles are 831 en 11.28ng.L^{-1}.

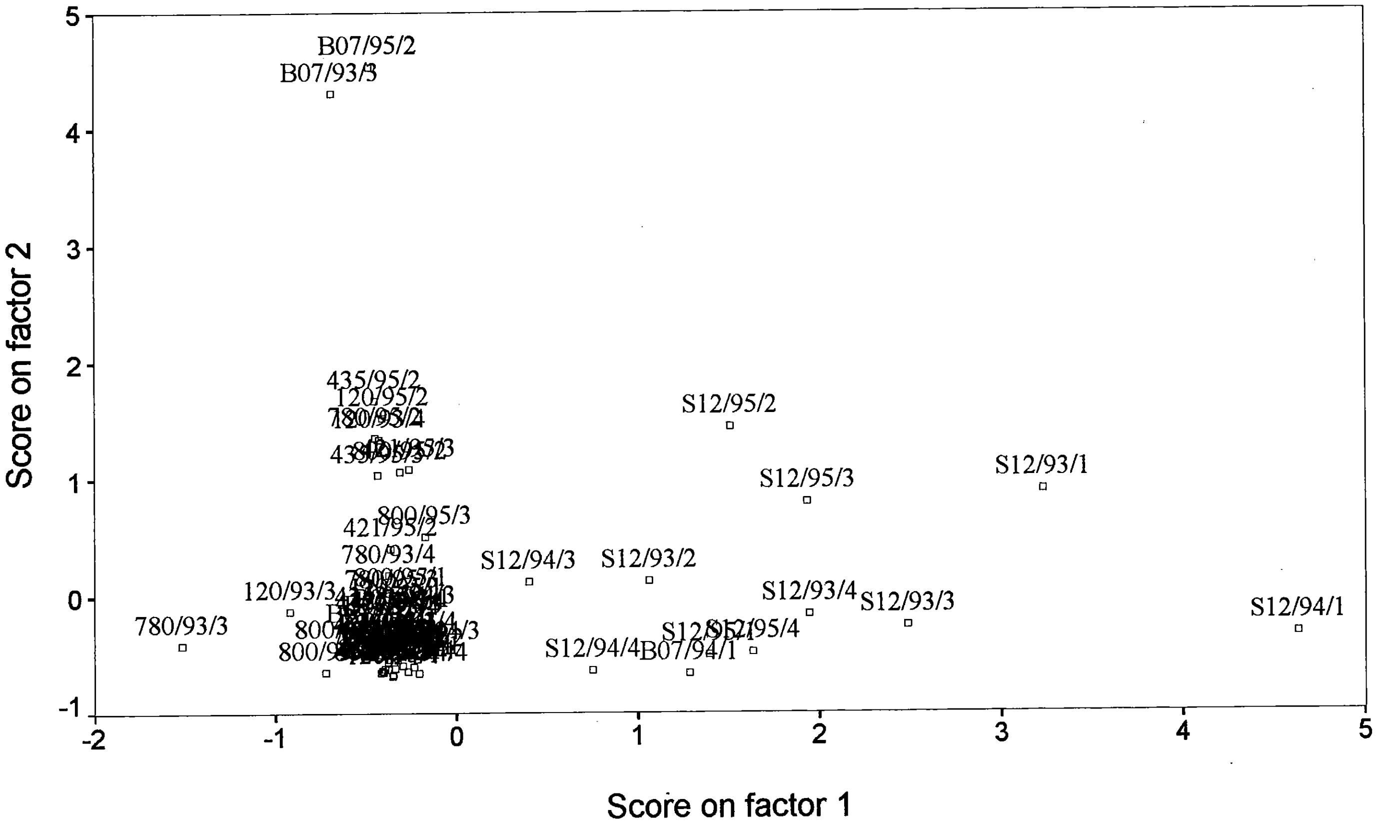


Figure III.2.8.a. Factor score plot of the PCA on all individual VOCs (factors 1 and 2)

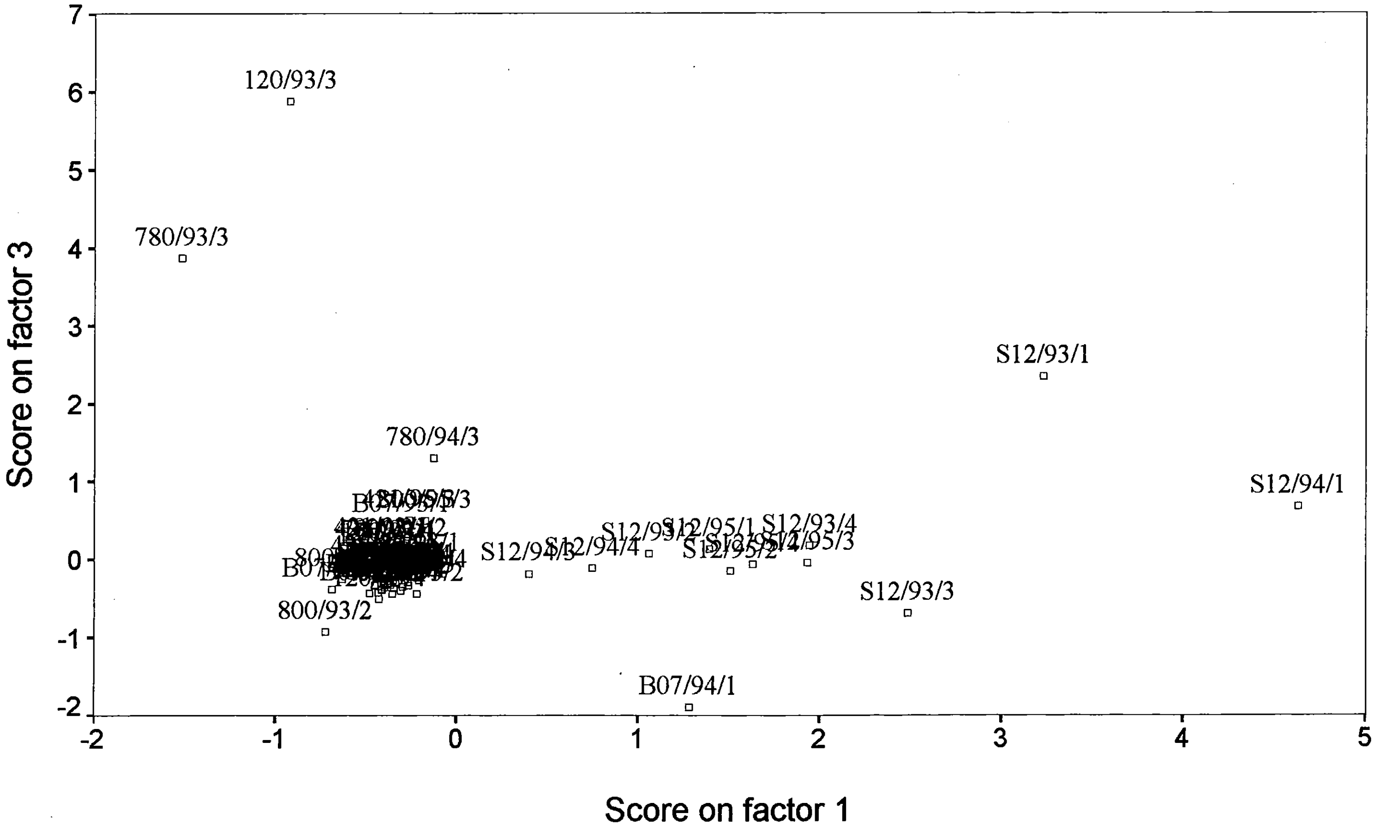


Figure III.2.8.b. Factor score plot of the PCA on all individual VOCs (factors 1 and 3)

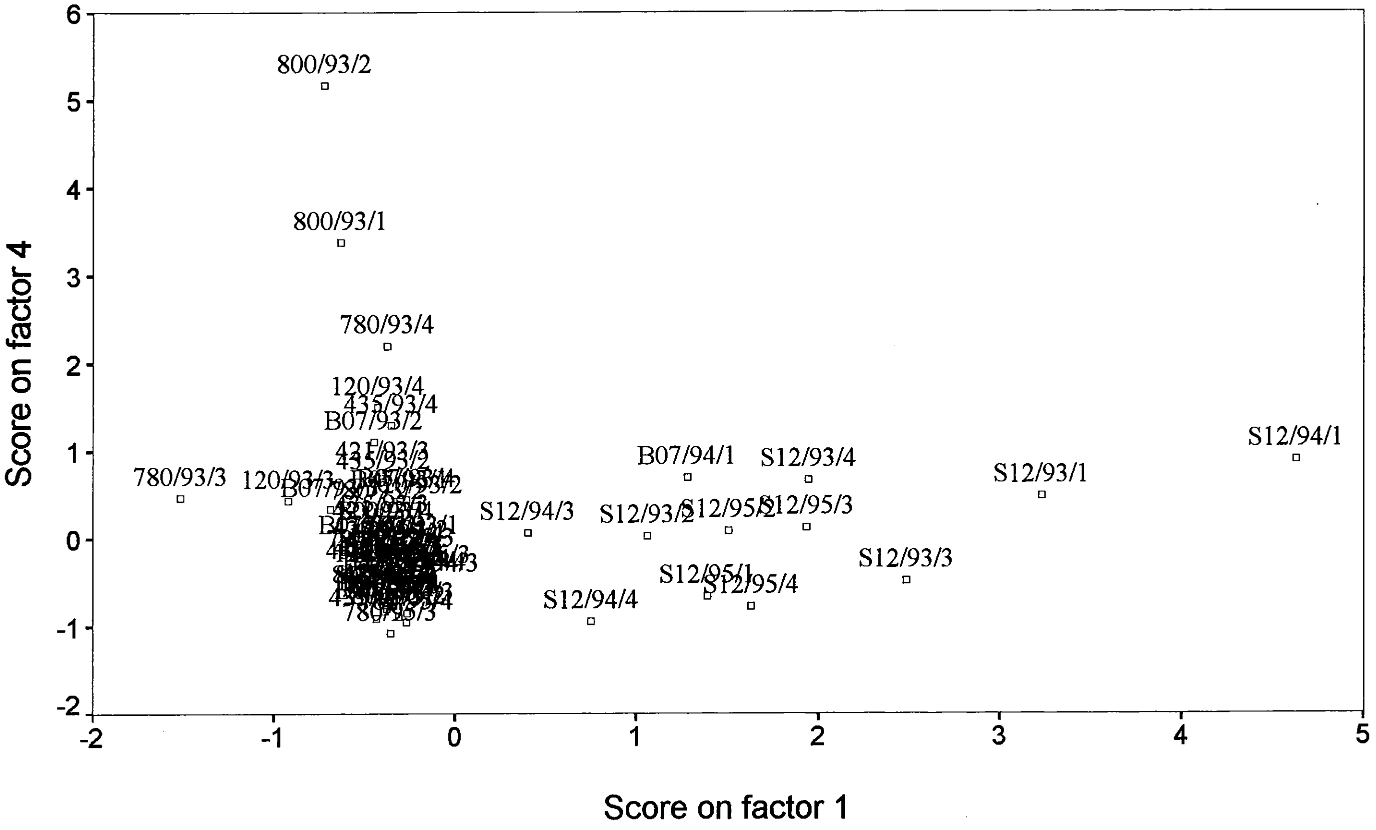


Figure III.2.8.c. Factor score plot of the PCA on all individual VOCs (factors 1 and 4)

A last group of samples which are separated, are isolated by a fourth factor, determined by benzene and toluene (Figure III.2.8). It are the samples 800/93/2, 800/93/1 and 780/93/4. They show scores on factor four of 5.17, 3.38 and 2.20. All other sample have scores below 1.5. The two samples from the location 800 have high benzene (96.9 resp. 85.0ng.L^{-1}) and toluene (96.2 resp. 43.7ng.L^{-1}) concentrations, in comparison with the 75 percentiles (25.1 en 41.0ng.L^{-1}). Sample 780/94/3 has only an elevated toluene concentration (114.5ng.L^{-1}).

For possible explanations for the different distinctions observed in this analysis, it is referred to the two previous analyses. In conclusion, this analysis confirmed the two previous ones. In addition, it revealed that no relationships between individual CHCs and individual MAHs were remarked.

III.2.2.3.4. Correlations between individual VOCs

Correlations between all individual VOCs, the sum of CHCs, the sum of MAHs and the sum of VOCs were investigated considering all samples. The correlation coefficient matrix is presented in Annex III.2.13.

The highest significant correlations (>0.70) between individual VOCs consist of a first group of correlations between some CHCs and of a second group of correlations between some MAHs. The correlations between the CHCs are between 1,1-dichloroethane and 1,1,1-trichloroethane (0.77), between 1,1-dichloroethane and tetrachloroethylene (0.74) and between 1,1,1-trichloroethane and tetrachloroethylene (0.94). This means that these three compounds are all strongly correlated.

Correlation coefficient higher than 0.70 between MAHs are those between ethylbenzene and m/p-xylene (0.79), between ethylbenzene and o-xylene (0.89) and between m/p-xylene and o-xylene (0.82). This illustrates that all C_2-substituted MAHs are strongly correlated.

Correlation coefficients between individual CHCs and individual MAHs are not higher than 0.5.

III.2.2.3.5. Factor analysis

III.2.2.3.5.1. Factor year

The measurement results of all individual VOCs and of the sum of CHCs, MAHs and VOCs can be presented as a function of the year of sampling by means of boxplots, as illustrated for 1,1,1-trichloroethane and toluene in Figure III.2.9. For all VOCs and for the sum of CHCs, MAHs and VOCs, the representation in boxplots is given in Annex III.2.14.

All VOCs and sums of CHCs, MAHs and VOCs showed normal distribution after logaritmic transformation except 1,1-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene. It was shown that also 1,1,1-trichloroethane and tetrachloroethylene had a normal distribution when the samples from location S12 (Scheldt estuary) were not considered. From this it was concluded that it is allowed to do a one way analysis of variance on all individual VOCs and on the sums of CHCs, MAHs and VOCs (except 1,1-dichloroethane), combined with a least square difference test for the factor year. The results are presented in Annex III.2.15. For 1,1-dichloroethane a one way analysis of variance test by means of the Kruskal-Wallis test was carried out. The results are presented in Annex III.2.16.

Chloroform and the sum of CHCs showed higher concentrations in 1993 than in 1995, whereas tetrachloromethane had higher concentrations in 1993 than in 1994. For the other CHCs no significant differences between concentrations measured in different years are noted. Benzene and toluene have significantly higher concentrations in 1993 than in 1994 and 1995. Ethylbenzene has higher concentrations in 1995 than in 1994. m/p-Xylene showed higher concentrations in 1995 than in 1993 and 1994. For o-xylene and the sum of VOCs no significant differences between the years considered are found, whereas the sum of MAHs is significantly higher in 1993 and 1995 than in 1994.

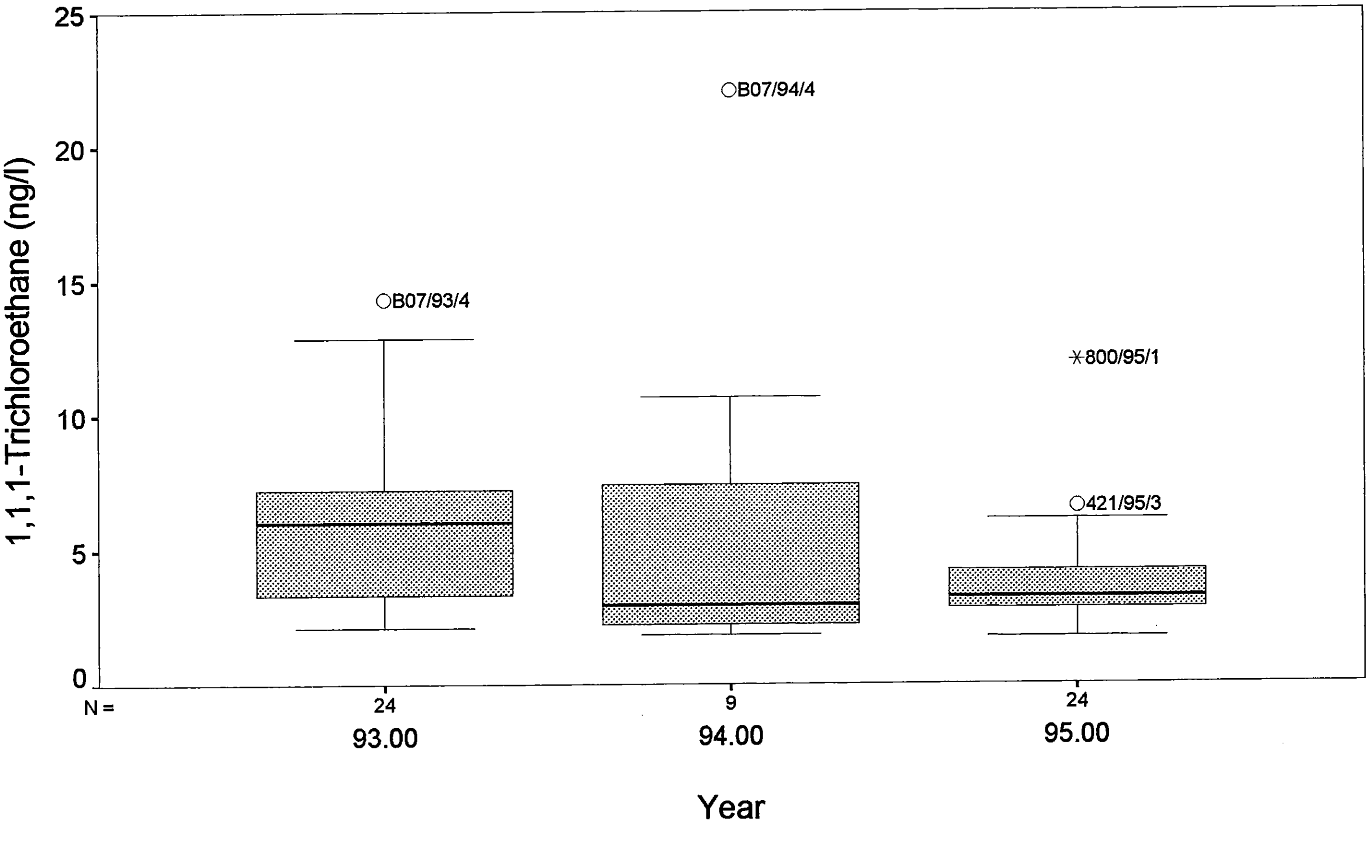


Figure III.2.9.a. Measurement results of 1,1,1-trichloroethane as a function of the year of sampling, represented by boxplots

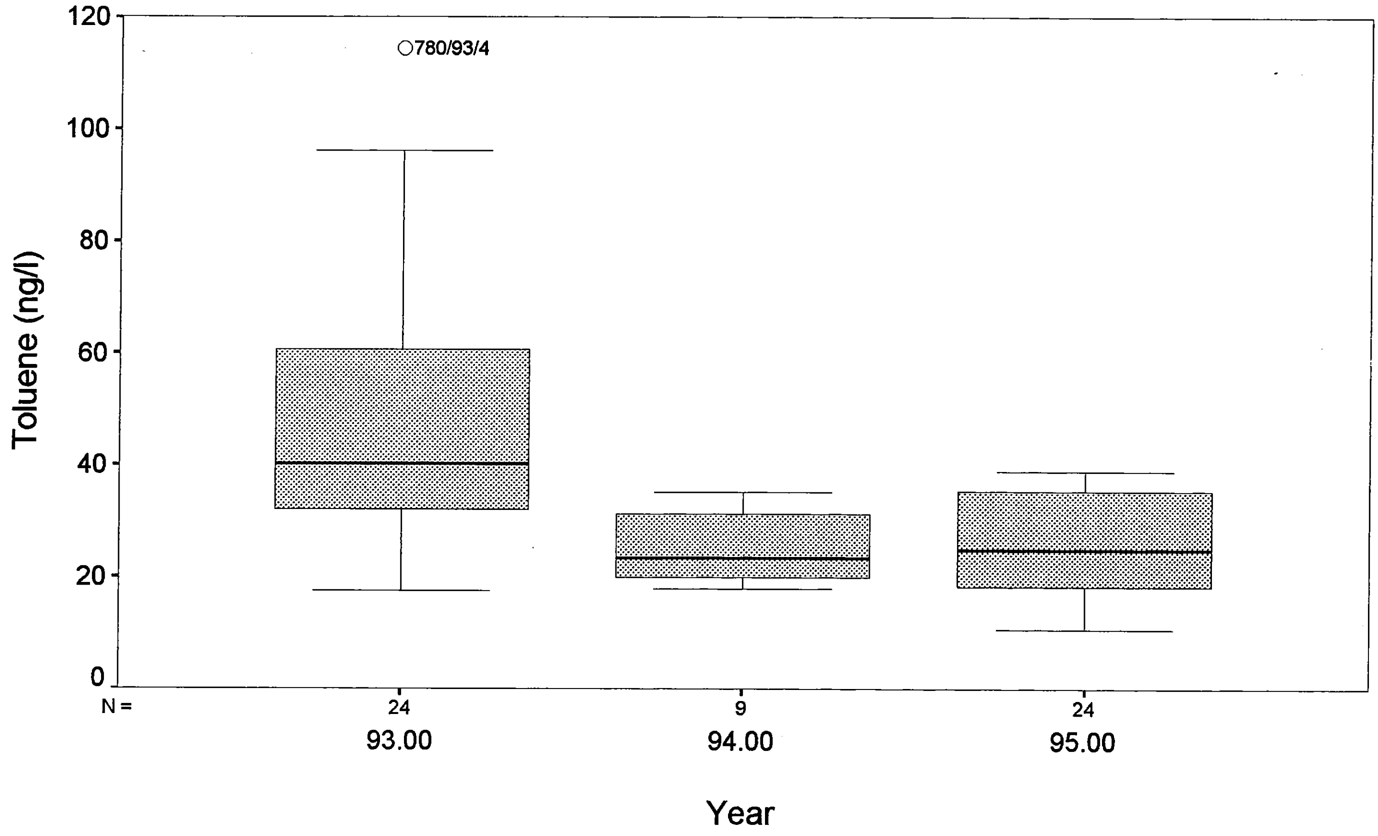


Figure III.2.9.b. Measurement results of toluene as a function of the year of sampling, represented by boxplots

III.2.2.3.5.2. Factor period

The data for all individual VOCs and of the sum of CHCs, MAHs and VOCs can be presented as a function of period during the year by means of boxplots, as illustrated for 1,1,1-trichloroethane and toluene in Figure III.2.10. For all VOCs and for the sum of CHCs, MAHs and VOCs, the representation in boxplots is given in Annex III.2.17.

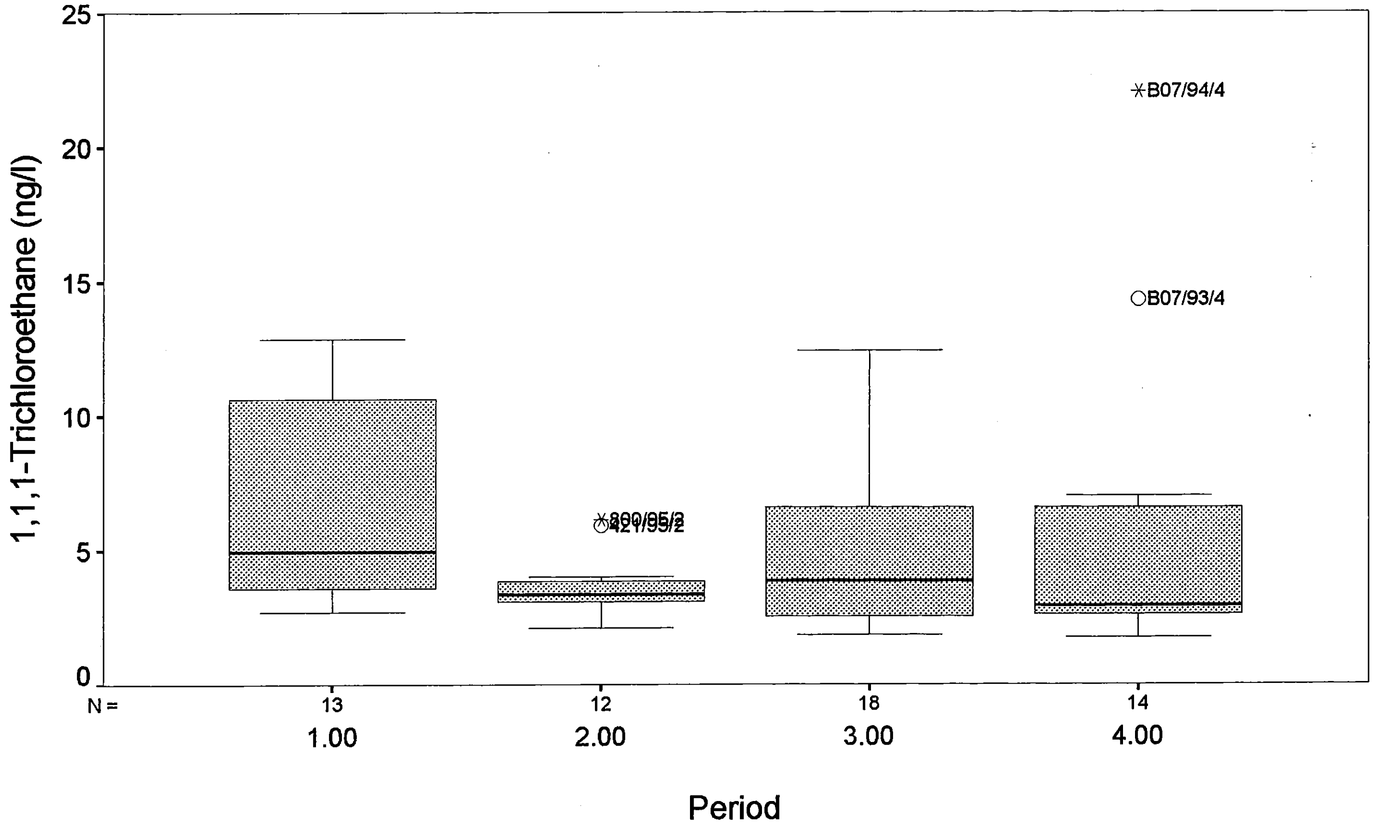


Figure III.2.10.a. Measurement results of 1,1,1-trichloroethane as a function of the period of sampling during the year, represented by boxplots

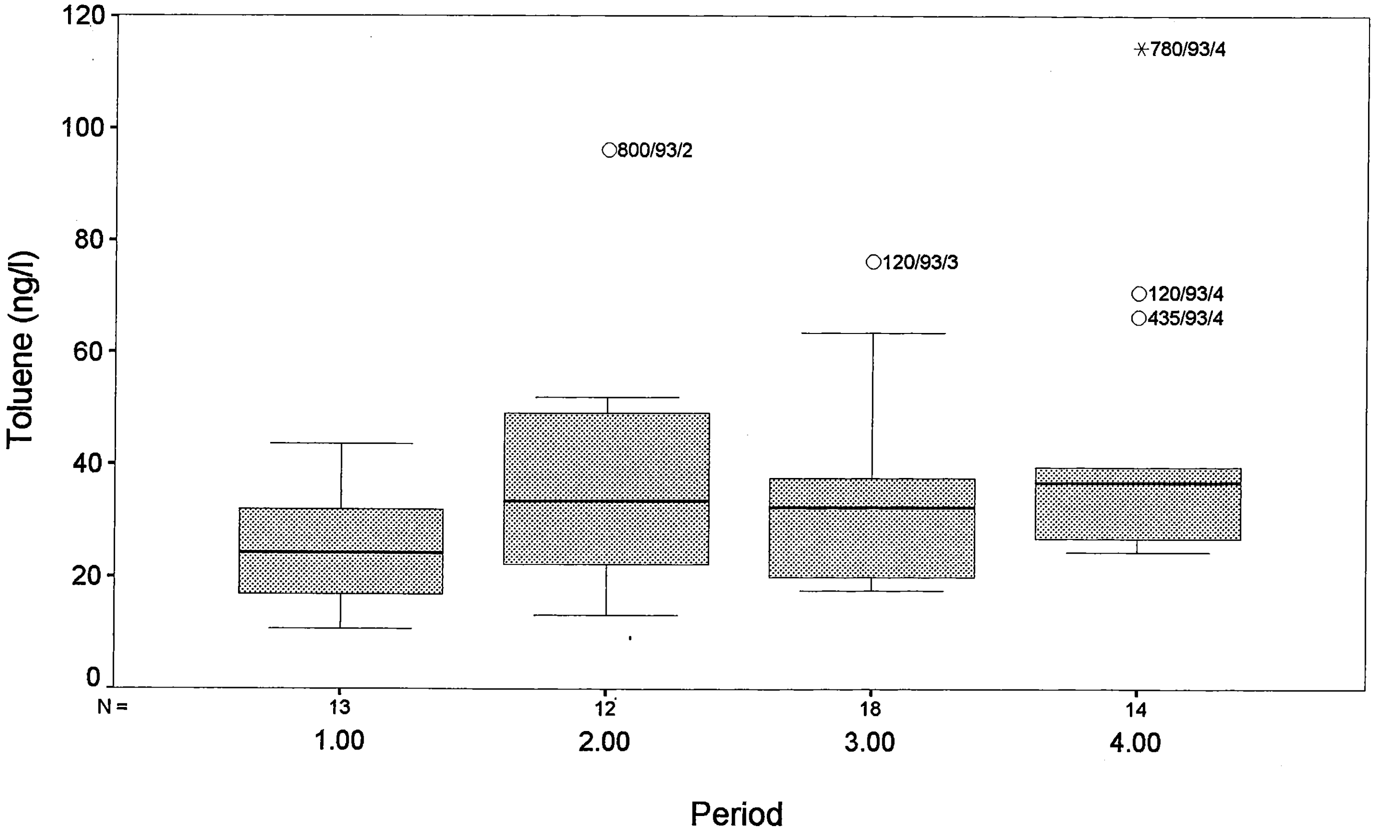


Figure III.2.10.b. Measurement results of toluene as a function of the period of sampling during the year, represented by boxplots

All VOCs and sums of CHCs, MAHs and VOCs showed normal distribution after logaritmic transformation except 1,1-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene. It was shown that also 1,1,1-trichloroethane and tetrachloroethylene concentrations were normally distributed when the samples from location S12 (Scheldt estuary) were not considered. From this it was concluded that it is allowed to do a one way analysis of variance on all individual VOCs and on the sums of CHCs, MAHs and VOCs, except 1,1-dichloroethane, combined with a least square difference test for the factor period in the year. The results are presented in Annex III.2.18. For 1,1-dichloroethane a one way analysis of variance test by means of the Kruskal-Wallis test was carried out. The results are presented in Annex III.2.19.

Chloroform concentrations in the third period are significantly higher than in the second and fourth period. In addition the first period shows higher concentrations than in the second period. Also trichloroethylene has higher concentrations in the first season, in comparison with season three and four. The other CHCs show no significant differences.

Within the group of MAHs, benzene showed significantly higher concentrations in the first and second period than in the thirth and fourth period. The C_2-substituted MAHs have higher concentrations in the second season. The concentrations in the second period for ethylbenzene are significantly higher than those for the third and fourth period, whereas those for m/p-xylene are higher than all other periods. o-Xylene concentrations in the third period are higher than in the first and fourth period. In addition, o-xylene shows higher concentrations in the third period when compared with the first and fourth period.

The sum of CHCs is significantly higher in the periods one and three in comparison with season two, whereas exactly season two has higher values for the sum of MAHs in comparison with all other periods. Finally the sum of all VOCs is significantly higher in the third period than in the fourth period.

III.2.2.3.5.3. Factor sampling location

The measurement results of all individual VOCs and of the sum of CHCs, MAHs and VOCs can be presented as a function of the sampling locations by means of boxplots, as illustrated for 1,1,1-trichloroethane and toluene in Figure III.2.11. For all VOCs and for the sum of CHCs, MAHs and VOCs, the representation in boxplots is given in Annex III.2.20.

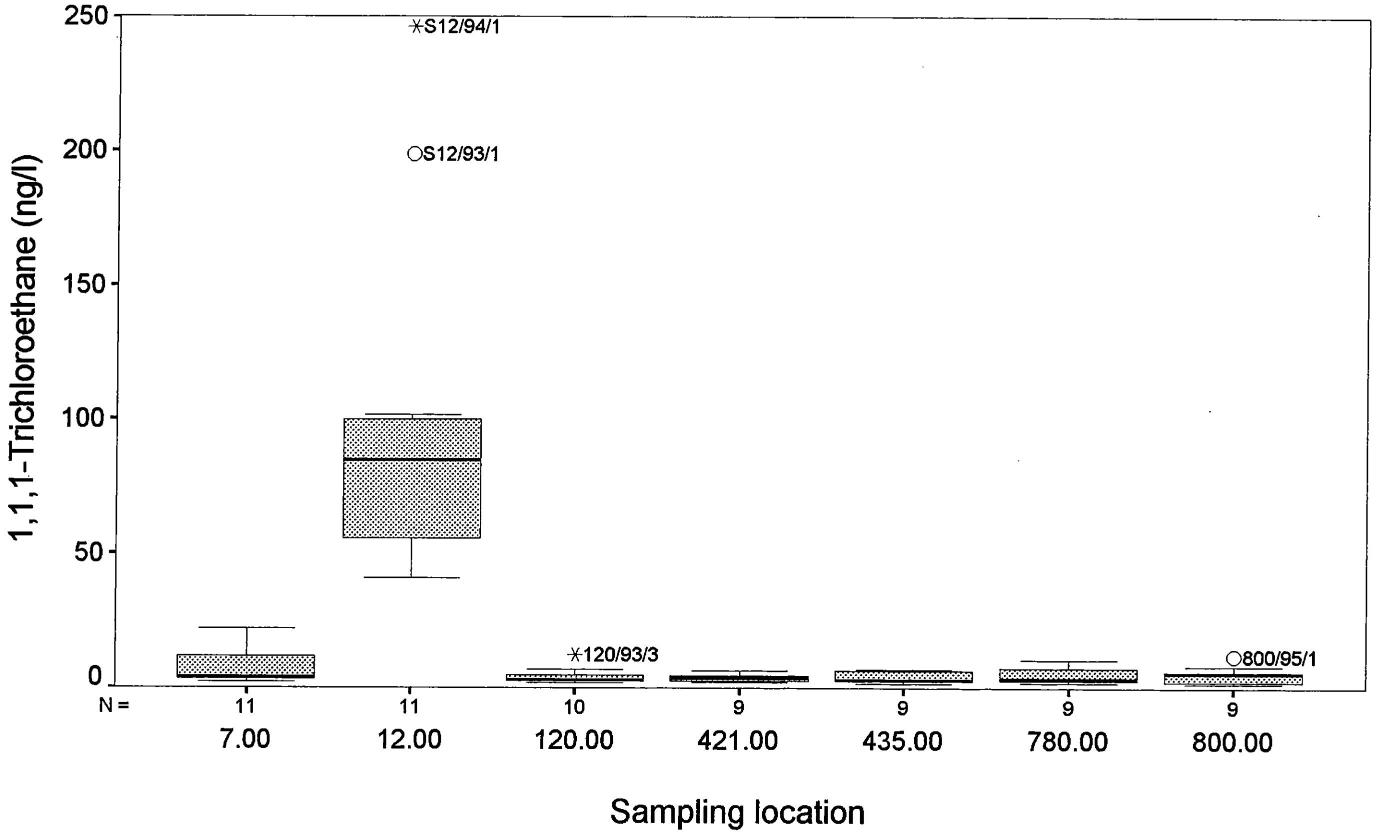


Figure III.2.11.a. Measurement results of 1,1,1-trichloroethane as a function of sampling location, represented by boxplots (7.00: location B07, 12.00: location S12)

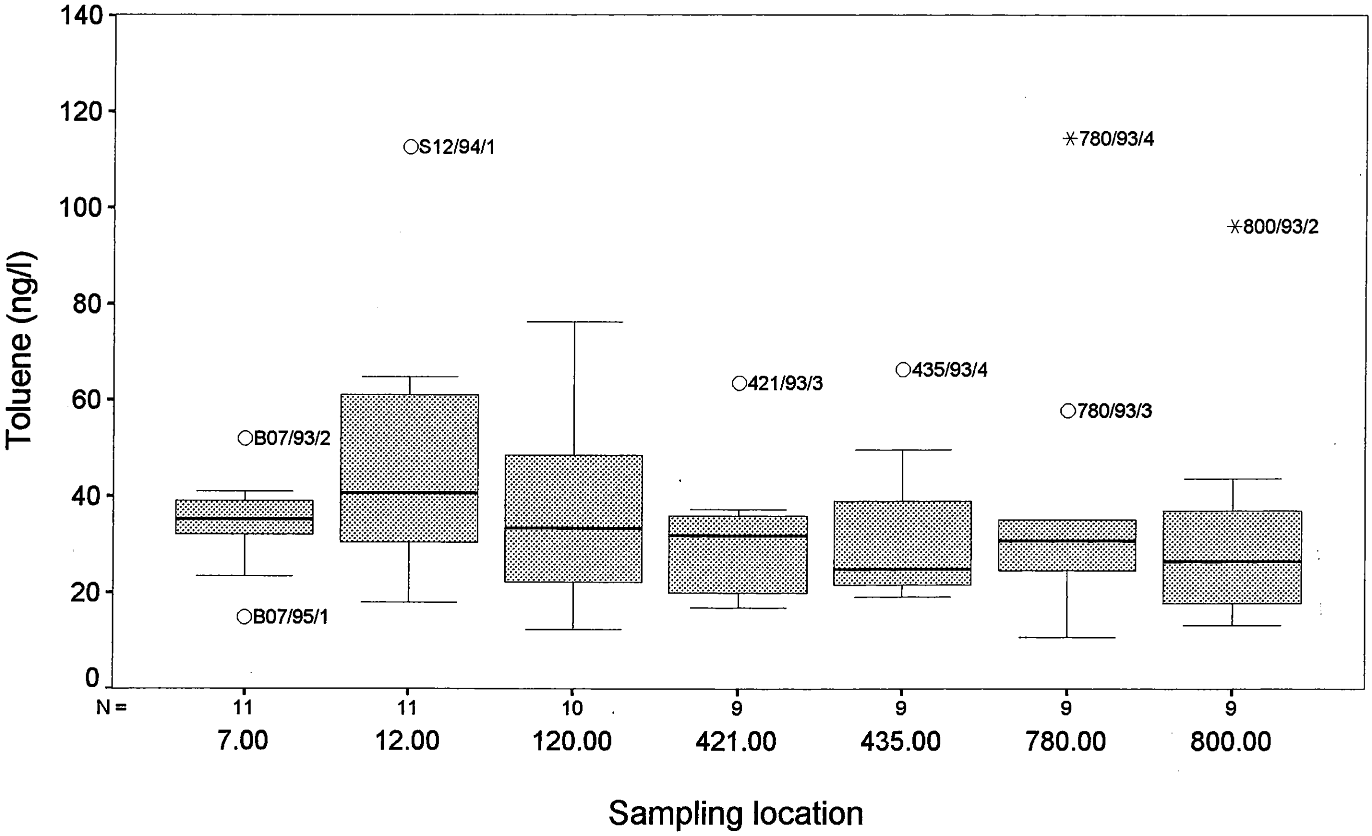


Figure III.2.11.b. Measurement results of toluene as a function of sampling location, represented by boxplots (7.00: location B07, 12.00: location S12)

All VOCs and sums of CHCs, MAHs and VOCs showed normal distribution after logaritmic transformation except 1,1-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene. It was shown that also 1,1,1-trichloroethane and tetrachloroethylene had a normal distribution when the samples from location S12 (Scheldt estuary) were excluded from the dataset. From this it was concluded that it is allowed to do a one way analysis of variance on all individual VOCs and on the sums of CHCs, MAHs and VOCs, except for 1,1-dichloroethane, combined with a least square difference test for the factor sampling location. The results are presented in Annex III.2.21. For 1,1-dichloroethane a one way analysis of variance test by means of the Kruskal-Wallis test was carried out. The results are presented in Annex III.2.22.

The CHCs tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene show all significantly higher concentrations at the sampling location in the Scheldt estuary (S12) in comparison with all other sampling locations. This is also noted for the sum of VOCs except in the case of S12 and 780: they are not significantly different. For the individual MAHs and the sum of MAHs no significant differences are noticed between all sampling locations.

In a second approach significant differences between the sampling locations in the Scheldt estuary (S12), at the mouth of the Scheldt estuary (B07) and at all other points (open sea locations) were investigated. The results are presented in Annex III.2.23 and III.2.24. First, the same trend is found as in the first approach for the CHCs. They showed significantly higher concentrations in the Scheldt estuary (location S12) than at the mouth of the Scheldt estuary (location B07) and than all open sea locations. Secondly, only 1,1,1-trichloroethane has a significantly higher concentration at the mouth of the Scheldt estuary than at open sea locations. For all other individual CHCs samples from the mouth of the Scheldt estuary and samples from the open sea locations cannot be distinguished. Finally, MAHs are not significantly different for sampels from the Scheldt estuary, from the mouth of the Scheldt or from open sea locations.

In a third step it was investigated if the distance to the coast for the open sea locations was significant for the concentrations. Three groups were composed: sampling locations near the coast (120 and 780), far from the coast (421 and 435) and one location as a reference (800). The factor analysis results are presented in Annex III.2.25 and III.2.26. No one of all individual VOCs or of the sums of CHCs, MAHs and VOCs are related to the distance to the coast.

III.2.2.3.5.4. Factor analysis without considering the samples taken on the location at the Scheldt estuary

From the previous analyses it was clear that the samples from the Scheldt estuary have some significant differences in comparison with all other samples, especially for the concentrations of CHCs. Therefore, it is useful to look if the same conclusions can be made without the consideration of samples taken from the location S12. In this approach, all populations of the individual VOCs and of the sum of CHCs, MAHs and VOCs show a normal distribution after logaritmic transformation except 1,1-dichloroethane.

In a first analysis the factor year was considered (*See* Annex III.2.27 and III.2.28). Chloroform, tetrachloromethane, 1,1,1-trichloroethane and the sum of CHCs are significantly higher in 1993 than in 1994 or 1995, whereas for 1,2-dichloroethane, trichloroethylene, tetrachloroethylene and 1,1-dichloroethane no significant differences are noticed. For the MAHs benzene and toluene concentrations in 1993 are significantly higher than in 1994 and 1995. Ethylbenzene is significantly higher in 1995 than in 1994; m/p-xylene is higher in 1995 than in 1993 and 1994 whereas o-xylene show no significant differences.

In a second analysis the factor period of the year was investigated (*see* Annex III.2.29 and III.2.30). The results for chloroform are the same as in the analysis where S12 was included. 1,2-Dichloroethane shows now significantly lower concentrations in the third period in comparison with all other periods. 1,1,1-Trichloroethane has higher concentrations in the first period when it is compared with period two. Trichloroethylene, which already showed significantly higher concentrations in the first period in comparison with the third and fourth period, has now also in the second period higher concentrations in comparison with the third and fourth period. Tetrachloroethylene has higher concentrations in the fourth season when compared with season two. No significant differences are noted for tetrachloromethane and 1,1-dichloroethane.

Benzene shows the same result as in the previous analysis, except that period one and four are no longer significantly different. Toluene show higher concentrations in the fourth period in comparison with season one. C_2-substituted MAHs have higher concentrations in the second season. This is the case as well for ethylbenzene (in comparison with the fourth period), as for m/p-xylene and o-xylene (in comparison with the first and fourth period). In addition the o-xylene concentrations are significantly higher in the third season when compared to the first and fourth season. The sum of CHCs show the same significant differences as in the previous analysis. In addition, the third period has significantly higher values than the fourth period. The results for the sum of MAHs and VOCs are the same as in the previous analyses.

III.2.2.4. CONCLUSIONS

III.2.2.4.1. Conclusions with respect to concentration levels

The concentrations of the individual VOCs are in general in the 1 to 50ng.L^{-1} concentration range. This can be seen from the 25 and 75 percentiles. A schematic representation is given in Figure II.2.12. They are for tetrachloromethane 1.2 and 4.3ng.L^{-1}, for 1,1-dichloroethane 1.1 and 1.9ng.L^{-1}, for 1,2-dichloroethane 5.3 and 23.3ng.L^{-1}, for 1,1,1-trichloroethane 3.0 and 10.6ng.L^{-1}, for trichloroethylene 5.0 and 21.1ng.L^{-1}, for tetrachloroethylene 1.7 and 5.4ng.L^{-1}, for benzene 14.2 and 25.1ng.L^{-1}, for toluene 22.6 and 41.0ng.L^{-1}, for ethylbenzene 7.8 and 29.8ng.L^{-1}, for m/p-xylene 9.7 and 32.4ng.L^{-1} and for o-xylene 8.6 and 23.8ng.L^{-1}. Only chloroform shows higher concentration ranges. The 25 and 75 percentiles are 11.7 and 120ng.L^{-1} respectively.

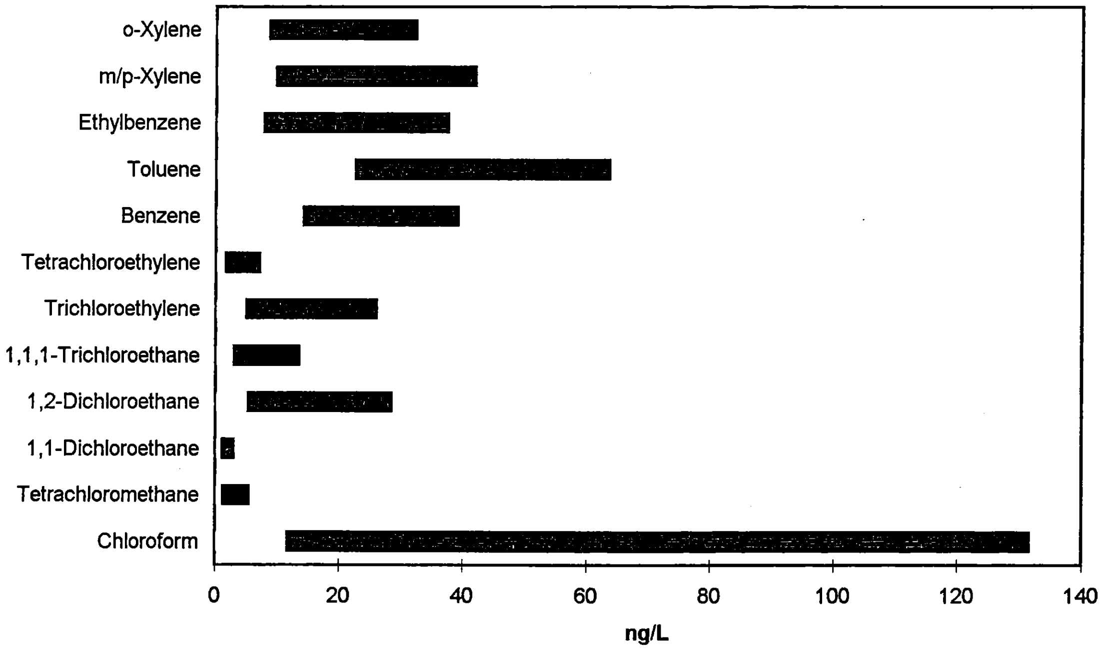


Figure III.2.12. Representation of the 25- to 75-percentile range of all individual VOCs of all samples

III.2.2.4.2. Conclusions with respect to relationships between individual VOCs

From the principal component analysis on all individual VOCs and from the correlation coefficients between all individual VOCs, some conclusions with respect to relationships between the VOCs can be made.

First, it is clear that no relationship between individual CHCs and individual MAHs could be found. This means that the two groups have different input pathways and/or different environmental behaviour and/or different environmental sinks.

Secondly, within the groups of CHCs, relations between chloroform and tetrachloromethane and between 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene were found in the principal component analysis on individual CHCs. The correlation coefficient matrix confirmed the relationships between 1,1-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene.

Finally, also relations between individual MAHs were observed in principal component analysis and from the correlation coefficients. The principal component analysis revealed relationships between benzene and toluene whereas both principal component analysis and the correlation coefficient matrix indicate relations between all C_2-substituted MAHs, i.e. ethylbenzene, o-xylene and m/p-xylene. The relationships are schematically represented in Figure III.2.13.

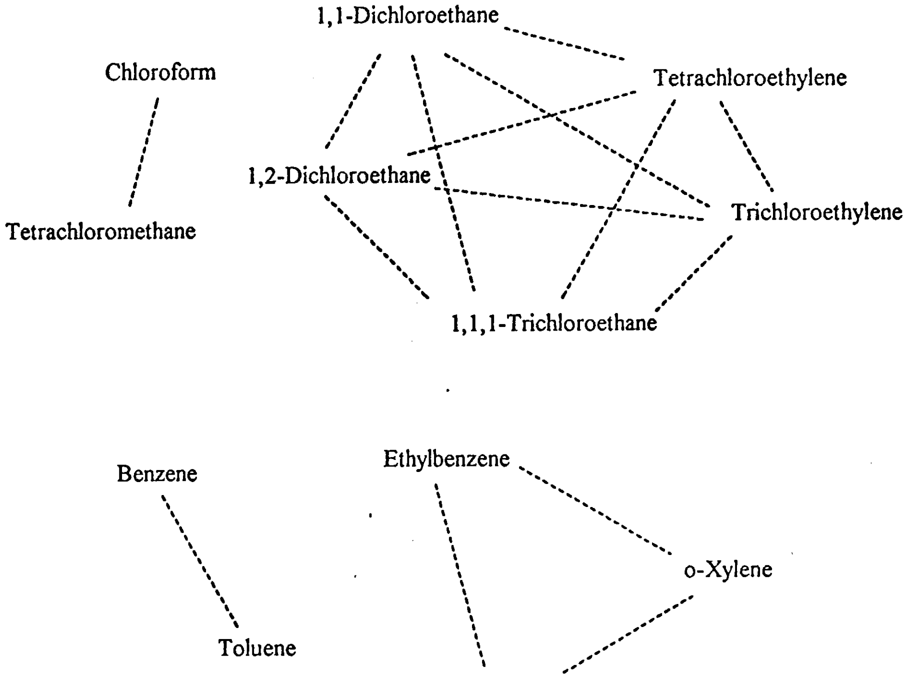


Figure III.2.13. Relationships between individual VOCs, observed in the PCAs

III.2.2.4.3. Conclusions with respect to sampling location

From the statistical tests it was found that for all individual CHCs except for chloroform the sampling location in the Scheldt estuary has to be distinguished from all other sampling locations, including those at open sea and at the Scheldt mouth because of higher concentrations for these compounds. This conclusion was supported by cluster analysis, principal component analysis and factor analysis. It has to be noted that this difference could not be proven for the MAHs.

When the samples from the sampling location at the Scheldt mouth were compared to the open sea locations no difference could be noted except for 1,1,1-trichloroethane. With factor analysis it was proven that water samples taken at the mouth of the Scheldt showed significantly higher concentrations than those taken at open sea locations.

For all open sea locations the concentrations of all VOCs were investigated with respect to the distance to the coast. No compound proved to have higher (or lower) concentrations near the coast than at locations further from the coast or than at a reference location on the Belgian Continental Plat (location 800).

III.2.2.4.4. Conclusions with respect to the time of sampling

Firstly, it was found that the concentrations at coastal sampling locations (locations 120 and 780) showed very high concentrations of chloroform (up to ± 10 000ng.L^{-1}) and elevated concentrations of tetrachloromethane in the third period of the year (end of September - October). This was proven by cluster analysis, principal component analysis and factor analysis. It can be suggested that this is related to biogenic sources (*see* Part I, Literature Study). Also the high concentration of trichloroethylene at the mouth of the Scheldt estuary in the first period of 1994 could be related to biogenic sources, though also anthropogenic sources cannot be excluded in this case.

Secondly, C_2-substituted MAHs had elevated concentrations in the second sample period in 1995 for all open sea locations and at the Scheldt mouth. This was confirmed by cluster analysis, principal component analysis and factor analysis. No direct explanation can be found since local (accidental) inputs can be excluded because it was found at all sampling locations over the whole Belgian Continental Plat at the same time. Biogenic sources could be suggested but this suggestion is poorly supported by the Literature Study.

III.2.3. MONITORING OF THE CONCENTRATIONS OF THE TARGET COMPOUNDS IN WATER SAMPLES FROM THE SCHELDT ESTUARY, ADDITIONAL TO THE PROGRAMME

III.2.3.1. OBJECTIVE

From the results obtained during the monitoring campaigns, it could be seen that the concentrations measured at the sampling location in the Scheldt estuary (location S12) were higher than at all other locations for all individual CHCs (except chloroform). Therefore, it was decided to take additional samples in the Scheldt estuary in 1995.

III.2.3.2. RESULTS

Samples were taken on 8 to 10 sampling locations on the trajectory Vlissingen-Antwerp. The sampling locations are presented in Figure III.2.14. Their coordinates are presented in Table III.2.5. The dates and hours on which samples were taken are presented in Table III.2.6. In addition, water depth, salinity and water temperature were noted and are also presented in Table III.2.6.

The measurement results of the four campaigns are presented in Table III.2.7. The measurement results are from samples taken on 27 March 1995 (Table III.2.7.a), 18 May 1995 (Table III.2.7.b), on 18 October 1995 (Table III.2.7.c) and on 4 December 1995 (Table III.2.7.d).

Table III.2.5. Coordinates of the sampling locations in the Scheldt estuary in the trajectory Vlissingen - Antwerp.

Location	N	E
S01	51 25.00	3 34.20
S04	51 20.70	3 49.50
S07	51 26.20	4 00.00
S09	51 22.20	4 04.70
S12	51 21.90	4 13.50
S15	51 18.80	4 16.40
S15b	51 17.35	4 19.34
S18	51 16.00	4 18.00
S18b	51 15.29	4 19.05
S22	51 13.13	4 23.50

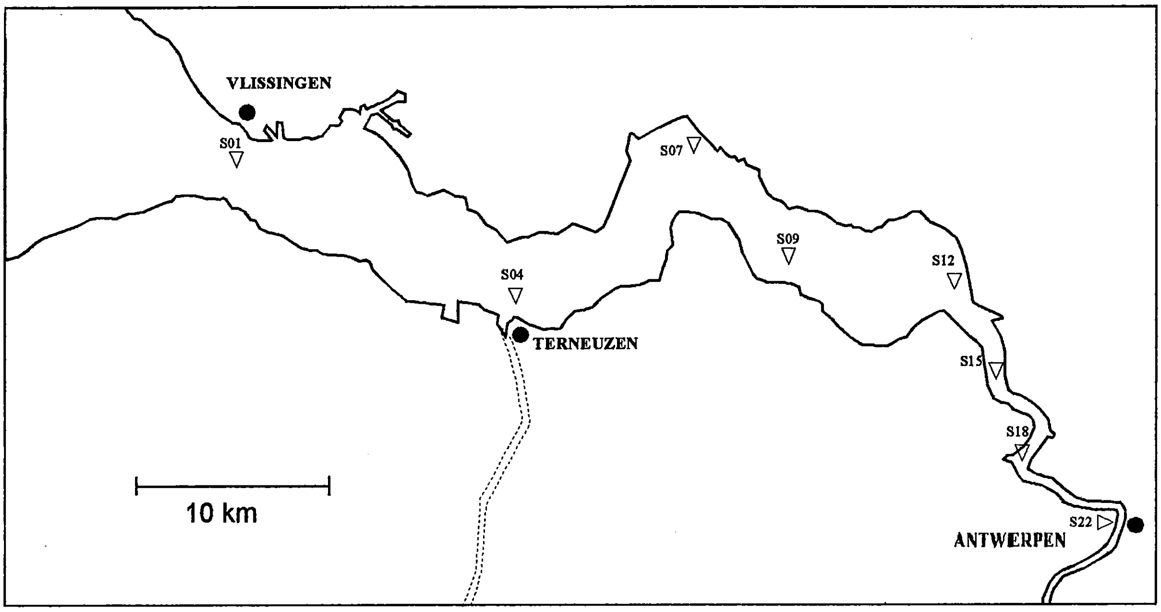


Figure III.2.14. Sampling locations in the Scheldt estuary between Antwerp and Vlissingen

Table III.2.6. Parameters of sampling in the Scheldt Estuary.

Date	Hour	Station	Period	Depth (m)	Salinity (g/L)	Temperature (°C)
27/03/95	14:13	S01	1	26.6	26.6	7.7
27/03/95	15:56	S04	1	8.5	18.8	7.9
27/03/95	17:21	S07	1	28.4	11.6	8.0
27/03/95	18:18	S09	1	17.3	6.4	8.4
27/03/95	19:15	S12	1	22.6	2.7	9.4
27/03/95	20:03	S15	1	10.2	1.8	9.7
27/03/95	20:44	S18	1	15.5	1.0	9.2
27/03/95	21:31	S22	1	15.1	0.5	9.2
18/05/95	5:43	S01	2	24.8	28.2	11.8
18/05/95	7:27	S04	2	48.4	22.7	12.4

continued

18/05/95	8:56	S07	2	27.1	17.5	12.6
18/05/95	10:07	S09	2	17.5	12.6	12.9
18/05/95	11:20	S12	2	20.2	7.1	14.0
18/05/95	12:04	S15	2	15.2	4.8	14.4
18/05/95	12:41	S15b	2	14.9	3.7	14.5
18/05/95	13:07	S18	2	14.3	2.2	14.7
18/05/95	13:27	S18b	2	13.6	1.5	14.7
18/05/95	14:04	S22	2	12.6	0.7	14.7
18.10.95	10:45	S01	3	23.1	29.9	15.9
18.10.95	12:30	S04	3	49.2	25.8	14.9
18.10.95	13:50	S07	3	27.2	22.3	16.0
18.10.95	14:45	S09	3	16.6	18.2	16.4
18.10.95	15:50	S12	3	12.4	13.4	17.4
18.10.95	16:20	S15	3	10.9	11.1	17.6
18.10.95	16:50	S15b	3	12.3	9.9	17.5
18.10.95	17:15	S18	3	12.9	8.0	17.3
18.10.95	17:35	S18b	3	11.1	6.1	17.1
18.10.95	18:25	S22	3	13.2	2.5	17.0
04.12.95	14:35	S01	4	21.2	30.0	8.4
04.12.95	16:10	S04	4	34.9	26.0	8.2
04.12.95	17:35	S07	4	24.3	22.0	7.9
04.12.95	18:25	S09	4	16.9	18.3	8.0
04.12.95	19:35	S12	4	19.1	12.9	9.2
04.12.95	20:25	S15	4	14.8	10.0	9.3
04.12.95	21:05	S18	4	13.3	6.1	8.8
04.12.95	21:50	S22	4	9.6	1.2	8.2

Table III.2.7.a. Results of the sample campaign on the Scheldt for the trajectory Vlissingen - Antwerp on 27 March 1995.

	S01	S04	S07	S09	S12	S15	S18	S22
Chloroform	26.5	473	1281.3	35.3	184.4	91.4	134.0	266.4
Tetrachloromethane	1.8	3.2	3.6	3.9	3.3	27.7	33.9	15.9
1,1-Dichloroethane	1.5	7.2	6.6	5.3	7.4	14.2	23.4	42.6
1,2-Dichloroethane	8.9	18.4	22.5	20.4	42.4	9.5	84.2	72.2
1,1,1-Trichloroethane	5.3	12.8	19.6	43.3	98.3	185.7	269.4	460.7
Trichloroethylene	9.4	9.6	17.6	38.5	94.1	150.2	209.3	327.1
Tetrachloroethylene	1.7	4.7	14.4	45.7	108.8	158.1	255.4	486.3
Benzene	13.8	28.8	18.4	16.4	18.8	29.5	25.7	16.2
Toluene	9.8	16.0	21.3	15.5	23.9	24.6	90.5	116.0
Ethylbenzene	25.0	22.3	13.7	15.1	14.8	12.9	10.4	18.4
m/p-Xylene	10.6	8.6	5.6	6.8	10.4	9.4	10.6	9.2
o-Xylene	9.9	7.5	4.8	6.1	8.4	7.4	10.3	7.9

Table III.2.7.b. Results of the sample campaign on the Scheldt for the trajectory Vlissingen - Antwerp on 18 May 1995.

	S01	S04	S07	S09	S12	S15	S15b	S18	S18b	S22
Chloroform	22.9	83.4	77.5	49.3	78.1	79.6	152.7	181.7	210.8	390.0
Tetrachloromethane	2.2	2.5	2.4	3.3	4.7	7.0	6.2	5.5	5.2	4.9
1,1-Dichloroethane	3.4	0.3	1.7	2.5	5.4	10.1	18.8	23.7	26.9	44.9
1,2-Dichloroethane	20.2	38.9	39.7	59.8	157.3	153.2	224.2	175.0	118.0	62.1
1,1,1-Trichloroethane	6.2	9.4	14.8	25.5	84.7	112.2	221.0	299.0	428.7	718.5
Trichloroethylene	16.0	26.6	66.3	25.6	75.3	120.0	173.6	225.3	248.9	252.2
Tetrachloroethylene	3.2	6.2	13.1	29.9	91.6	156.2	227.6	357.4	501.4	900.6
Benzene	111.1	123.1	48.7	36.4	27.1	26.4	15.7	9.2	7.1	10.4
Toluene	29.4	58.1	23.4	21..0	40.7	77.4	55.2	53.2	45.0	38.4
Ethylbenzene	30.3	51.4	164.2	30.9	52.5	44.6	35.0	47.4	30.5	56.4
m/p-Xylene	86.1	120	557.9	79.8	147.9	104.9	72.7	128.6	87.4	177.4
o-Xylene	31.7	38.2	143.8	30.2	41.8	37.0	22.1	37.5	37.3	111.6

Table III.2.7.c. Results of the sample campaign on the Scheldt for the trajectory Vlissingen - Antwerp on 18 October 1995.

	S01	S04	S07	S09	S12	S15	S15b	S18	S18b	S22
Chloroform	14.7	29.3	51.3	56.2	51.5	823.4	298.8	244.6	245.9	299.2
Tetrachloromethane	1.2	4.9	2.1	3.6	4.8	18.6	8.3	6.5	6.7	2.8
1,1-Dichloroethane	1.0	4.3	1.7	3.4	5.2	25.8	21.6	24.0	24.1	34.8
1,2-Dichloroethane	10.5	16.8	37.7	117.5	178.8	211.2	365.5	321.6	320.6	78.8
1,1,1-Trichloroethane	3.4	9.8	15.0	43.3	96.1	127.3	298.3	286.7	287.9	192.7
Trichloroethylene	4.8	9.7	7.6	20.0	29.9	52.6	95.2	111.0	112.2	133.7
Tetrachloroethylene	2.6	11.5	20.7	69.6	144.0	215.6	533.4	662.3	668.6	698.7
Benzene	13.8	23.2	346.5	39.2	19.1	29.7	24.1	22.4	22.3	23.6
Toluene	44.3	28.6	38.0	119.8	63.0	72.9	56.2	50.6	51.0	44.6
Ethylbenzene	7.6	23.4	50.6	47.2	32.2	32.3	46.8	26.2	26.2	41.1
m/p-Xylene	13.8	49.1	126.1	108.6	68.3	65.6	83.4	52.4	52.6	69.1
o-Xylene	8.8	33.4	78.6	84.2	50.7	54.3	72.3	51.2	50.5	63.3

Table III.2.7.d. Results of the sample campaign on the Scheldt for the trajectory Vlissingen - Antwerp on 4 December 1995.

	S01	S04	S07	S09	S12	S15	S18	S22
Chloroform	7.4	14.1	24.6	46.6	73.9	74.0	130.9	224.3
Tetrachloromethane	0.8	1.8	2.6	2.6	2.8	2.4	3.8	3.6
1,1-Dichloroethane	0.7	1.6	1.1	2.9	6.2	7.2	17.1	25.5
1,2-Dichloroethane	12.9	21.2	29.4	67	106.7	98.8	160.3	58.9
1,1,1-Trichloroethane	2.4	5.1	10	25.7	51.0	69.8	158.2	173.2
Trichloroethylene	3.7	4.8	13.2	22.4	39.0	55.5	148.2	215.8
Tetrachloroethylene	1.6	4.6	14.5	77.3	183.5	109.5	959.1	1081.5
Benzene	13.8	13.2	17.5	20.5	14.7	13.4	15.7	14.4
Toluene	20.7	27.3	38.4	42.1	30.6	40.3	46.4	22.8
Ethylbenzene	5.2	4.9	9.2	16.2	12.1	7.9	8.3	5.3
m/p-Xylene	5.8	6.1	9.4	15.6	9.7	8.0	10.0	9.2
o-Xylene	6.1	6.2	9.2	18.1	12.4	10.6	12.9	13.7

From the results it can be seen that chloroform show large variations in concentration along the trajectory. Concentrations from below 10ng.L^{-1} up to above 1000ng.L^{-1} are observed. The other CHCs all show generally increasing concentrations towards Antwerp and minimum concentrations near Vlissingen. The concentration gradients are illustrated in Figure III.2.15 for trichloroethylene and toluene. For all compounds the same representation is given in Annex III.2.31. The concentration can be plotted as a function of salinity as is illustrated for 1,1,1-trichloroethane and toluene in Figure III.2.16. For all VOCs the same plot is given in Annex III.2.32.

The gradients observed for the CHCs cannot be recognised for the MAHs except for toluene on 27 March 1995. On 18 May 1995 benzene proved to give an opposite gradient with the highest concentration near Vlissingen (111.1ng.L^{-1}) and the lowest concentration near Antwerp (7.1 to 10.4ng.L^{-1}). The variations in concentration along the sampling trajectory is different from one sampling campaign to another one. On 27 March 1995 and 4 December 1995 all MAHs except toluene on 27 March show low variations in concentration (e.g. m/p-xylene concentrations on 27 March between 5.6 and 10.6ng.L^{-1}) and rather low concentrations: all individual MAHs concentrations are below 50ng.L^{-1}. However, on 18 May and 18 October 1995, MAHs concentrations are varying strongly (e.g. m/p-xylene concentrations on 18 October 1995 between 13.8 and 126.1ng.L^{-1}). In addition some concentrations are higher than in the two other sampling campaigns. Concentrations of all individual MAHs show in both campaigns samples with concentrations abovc 50ng.L^{-1} whereas C_2-substituted MAHs have some concentrations over 100ng.L^{-1}.

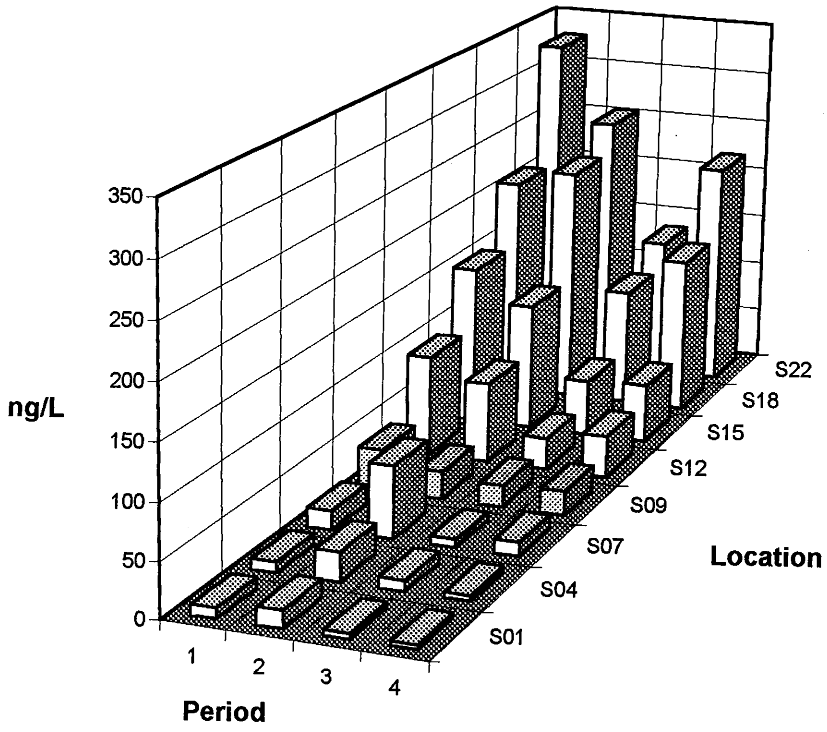


Figure III.2.15.a. Measurement results of trichloroethylene during 4 periods in 1995 and all sampling locations in the Scheldt estuary, represented by a bar chart

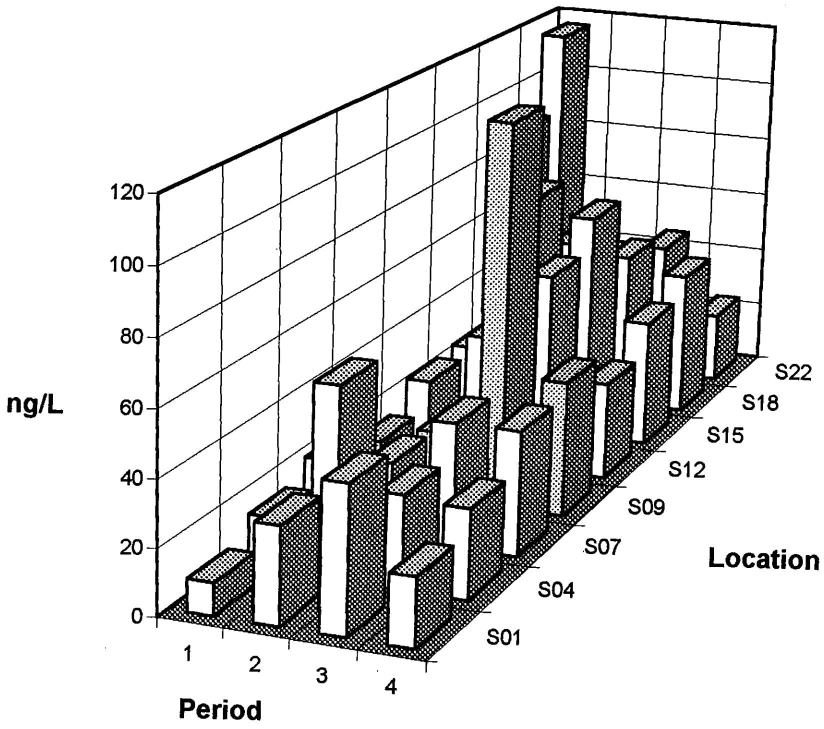


Figure III.2.15.b. Measurement results of toluene during 4 periods in 1995 and all sampling locations in the Scheldt estuary, represented by a bar chart

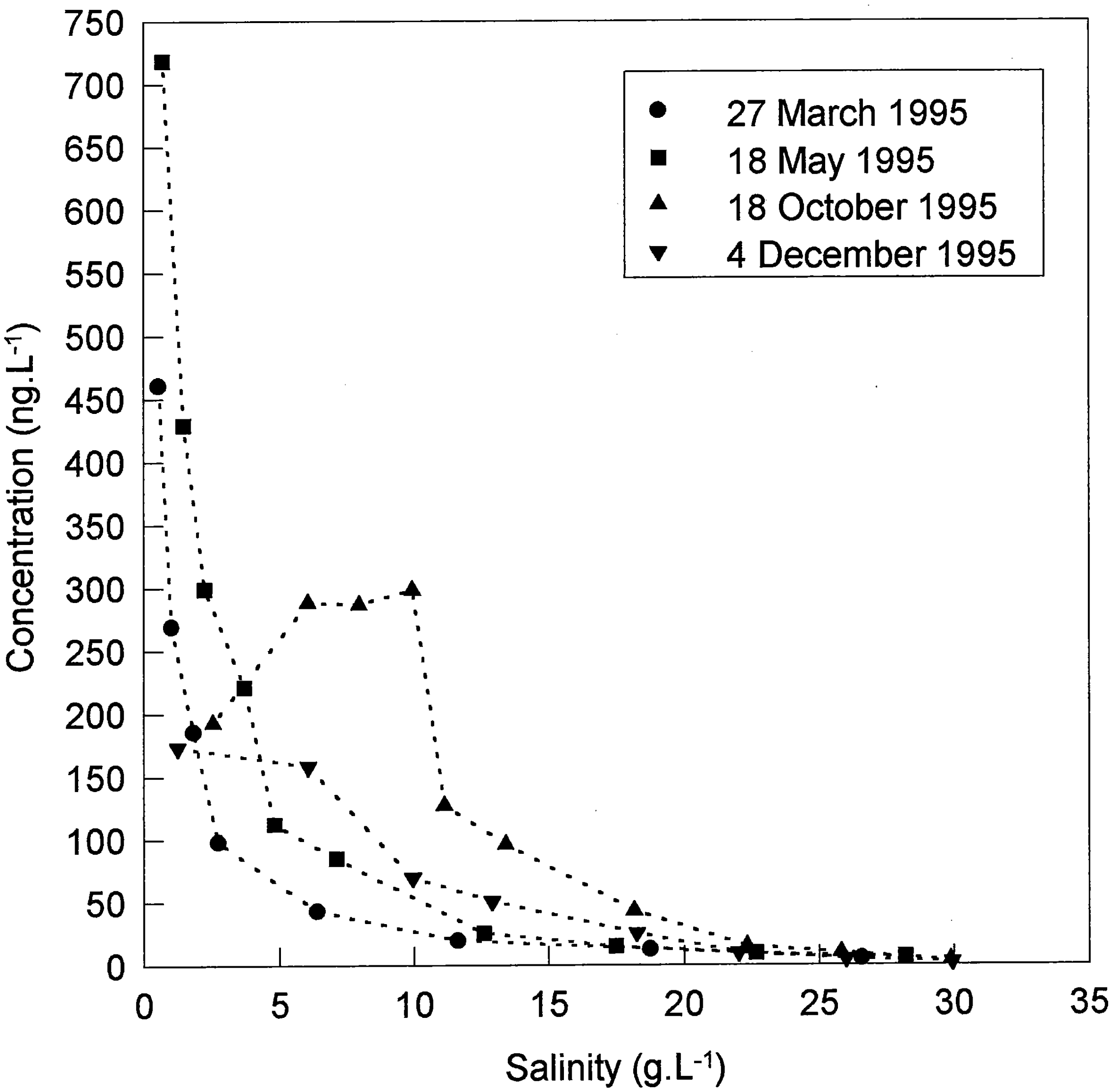


Figure III.2.16.a. Measurement results of 1,1,1-trichloroethane during 4 periods in 1995 and all sampling locations in the Scheldt estuary, represented by an x,y-plot

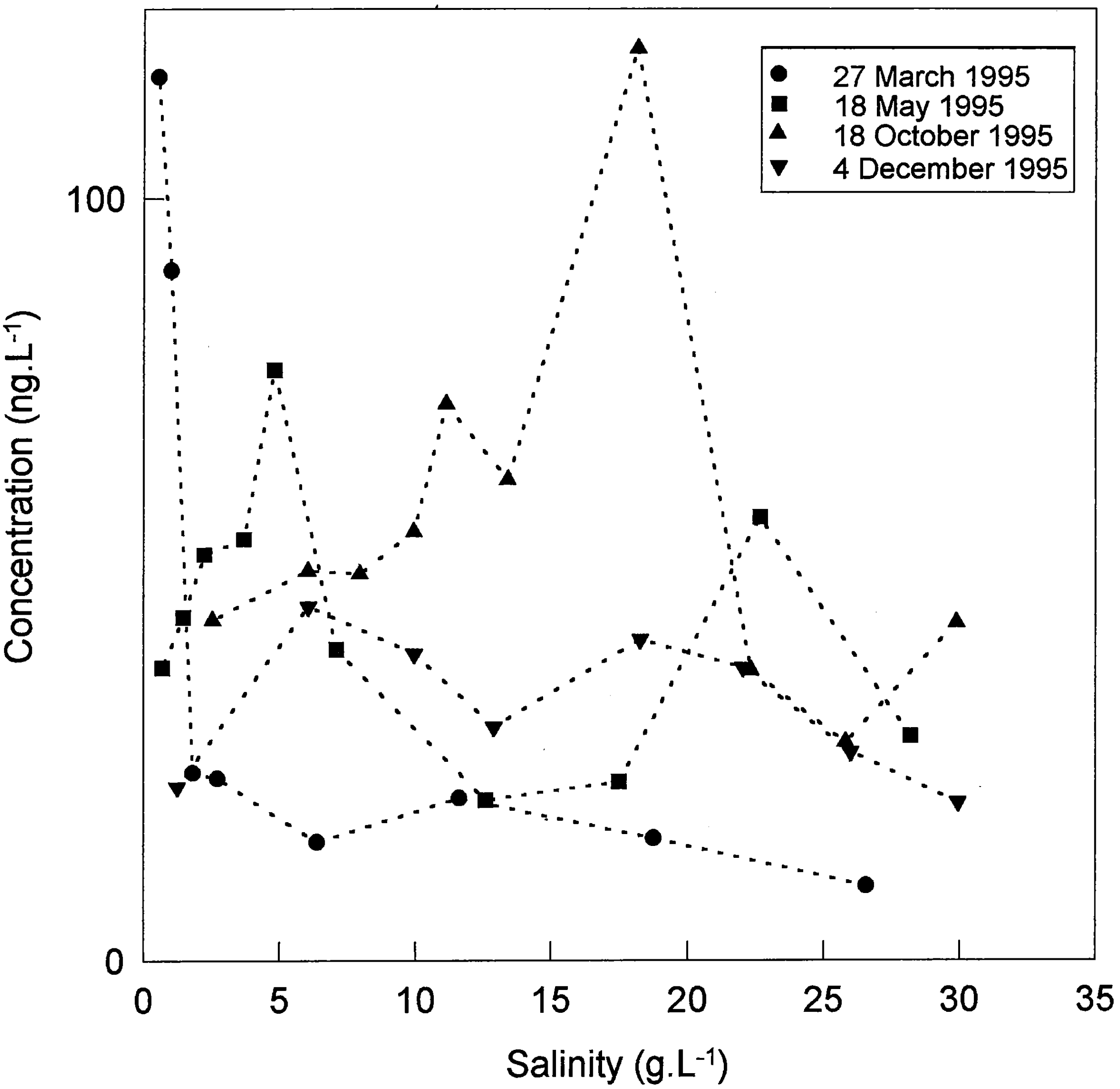


Figure III.2.16.b. Measurement results of toluene during 4 periods in 1995 and all sampling locations in the Scheldt estuary, represented by an x,y-plot

III.2.3.3. CONCLUSIONS

In conclusion the CHCs and MAHs show a different concentration pattern in the Scheldt estuary trajectory Vlissingen-Antwerp. The gradient and the concentration levels of the CHCs can be explained by anthropogenic inputs. Plots of concentrations versus salinity indicate the rapid concentration decrease towards Vlissingen, suggesting removal mechanisms additional to dilution with less polluted salt seawater.

The MAHs show in two campaigns higher concentrations than at open sea locations whereas the measurements in the two other campaigns are of a same level as at open sea locations. It is clear that there is insufficient information to date to explain these differences and to interprete the concentration patterns.

III.3. SEDIMENTS

III.3.1 INTRODUCTION

The sediment samples collected during the monitoring campaign were only analysed twice for the presence of the target compounds. The first occasion was at the onset of the monitoring campaign with as primary goal the determination of the variability of the sampling at a selected sampling station. The result were, however mostly below the detection limits of the analytical technique and for that reason the research focused on the determination of the target compounds in marine biota, where many difficulties were encountered. As a method was developed for the determination of VOCs in biota, it was tested for the analysis of sediments as well (see II.3.3.3) with excellent results. The samples collected during the 1995 campaign were then analysed using the new improved method, again with little concentrations above the detection limits. As a result, the research was further focused on the analysis of the target compounds in biota.

III.3.2 VARIABILITY AT ONE MONITORING STATION

III.3.2.1 INTRODUCTION

In order to determine the variability 5 sediment samples were independently collected at one sampling location (120) (figure III.3.1) and analysed using the analytical technique described in section II.3.3.2. As three independent samples were available for station 435 (figure III.3.1) they were also analysed.

III.3.2.2 RESULTS AND DISCUSSION

The results of the analysis are given in table III.3.1. For the sediments of sampling station 120, only ethylbenzene could be detected in sufficient amounts. The variability for the analysis of the different samples is however very small. For sampling station 435 trichloroethylene, m&p-xylene and o-xylene were detected. For the CHC the variability was small, but for the MAHs it was considerably higher. In those cases sampling would contribute considerably to the eventual outcome of analyses. Care should in any case be taken, interpreting these results as all observed concentrations are close to the detection limits of the analytical methodology and this is precisely the area were the greatest error of the methodology is expected. Further study of these phenomena would in any case require a methodology with a still lower detection limit or a sampling location with much higher concentrations.

Table III.3.1: Variability of VOCs at one sampling station.

Compound	120		435	
	Concentration in pg/g	RSD % (n=4)	Concentration in pg/g	RSD % (n=3)
Chloroform	nd	na	nd	na
Trichloroethane	nd	na	nd	na
Tetrachloromethane	nd	na	nd	na
Benzene	nd	na	nd	na
Trichloroethylene	nd	na	23	6
Toluene	nd	na	nd	na
Tetrachloroethylene	nd	na	nd	na
Ethylbenzene	4	7	nd	na
m&p-Xylene	nd	na	6	50
o-Xylene	nd	na	4	60
1,2-Dichloroethane	nd	na	nd	na
1,1-Dichloroethane	nd	na	nd	na

n = number of samples, RDS = relative standard deviation, nd = not detected, na = not applicable

III.3.3 SEASONAL AND SPATIAL DISTRIBUTION OF VOC CONCENTRATIONS IN MARINE SEDIMENTS

III.3.3.1 INTRODUCTION

For the sediment samples collected in 1995 a new series of analyses was carried out using the analysis method developed for biological samples. The seasonal variability of VOC concentration in sediments was estimated by analysing the sediment samples from station 780 collected during the different campaigns. The spatial distribution of VOC concentrations was estimated by analysing the samples of the different stations collected during one period, namely the winter of '95-'96. The monitoring stations are spread over the continental shelf in such a way that they roughly represent a west-east axis, a north-south axis and included suspected points of entry of contaminants such as the Scheldt estuary and the harbour of Zeebrugge (figure III.3.1).

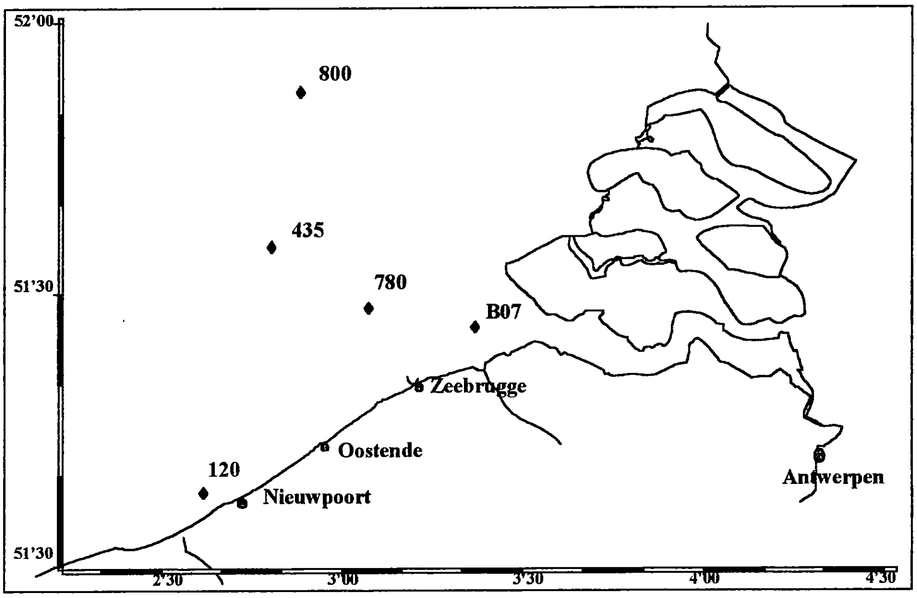


Figure III.3.1: Sampling stations on the Belgian Continental shelf for the monitoring of VOCs in marine sediments.

III.3.3.2 RESULTS AND DISCUSSION

The results of the analysis of the sediment samples for seasonal and spatial distribution is given in table III.3.2.

For the samples that were analysed for the seasonal variation only trichloroethane, tetrachloromethane, tetrachloroethylene and 1,1-dichloroethane could be detected on respectively one, three, one and two occasions. It is evident that this small set of data does not allow any form of comparison. Moreover, concentrations are again very close to the detection limits.

For the samples that were analysed for the determination of the spatial distribution only chloroform, tetrachloromethane and 1,1-dichloroethane were detected on one occasion. Obviously, this does not allow any form of comparison.

III.3.4 CONCLUSIONS

The analysis of sediment samples was only executed on a number of occasions which revealed that the concentration of VOCs in sediments along the Belgian coast were generally below or at the detection limits of the analytical method. Seriously studying an alternative and still more sensitive method was not feasible in the framework of this project. It is further to be questioned if this is necessary as the LODs obtained with the current methodology are well in the range of those reported in literature by authors e.g. Bianchi and Varney, 1989; Bianchi *et al.*, 1991; Al-Rekabi *et al.*, 1995).

III.3.5 REFERENCES

Al-Rekabi H., Sojak L. and Kminiak M., Water Air Soil Pollut., 81, 193-200 (1995).

Bianchi A. and Varney M.S., J. High Resolut. Chromatogr., 12, 184-186 (1989).

Bianchi A., Varney M.S. and Phillips J., J. Chromatogr., 542, 413-450 (1991).

Table III.3.1: Results of the analysis of VOC concentrations for the determination of seasonal and spatial variability. Concentrations are expressed as pg/g.

Compound	Station 780				Station 435	Station S12	Station 435	Station B08	Station 800	Station 120
	03/95	05/95	10/95	11/95	10/95	11/95	12/95	01/96	02/96	03/96
Chloroform	nd	nd	nd	nd	nd	nd	nd	nd	60	nd
Trichloroethane	nd	nd	10	nd	nd	nd	nd	nd	nd	nd
Tetrachloromethane	4	nd	6	6	2	nd	nd	nd	nd	nd
Benzene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Trichloroethylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Toluene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Tetrachloroethylene	nd	nd	37	nd	nd	nd	nd	nd	nd	nd
Ethylbenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
m&p-Xylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
o-Xylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,2-Dichloroethane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,1-Dichloroethane	nd	nd	10	2	1	nd	nd	nd	nd	nd

nd = not detected

III.4. BIOTA

III.4.1. INTERSPECIES AND INTERSPECIMEN DISTRIBUTION

III.4.1.1 INTRODUCTION

To determine the interspecies and interspecimen distribution 25 specimen of 2 species (whiting, *Merlangius merlangus,* and dab, *Limanda limanda*) were collected during one trawl at sampling station 780. This to assure the fact that the fish were collected from the same population. Liver and muscle tissue was then individually analysed and the resulting data were used to perform a number of statistical tests.

For the muscle tissue of whiting an additional determination of 10 polychlorinated biphenyls (CBs), the organochlorine pesticide (OCP) hexachlorobenzene, the p,p'-DDT metabolite p,p'-DDE according to Roose *et al.* (1993) and a total lipid determination using the total lipid extraction of Bligh and Dyer (1959) was performed. This allowed to determine to what extent the concentrations of VOCs are related to those of other important contaminants and whether they are correlated with the fat content.

III.4.1.2 INTERSPECIES AND INTERSPECIMEN DISTRIBUTION IN WHITING

III.4.1.2.1 Distribution of VOCs in muscle tissue of whiting

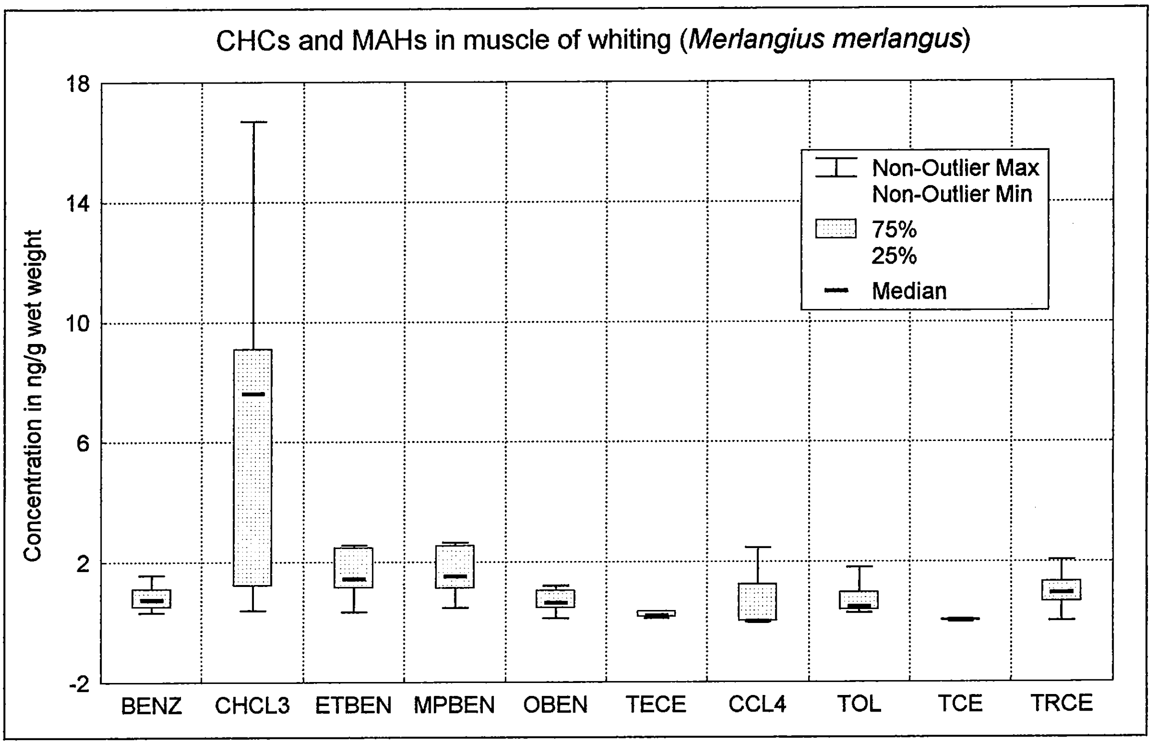
At the first instance, the minimum, maximum, 25% percentile, 75% percentile, median, mean, standard deviation (SDs), standard error, lower 95% confidence interval, coefficient of variation and the geometric mean was determined for VOCs in muscle of whiting originating from one sample. Although 25 individual samples were initially analysed, the results of four had to be discarded for reasons of quality assurance. VOCs could be determined in all the other samples.

The results of the analyses are given in table III.4.1. For certain compounds such as tetrachloromethane and trichloroethane the data set is small as only few concentrations were above the detection limit. This is especially the case for tetrachloromethane, for which only four valid concentrations could be determined.

Table III.4.1: Concentrations in ng/g wet weight of VOCs in muscle of whiting (*Merlangius merlangus*) of one sampling location.

Sample	Benzene	Chloroform	Ethyl-benzene	m&p-Xylene	o-Xylene	Tetrachloro-ethylene	Tetrachloro-methane	Toluene	Trichloro-ethane	Trichloro-ethylene
Whiting 1	0.83	nd	1.22	1.53	0.69	nd	nd	1.63	0.06	1.08
Whiting 2	0.50	nd	0.66	0.85	0.37	nd	nd	0.83	0.02	0.78
Whiting 3	0.97	nd	5.72	6.43	3.33	nd	nd	0.75	0.03	1.08
Whiting 4	1.12	nd	1.45	1.88	1.06	nd	nd	0.99	0.10	1.53
Whiting 5	1.58	nd	1.68	1.81	0.91	nd	2.49	1.83	0.05	1.48
Whiting 6	1.36	nd	2.57	2.66	1.23	nd	nd	1.52	0.03	0.97
Whiting 7	nd	7.92	1.10	1.21	0.46	0.22	0.01	0.40	0.04	0.28
Whiting 8	0.63	13.50	1.45	1.13	0.54	0.15	nd	0.39	0.05	2.51
Whiting 9	0.44	9.11	1.22	1.17	0.50	0.16	nd	0.42	0.10	2.09
Whiting 10	1.19	16.71	2.02	2.18	0.68	0.37	0.04	0.88	0.20	1.39
Whiting 11	0.34	7.33	1.64	1.84	0.65	0.23	nd	0.48	0.04	0.76
Whiting 12	nd	nd	0.38	0.53	0.15	nd	nd	nd	nd	0.27
Whiting 13	nd	nd	1.27	1.34	0.49	nd	nd	0.52	nd	0.61
Whiting 14	nd	nd	2.42	2.56	0.95	nd	nd	nd	nd	1.21
Whiting 15	nd	nd	1.20	1.13	0.48	nd	nd	nd	nd	0.83
Whiting 16	nd	8.51	nd	1.54	0.64	0.71	nd	nd	nd	1.29
Whiting 17	0.59	2.56	8.05	7.44	3.31	0.38	nd	0.39	nd	0.74
Whiting 18	0.52	1.23	4.58	5.15	2.48	0.17	nd	0.32	nd	0.61
Whiting 19	0.76	nd	17.71	14.31	7.03	0.16	nd	0.50	0.03	0.95
Whiting 20	nd	0.40	0.35	0.50	0.26	nd	0.03	nd	nd	0.05
Whiting 21	nd	0.48	0.73	0.92	0.48	nd	nd	nd	nd	nd

nd = not detected



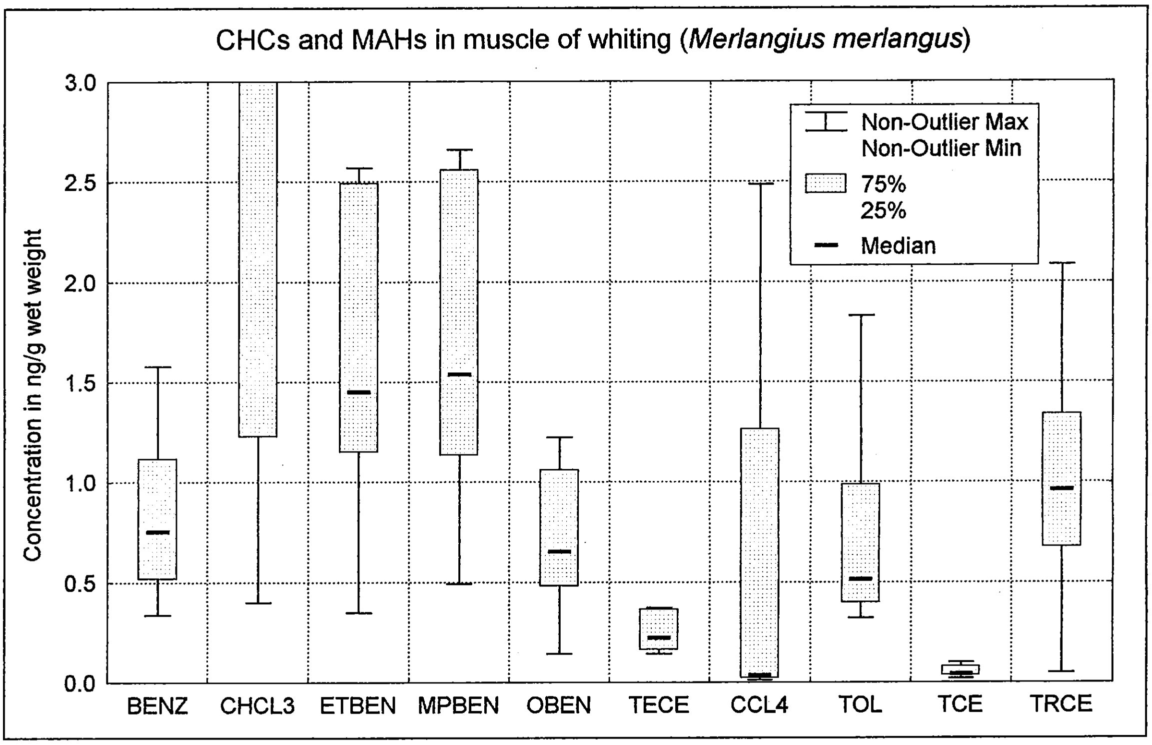


Figure III.4.1: Box and whisker plot of VOCs in muscle tissue of whiting. Overview (upper graph) and detail (lower graph) with BENZ = benzene, CHCL3 = chloroform, ETBEN = ethylbenzene, MPBEN = m&p-xylene, OBEN = o-xylene, TECE = tetrachloroethylene, CCL4 = tetrachloromethane, TOL = toluene, TCE = trichloroethane, TRCE = trichloroethylene.

Table III.4.2: Basic statistics of VOCs in muscle of whiting from one sample. The calculations were based on the concentrations expressed as ng/g wet weight.

Parameter	n	Minimum	25% Percentile	Median	75% Percentile	Maximum	Mean	SD	SEM	CV
Benzene	13	1.4	2.4	4.4	5.4	6.8	4.0	2.0	0.5	46%
Chloroform	10	1.6	31.5	41.7	74.7	1235.0	197.6	386.8	122.3	83%
m&p-Xylene	20	1.3	5.3	6.4	10.6	112.5	13.9	24.4	5.4	139%
Ethylbenzene	21	1.2	3.9	5.7	8.7	52.7	10.8	13.2	2.9	117%
o-Xylene	21	0.4	2.3	3.1	4.3	63.4	8.6	14.6	3.2	126%
Tetrachloroethylene	12	0.1	0.1	0.2	0.4	0.9	0.3	0.2	0.1	64%
Tetrachloromethane	4	0.2		0.7		11.4	3.2	5.5	2.7	191%
Toluene	15	1.3	1.8	2.6	4.2	7.7	3.4	2.0	0.5	63%
Trichloroethane	9	0.6	0.6	1.0	1.0	2.5	1.2	0.7	0.2	79%
Trichloroethylene	20	0.1	3.0	4.6	6.4	12.4	4.6	2.8	0.6	58%

n = number of samples, SD = standard deviation, SEM = standard error of the mean, CI = confidence interval, CV = coefficient of variation

The results of the statistical analysis are given in table III.4.2. The large variability of the concentrations becomes immediately evident as the standard deviation is generally high. The discrepancy between the mean and the median suggests that the values are not normally distributed. The variability and the distribution of the VOCs is illustrated in figure III.4.1.

The fact whether a normal distribution can be assumed is extremely important for the choice of statistical tests later on. A Kolmogorov-Smirnov test was therefore executed to determine whether the distribution is normal. The P value of the test is obtained with the Dallal and Wilkinson's approximation to Lilliefors' method (GraphPad Prism ver. 2.00) . The test results in the Kolmogorov-Smirnov (KS) distance and a P value. The KS distance is a measure of the deviation of the normal distribution. A KS distance of zero indicates that the sample is normally distributed. The P value gives the probability that a randomly selected sample of this size would deviate as much of the Gaussian distribution than observed in the test, or better the probability that it has a KS distance as large or larger than the one observed. The results of these tests are given in table III.4.3.

Table III.4.3: Results of the Kolmogorov-Smirnov test for VOCs in muscle of whiting.

	KS distance	P value	Passed normality test (P>0.05)?
Benzene	0.1508	$P > 0.10$	Yes
Chloroform	0.4167	0.062	Yes
m&p-Xylene	0.372	0.0079	No
Ethylbenzene	0.322	0.0257	No
o-Xylene	0.3855	0.0039	No
Tetrachloroethylene	0.2444	$P > 0.10$	Yes
Tetrachloromethane	0.4178	$P > 0.10$	Yes
Toluene	0.1875	$P > 0.10$	Yes
Trichloroethane	0.268	$P > 0.10$	Yes
Trichloroethylene	0.1266	$P > 0.10$	Yes

For the m&p-xylene, ethylbenzene and o-xylene the tests indicates that the population in not normally distributed. This does however not mean that for the other cases a normal distribution can be assumed as the sample size is generally small. The test only indicates that the P values, in those cases, are not inconsistent with a Gaussian population. To further investigate the distribution of the VOCs in muscle tissue of whiting, a normal probability plot was made for each compound. For this plot the deviations of the mean are first rank ordered. For these ranks a z value is calculated based on the assumption that samples come from a population with a normal distribution. The z values are then plotted against the observed residuals. Ideally, the resulting points on the graph should have a linear correlation. The results of these plots are given in figures III.4.2 and III.4.3 for the different VOCs. Most of the plots with perhaps the exception of trichloroethylene show an s shaped pattern around the expected straight line. For certain cases, such as trichloroethylene, a normal distribution could be accepted, yet it seemed advisable to consider the contrary as the number of data was limited. It was therefore concluded that both the MAHs and the CHCs are not normally distributed in muscle tissue of whiting. Ensuing statistical comparisons should as a results be made with non parametric tests.

The data for the VOCs were further analysed by comparing the values for the MAHs with each other and the values for CHCs with each other, using a non parametric Kruskall Wallis ANOVA test. This was to determine whether MAHs or CHCs can be considered as a group. For both cases, the test revealed that the difference between the medians was larger than expected by change ($P<0.001$). It could therefore be assumed that the data sets originate from different populations. The different MAHs and CHCs should therefore be treated as individual compounds in stead as a group. This was, however further investigated with Dunn's post test and the results of this test are given in table III.4.4.

The test revealed significant P values for the comparison between ethylbenzene and toluene for the MAHs and between chloroform and trichloroethane and tetrachloroethylene and tetrachloroethylene and trichloroethylene.

It was therefore concluded that VOCs are not normally distributed in muscle of whiting and that the concentrations of the different VOCs should be treated separately and not as a group of compounds, such as MAHs or CHCs, for statistical comparisons. The concentrations are further characterised by a substantial variability both between the VOCs in a given fish and between the different fishes. A substantial variability is also seen for the concentration of the same VOC in the different fishes. The test further indicated that the concentrations of VOCs are not related in muscle of whiting.

Table III.4.4: Results of Dunn's multiple comparison test.

Comparison	P value	Summary
Benzene vs Ethylbenzene	$P > 0.05$	ns
Benzene vs m&p-Xylene	$P > 0.05$	ns
Benzene vs o-Xylene	$P > 0.05$	ns
Benzene vs Toluene	$P > 0.05$	ns
Ethylbenzene vs m&p-Xylene	$P > 0.05$	ns
Ethylbenzene vs o-Xylene	$P > 0.05$	ns
Ethylbenzene vs Toluene	$P < 0.05$	*
m&p-Xylene vs o-Xylene	$P > 0.05$	ns
m&p-Xylene vs Toluene	$P > 0.05$	ns
o-Xylene vs Toluene	$P > 0.05$	ns
Chloroform vs Tetrachloroethylene	$P < 0.001$	*
Chloroform vs Tetrachloromethane	$P > 0.05$	ns
Chloroform vs Trichloroethane	$P < 0.01$	*
Chloroform vs Trichloroethylene	$P > 0.05$	ns
Tetrachloroethylene vs Tetrachloromethane	$P > 0.05$	ns
Tetrachloroethylene vs Trichloroethane	$P > 0.05$	ns
Tetrachloroethylene vs Trichloroethylene	$P < 0.001$	*
Tetrachloromethane vs Trichloroethane	$P > 0.05$	ns
Tetrachloromethane vs Trichloroethylene	$P > 0.05$	ns
Trichloroethane vs Trichloroethylene	$P > 0.05$	ns

ns = not significant, * significant

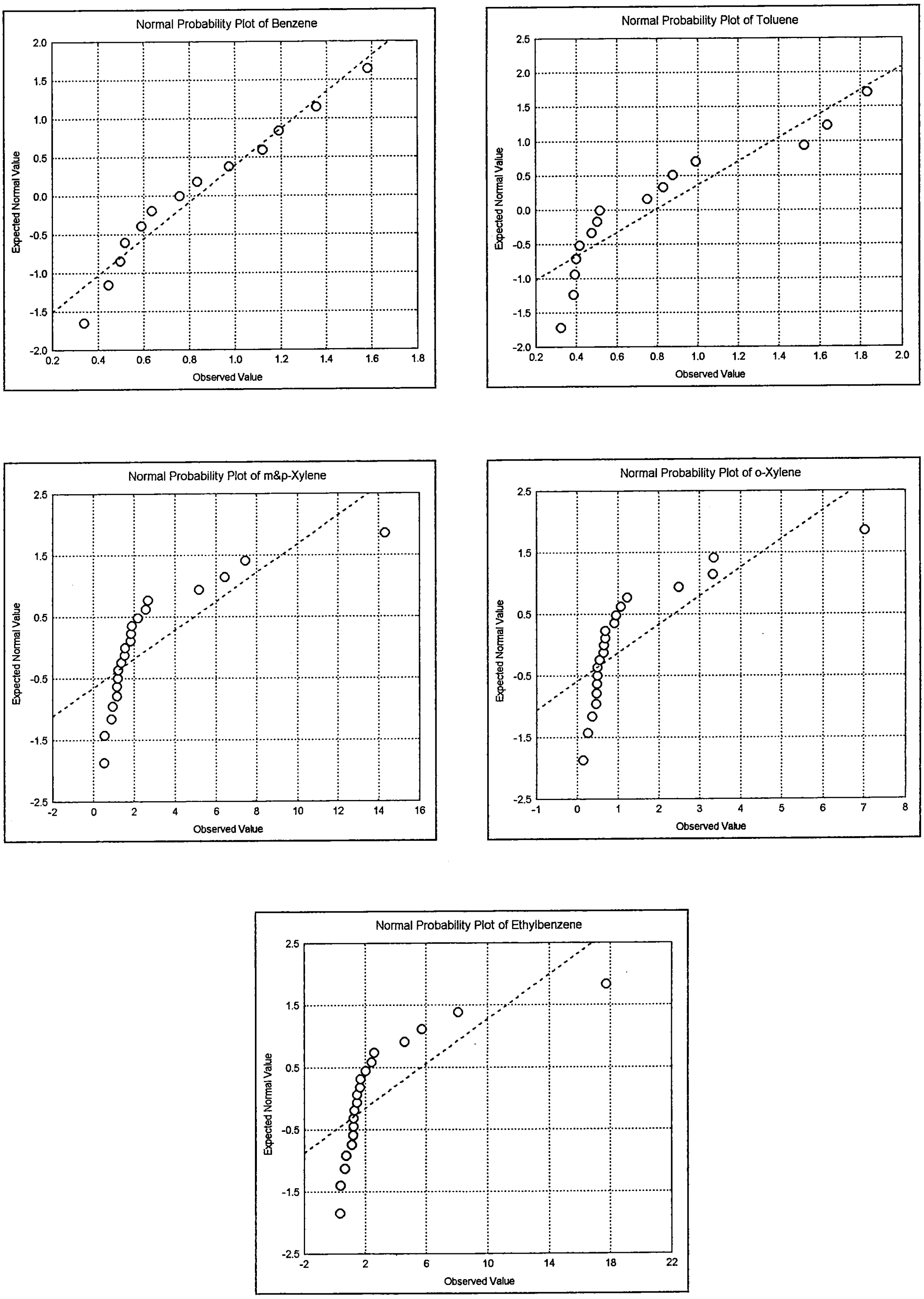


Figure III.4.2: Normal probability plot of benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in muscle tissue of whiting.

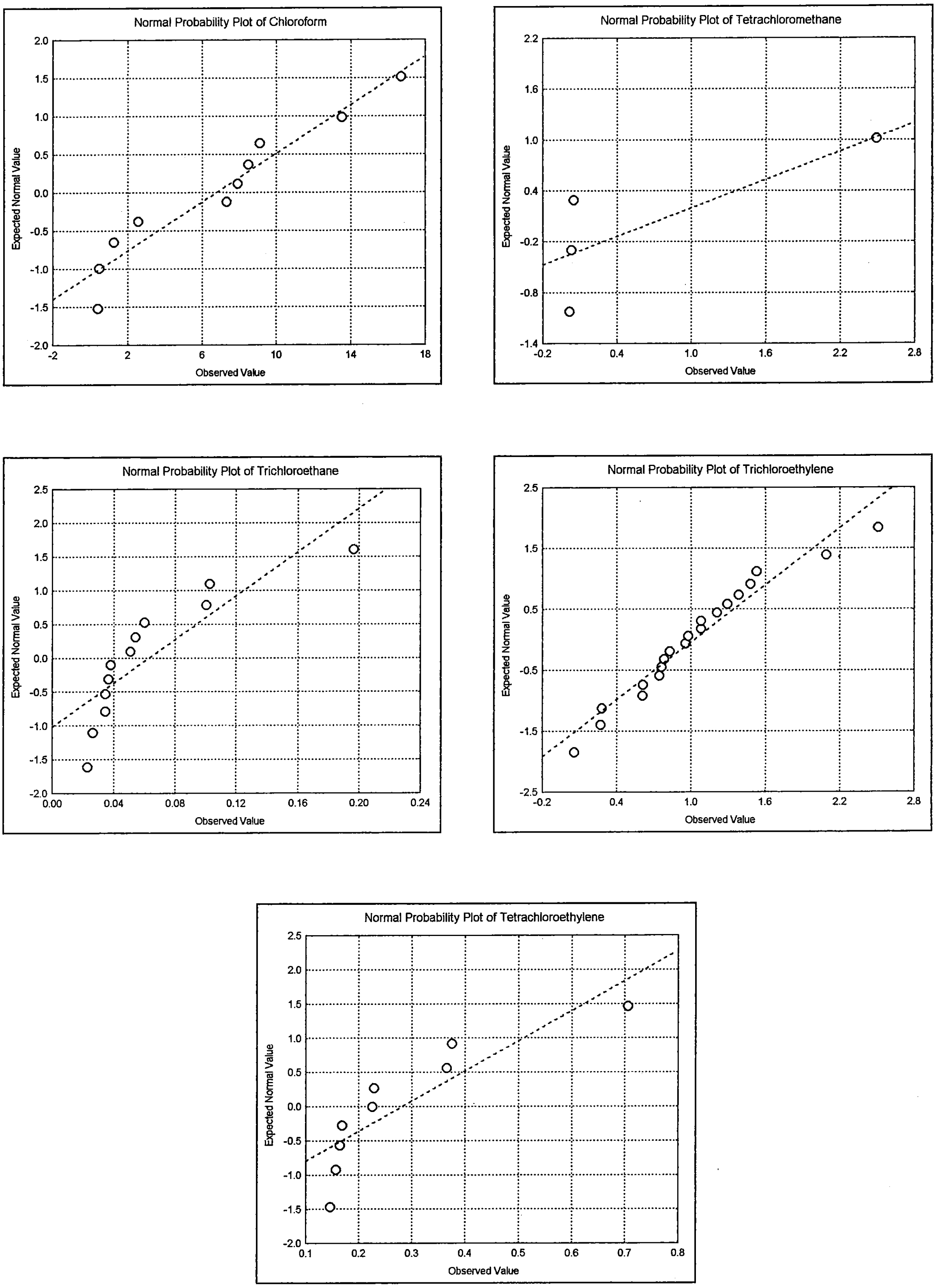


Figure III.4.3: Normal probability plot of chloroform (upper left), tetrachloromethane (upper right), trichloroethane (middle left), trichloroethylene (middle right) and tetrachloroethylene (bottom) in muscle tissue of whiting.

III.4.1.2.2 Distribution of CBs and OCPs in muscle tissue of whiting

As above, the distribution of the CBs and OCPs in muscle of whiting was first described by determining the minimum, maximum, 25% percentile, 75% percentile, median, mean, standard deviation (SDs), standard error, coefficient of variation and the geometric mean. Only 22 individual samples of the original 25 could be analysed by lack of material. For all samples the CBs with UIPAC n° 28, 31 52, 101, 105, 118, 138, 153, 156 and 180 (Ballschmiter and Zell, 1992) and the OCPs HCB and p,p'-DDE could be quantitatively determined. The results of the analyses are given in table III.4.5. The concentration of the CBs and the OCPs is in the same order of magnitude as those of VOCs. The results of the statistical analysis are given in table III.4.6. The standard deviation is generally again of the same order of magnitude as that for VOCs. The discrepancy between the mean and the median is smaller compared to the results for VOCs. This suggests that the values are normally distributed. The variability and the distribution of the CBs and OCPs is illustrated in figure III.4.4.

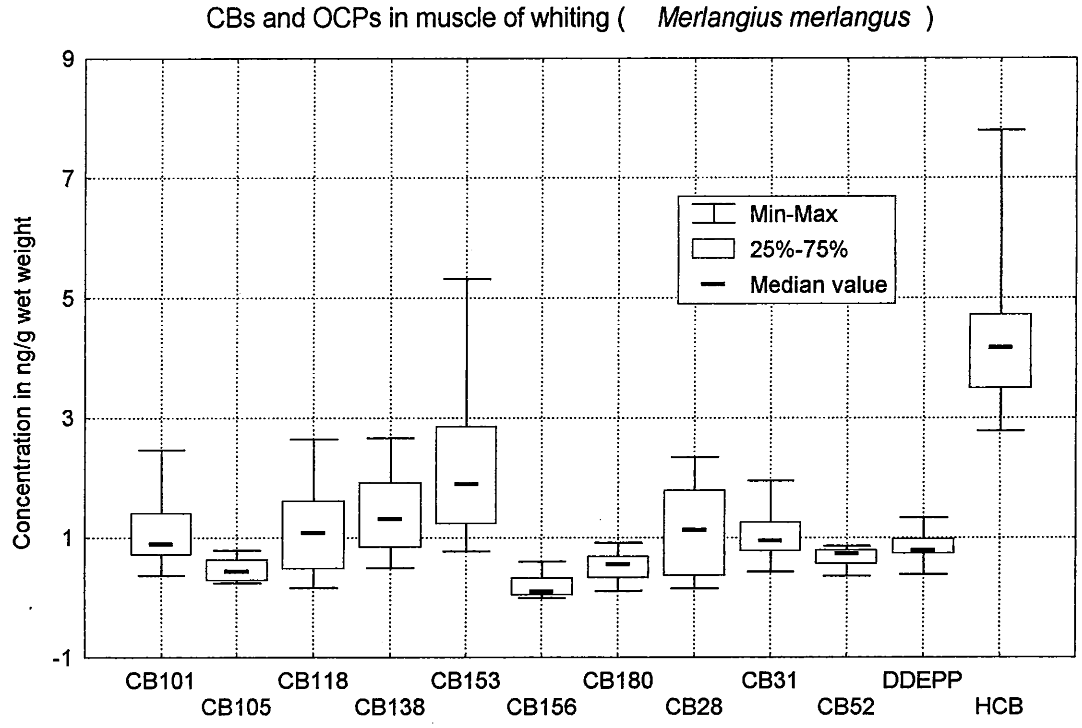


Figure III.4.4: Box and Whisker plot illustrating the variability and distribution of CBs and OCPs in muscle of whiting.

A Kolmogorov-Smirnov test was again used to determine whether the distribution is Gaussian. The results of these tests are given in table III.4.7.

Table III.4.7: Results of the Kolmogorov-Smirnov test for CBs and OCPs in muscle of whiting.

Parameter	KS distance	P value	Passed normality test (P>0.05)?
CB101	0.1686	$P > 0.10$	Yes
CB105	0.1297	$P > 0.10$	Yes
CB118	0.1229	$P > 0.10$	Yes
CB138	0.1473	$P > 0.10$	Yes
CB153	0.1783	$P > 0.10$	Yes
CB156	0.2653	0.0903	Yes
CB180	0.1399	$P > 0.10$	Yes
CB28	0.1683	$P > 0.10$	Yes
CB31	0.1402	$P > 0.10$	Yes
CB52	0.1355	$P > 0.10$	Yes
DDEPP	0.3773	0.0038	No
HCB	0.09747	$P > 0.10$	Yes

All CBs and OCPs with the exception of p,p'-DDE pass the normality test. This would lead to the assumption that the concentrations of CBs and OCPs exhibit a normal distribution in the muscle tissue of whiting from the same population. However, the sample size is again small. The results of the test should therefore be interpreted with the necessary caution. The distribution was therefore further investigated by means of normal probability plots. The plots for the various CBs and OCPs are given in figures III.4.5 and III.4.6..

Although the results of the Kolomogorov-Smirnov test suggest a normal distribution, the contrary is suggested by the normal probability plots. For nearly all cases a s shaped pattern can be observed around the expected straight line This is consistent with previous observations (Roose *et al.*, 1996). Moreover, the s shaped pattern is identical to the one observed for most VOCs. This certainly certifies a correlation analysis between the concentrations of VOCs and CBs in the same fish. It could therefore be accepted that the CBs and the OCPs are not normally distributed in the muscle tissue of whiting. Non parametric tests are therefore preferred.

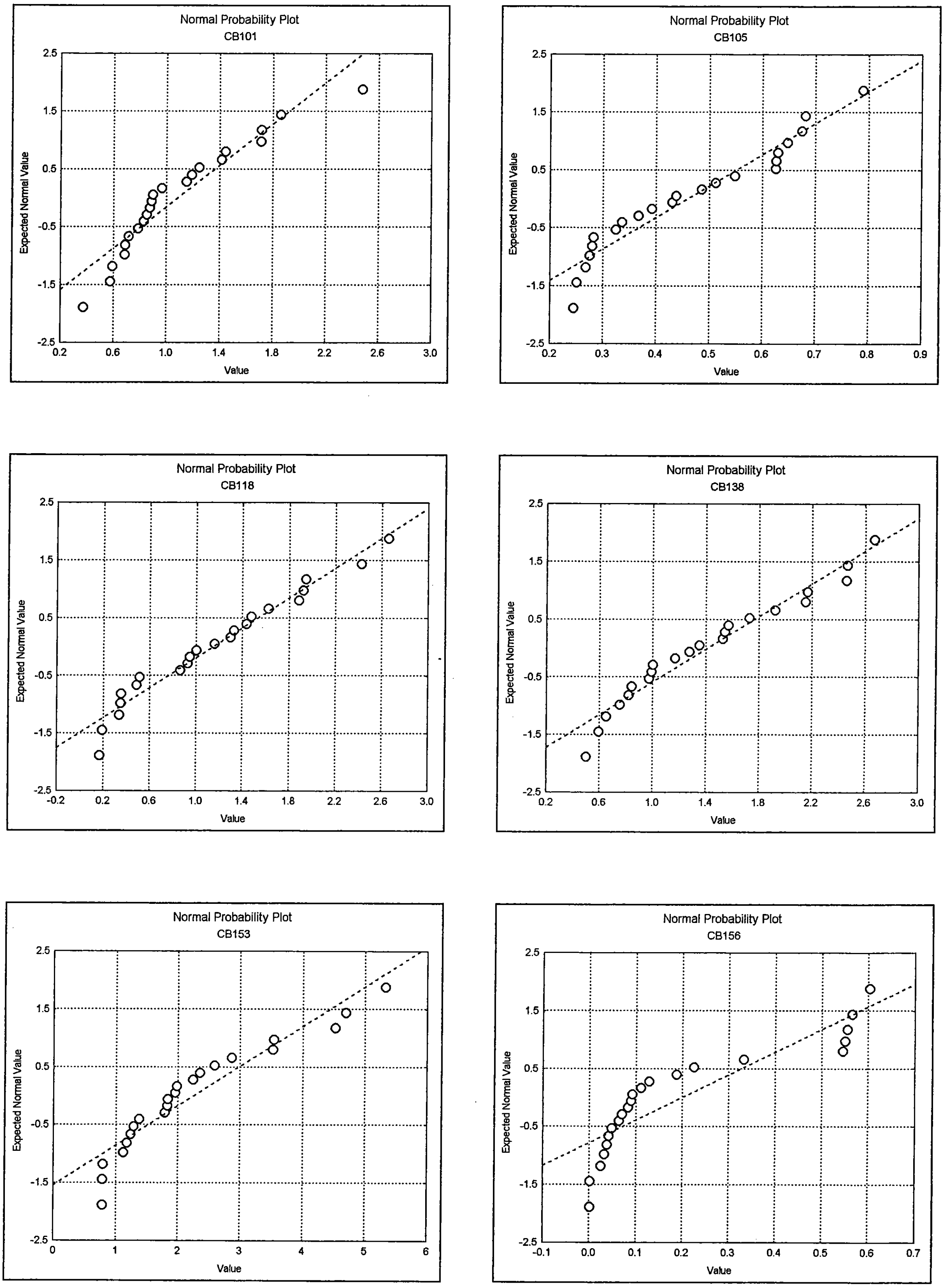


Figure III.4.5: Normal probability plot of CB 101 (upper left), CB 105 (upper right), CB 118 (middle left), CB 138 (middle right), CB 153 (bottom left) and CB 156 (bottom right) in muscle tissue of whiting.

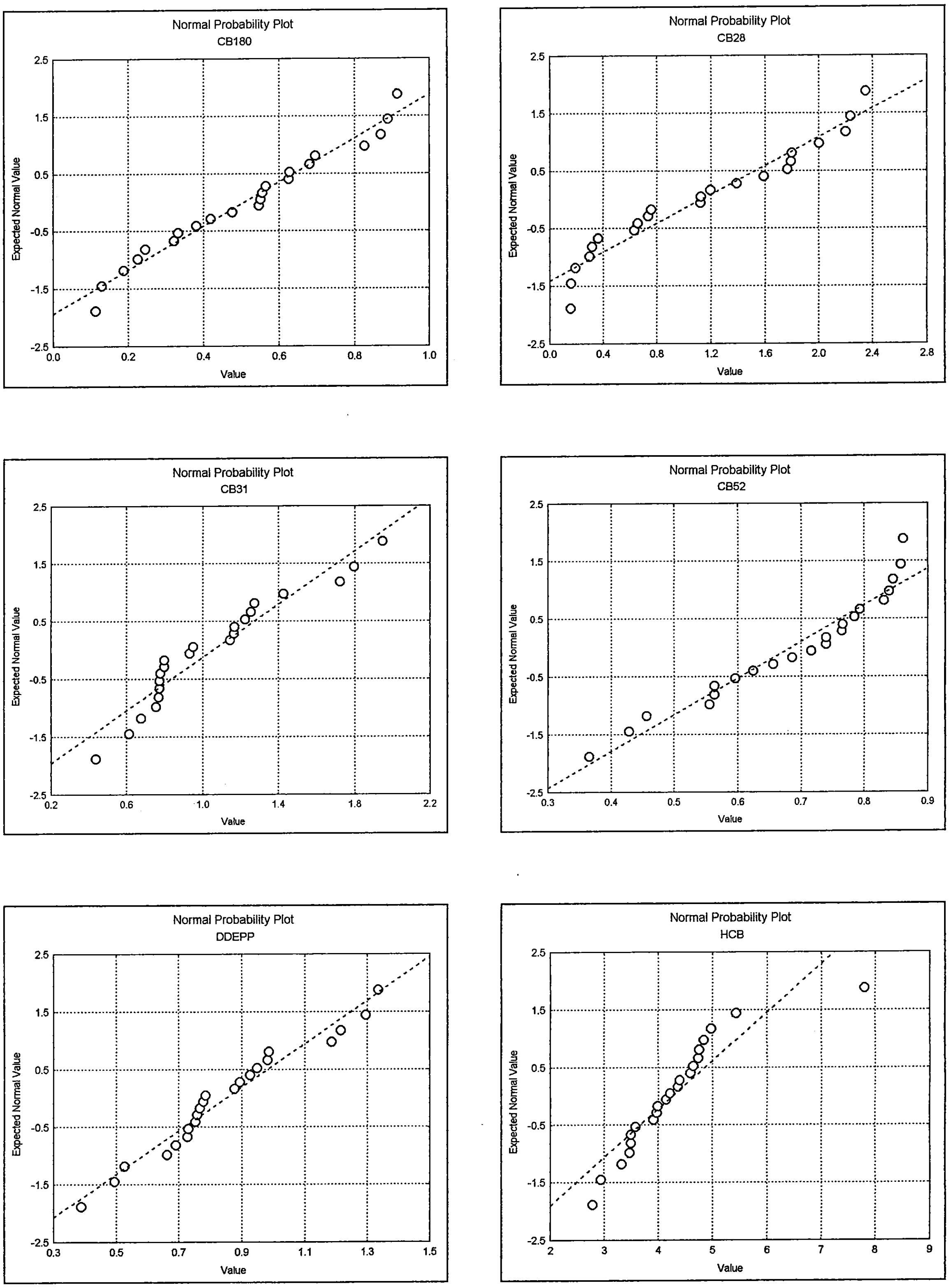


Figure III.4.6: Normal probability plot of CB 180 (upper left), CB 152 (upper right), CB 28 (middle left), CB 31 (middle right), p,p'-DDE (bottom left) and HCB (bottom right) in muscle tissue of whiting.

The data for the CBs and OCPs were further analysed, using a non parametric Kruskall Wallis ANOVA test. This to determine whether CBs and OCPs concentrations are originating form the same populations and could be treated as one group for statistical comparisons. The test revealed that the differences between the medians was larger than expected by chance ($P<0.001$). It could therefore be assumed that the data sets originate from different populations, and should thus be treated as individual populations.

III.4.1.2.3 Correlation between VOCs, CBs, OCPs in muscle tissue of whiting and the fat content

The concentrations of VOCs, CBs and OCPs were correlated with the total fat content as determined with the method of Bligh and Dyer (1959). As all the compounds under consideration are lypophylic organic compounds a relation with the fat content of the tissue may be expected. Such relations have already been established for CBs (Shaefer *et al.*, 1976; Goerke *et al.*, 1979; Schneider, 1981; Delbeke *et al.*, 1995; Roose *et al.*, 1996). A positive correlation with the fat content would require normalising the data for the fat content when spatial and temporal comparisons are made or when tissues and species are compared (Delbeke *et al.*, 1995; Roose *et al.*, 1996).

The data obtained from the lipid determinations were first statistically analysed for their distribution and variability. The results of the different tests is given in table III.4.8.

The coefficient of variation is a lot lower than for the contaminants. This is, however, to be expected as the lipid content of a fishes of the same catch will not vary significantly as it is a measure for the general condition of the population at that time and for that place. As is already indicated in table III.4.8, a Kolomogorov-Smirnov test was performed to determine whether the fat content is normally distributed in fish from the same population. The latter is to be expected and the results (table III.4.8) indicate it. However, when the distribution is further analysed using a normal probability plot, a certain deviation from the expected straight line is observed (figure III.4.7). The data points on the plot show again an s shaped pattern not unlike the one for the contaminants. It should again be stressed that the population was rather small and that the results should therefore be interpreted with the necessary caution.

Table III.4.8: Statisitical analysis of the fat content.

Parameter	Value
Number of values	22
Minimum	0.63
25% Percentile	0.68
Median	0.77
75% Percentile	0.88
Maximum	1.63
Mean	0.81
SD	0.21
SEM	0.05
Lower 95% CI	0.71
Upper 95% CI	0.90
Coefficient of variation	26.30%
Geometric mean	0.79
Normality Test	
Kolmogorov-Smirnov distance	0.20
P value	P > 0.10
Passed normality test (P>0.05)?	Yes

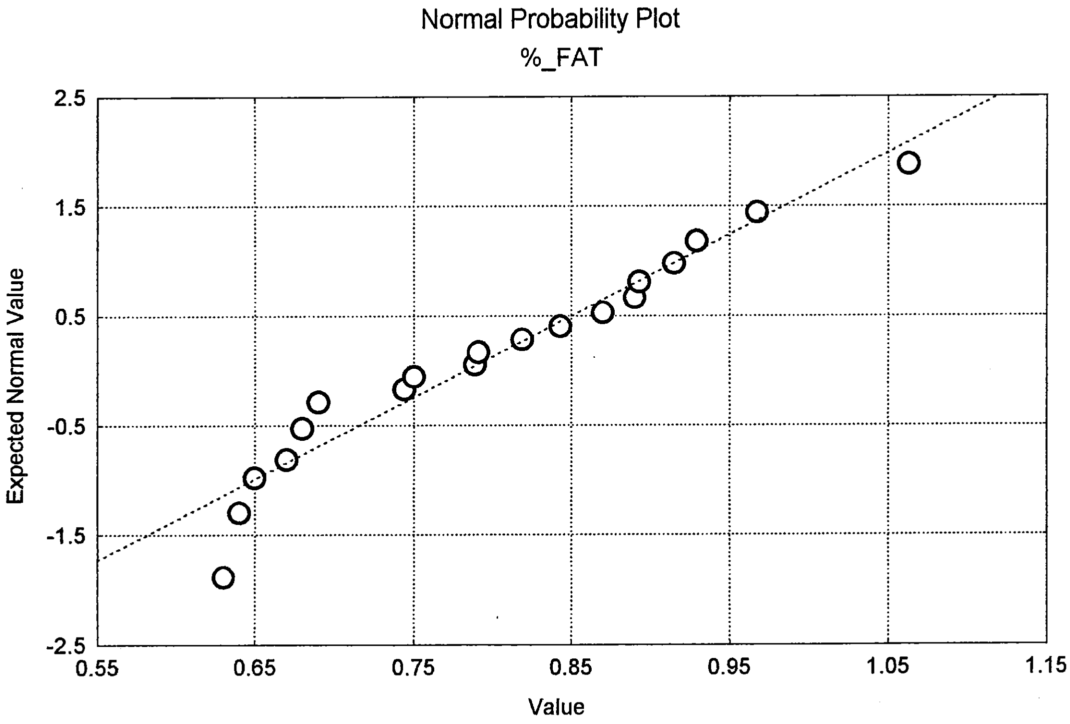


Figure III.4.7: Normal probability plot of the fat content in muscle tissue of whiting.

As a result, the correlation analysis was performed with the non parametric Spearman correlation, rather than transforming the data to approach a Gaussian distribution or to assume one. The results of this correlation analyses are given in table III.4.9. The correlation between the fat content and the various contaminants is further illustrated in figures III.4.8 to III.4.11.

Table III.4.9: Results of the correlation analysis between the fat content and VOCs, CBs and OCPs.

Parameter	n	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
Benzene	13	0.06	-0.52 to 0.60	0.844	ns
Ethylbenzen	20	-0.09	-0.52 to 0.38	0.698	ns
m&p-Xylene	22	-0.15	-0.55 to 0.30	0.507	ns
o-Xylene	22	-0.15	-0.55 to 0.30	0.504	ns
Toluene	15	0.17	-0.39 to 0.64	0.537	ns
Chloroform	11	0.65	0.054to 0.92	0.032	*
Tetrachloroethylene	10	-0.55	0.10	ns	na
Tetrachloromethane	4	0.00	1	na	na
Trichloroethane	12	0.11	-0.51 to 0.66	0.729	ns
Trichloroethylene	20	0.40	-0.07 to 0.72	0.084	ns
CB101	22	0.39	-0.05 to 0.71	0.071	ns
CB105	22	0.64	0.29 to 0.84	0.001	*
CB118	22	0.46	0.035 to 0.75	0.031	*
CB138	22	0.40	-0.042 to 0.71	0.067	ns
CB153	22	0.40	-0.037 to 0.71	0.064	ns
CB156	22	0.40	-0.04 to 0.71	0.068	ns
CB180	22	0.21	-0.25 to 0.59	0.351	ns
CB28	22	-0.05	-0.48 to 0.39	0.814	ns
CB31	22	0.36	-0.08 to 0.69	0.097	ns
CB52	22	0.39	-0.051to 0.70	0.073	ns
p,p'-DDE	22	0.18	-0.27to 0.57	0.420	ns
HCB	22	-0.07	-0.49 to 0.37	0.747	ns

n = number of samples, r = Pearson correlation coefficient, CI = confidence interval, ns = not significant, * = significant, na = not available

Using the Spearman correlation analysis a significant increase of contaminant concentration with fat content could be demonstrated for chloroform, CB 101 and CB 118. Looking at figure III.4.8 indeed suggests that the lipid content is not related to the concentration of the MAHs. A remarkable independence of the lipid content can even be observed for ethylbenzene and the xylenes. The data for the CHCs give a somewhat different picture. For chloroform a significant correlation was established and for the other CHCs the variability is such that it doesn't allow any predictions. It would be interesting to perform the same tests with a bigger data set. Strikingly, only CB 101 and CB 118 correlate significantly with the fat content. This is rather unexpected in view of earlier findings. This could be the result of the size of the data set or the correlation test that was used. The correlations were therefore recalculated assuming a Gaussian distribution for both the fat content and the CB and OCP concentrations. The results of this analysis are given in table III.4.10.

Table III.4.10: Results of the Pearson correlation analysis between fat content and the concentration of CBs and OCPs.

Parameter	n	Pearson r	95% CI	P value (two-tailed)	P value summary	r^2
CB101	22	0.57	0.20 to 0.80	0.0056	*	0.33
CB105	22	0.63	0.29 to 0.83	0.0016	*	0.40
CB118	22	0.48	0.072 to 0.75	0.024	*	0.23
CB138	22	0.48	0.076 to 0.75	0.0231	*	0.23
CB153	22	0.55	0.17 to 0.79	0.0074	*	0.31
CB156	22	0.57	0.20 to 0.80	0.0053	*	0.33
CB180	22	0.12	-0.32 to 0.51	0.6065	ns	0.01
CB28	22	-0.15	-0.54 to 0.29	0.5167	ns	0.02
CB31	22	0.36	-0.077 to 0.68	0.1037	ns	0.13
CB52	22	0.48	0.077to 0.75	0.0229	*	0.23
DDEPP	22	0.82	0.61 to 0.92	P<0.0001	*	0.67
HCB	22	-0.17	-0.55 to 0.28	0.4638	ns	0.027

n = number of samples, r = Pearson correlation coefficient, CI = confidence interval, ns = not significant, * = significant

When a Gaussian distribution is assumed, a significant positive correlation is established for CB 101, CB 105, CB 118, CB 138, CB 153, CB 156, CB 52 and p,p'-DDE. Only the results of CB 105 and CB 118 are therefore comparable with the previous test. Looking at figures III.4.20 to III.4.25 does not clarify this dilemma. The variability of the data is simply too large and the sample size is too small to make any firm conclusions. A positive correlation is, however, expected and CBs are therefore frequently normalised on the fat content for comparisons.

Therefore, for all practical purposes and based on the results mentioned above VOC, CB and OCP concentrations were not normalised on the fat content in the remainder of this report. All statistical tests and comparison can be made on a wet weight basis especially when the VOCs are considered.

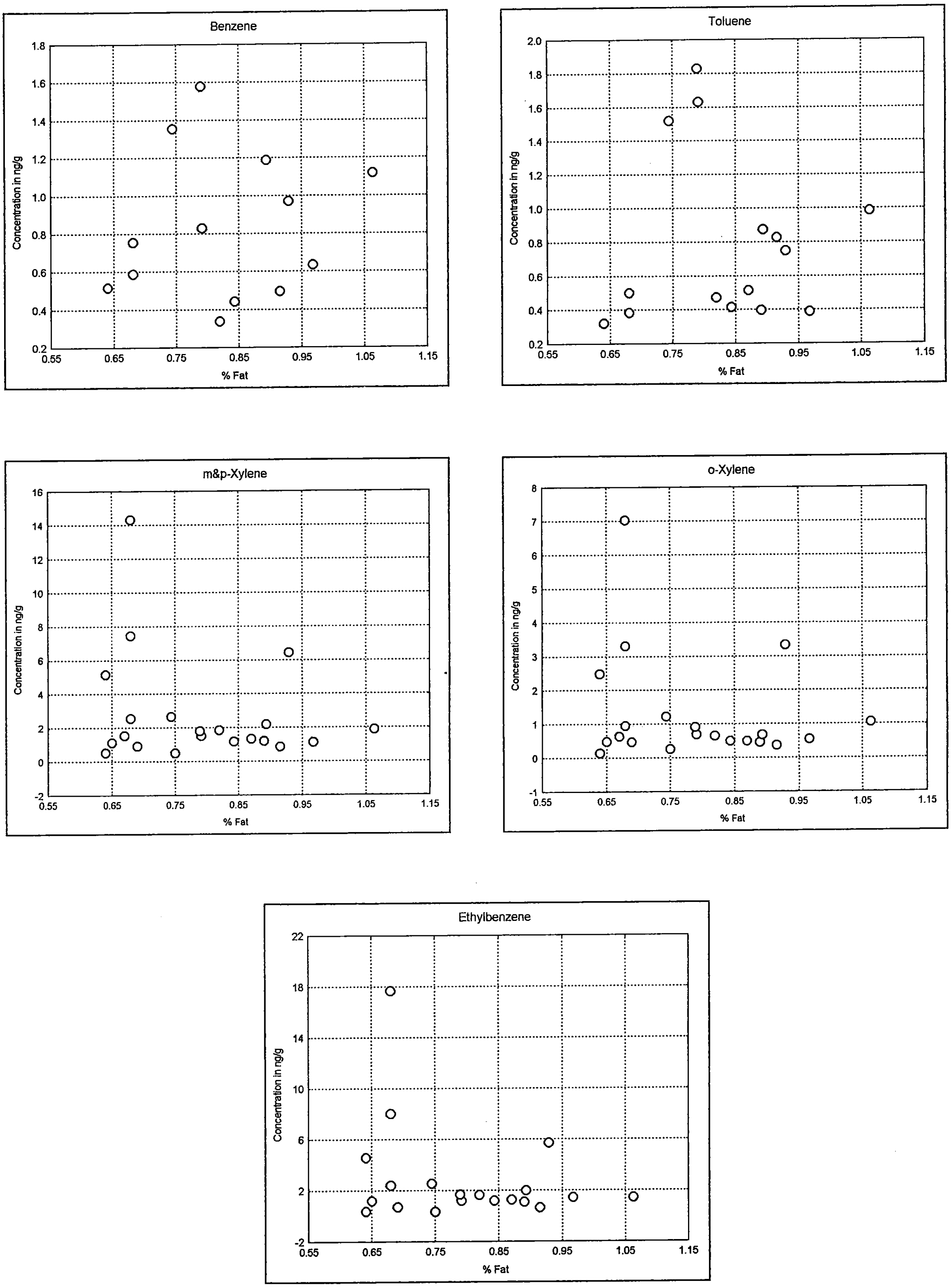


Figure III.4.8: Correlation between the fat content and benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in muscle tissue of whiting.

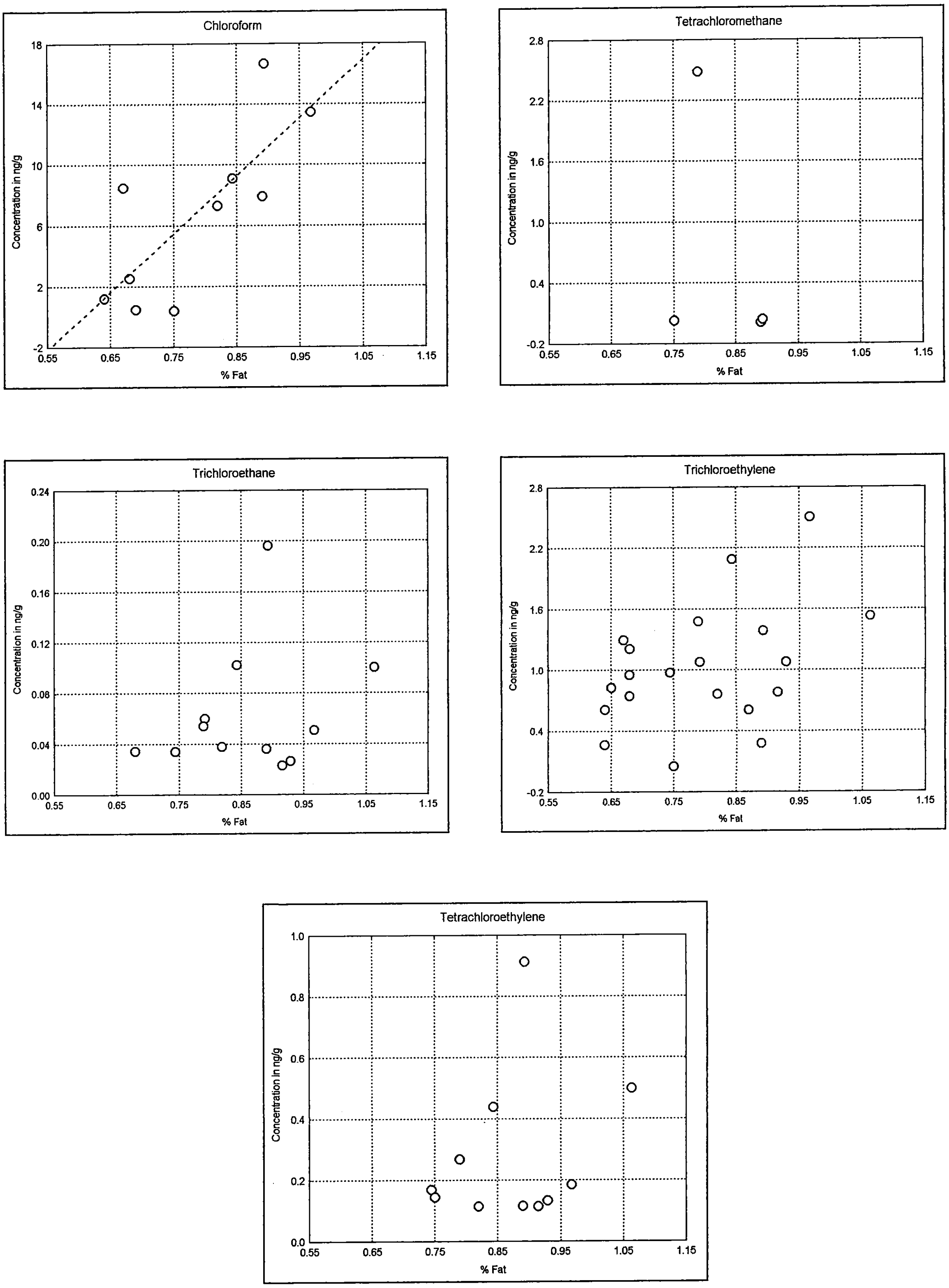


Figure III.4.9: Correlation between the fat content and chloroform (upper left), tetrachloromethane (upper right), trichloroethane (middle left), trichloroethylene (middle right) and tetrachloroethylene (bottom) in muscle tissue of whiting.

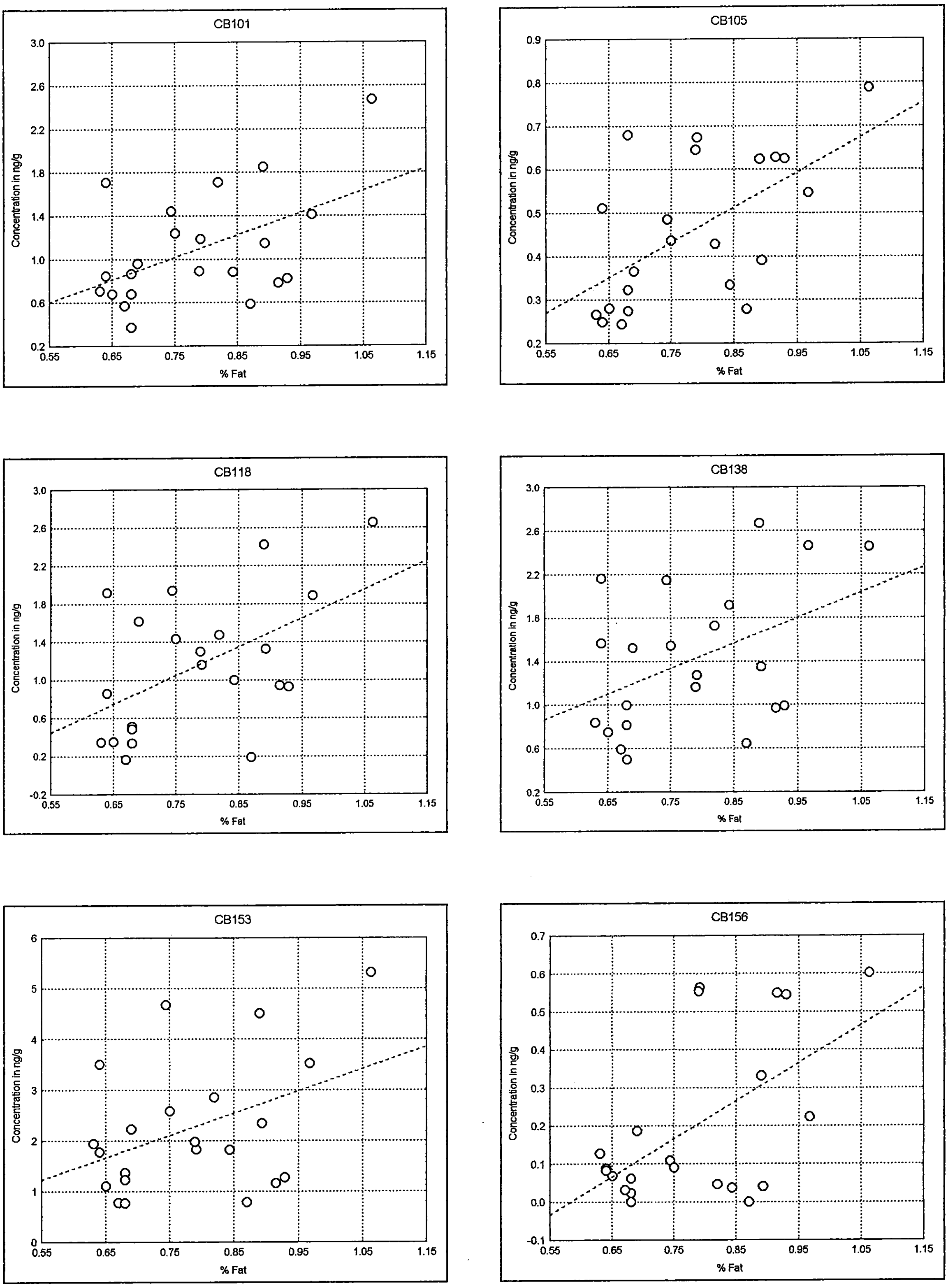


Figure III.4.10: Correlation between the fat content and CB 101 (upper left), CB 105 (upper right), CB 118 (middle left), CB 138 (middle right), CB 153 (bottom left) and CB 156 (bottom right) in muscle tissue of whiting.

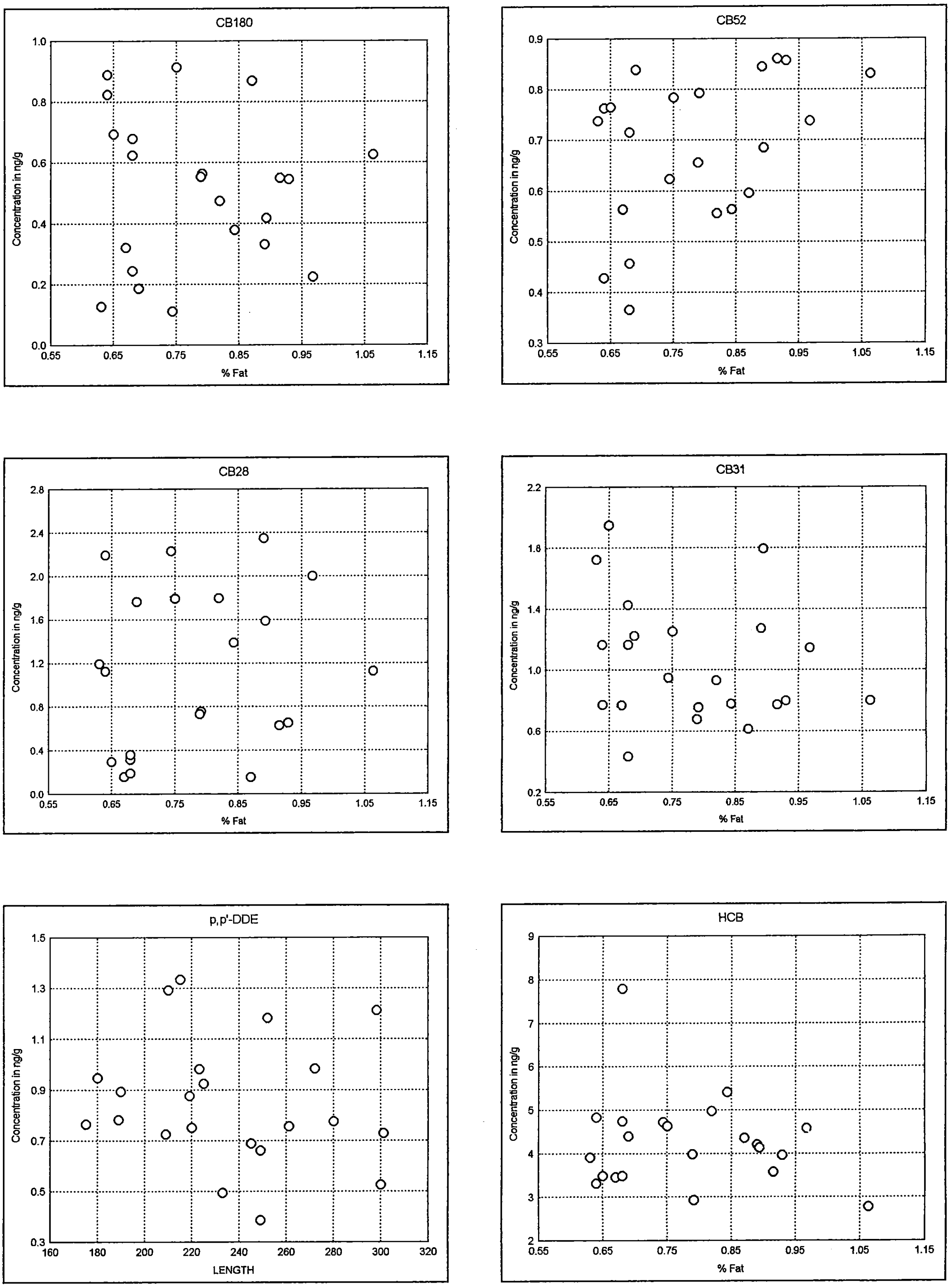


Figure III.4.11: Correlation between the fat content and CB 180 (upper left), CB 152 (upper right), CB 28 (middle left), CB 31 (middle right), p,p'-DDE (bottom left) and HCB (bottom right) in muscle tissue of whiting.

III.4.1.2.4 Correlation between VOCs, CBs, OCPs in muscle tissue of whiting and size of the fish

As for the fat content, the length of the fish was correlated with the concentrations of VOCs, CBs and OCPs. As length is a parameter for the age of the fish, an increase with length of the fish is indicative for biomagnification. Such increases with length were already noted for the concentrations of CBs in the liver of cod (de Boer, 1994) and OCPs (Kruse and Krüger, 1981).

Prior to investigating the correlation with the contaminants the length distribution was analysed statically. The result of this analysis is given in table III.4.11.

Table III.4.11: Statistical analysis of the length of the fish

Parameter	Value
Number of values	22
Minimum	175
25% Percentile	212.5
Median	229
75% Percentile	256.5
Maximum	301
Mean	236.1
Std. Deviation	38.15
Std. Error	8.134
Lower 95% CI	219.2
Upper 95% CI	253.1
Coefficient of variation	16.16%
Geometric mean	233.2
Normality Test	
KS distance	0.1148
P value	P > 0.10
Passed normality test (P>0.05)?	Yes

The fish in the sample were selected to obtain a representative sample for the length class 200 to 300 mm. The results in table III.4.11 show a variability of only 16 % and that the mean and the median are very close. The normality of the distribution was tested with the Kolmogorov-Smirnov test. An ideal sample should be normally distributed. The results of the KS test indeed indicate that the sample has a Gaussian distribution. This was further investigated, as before, with a normal probability plot. The result is illustrated in figure III.4.12.

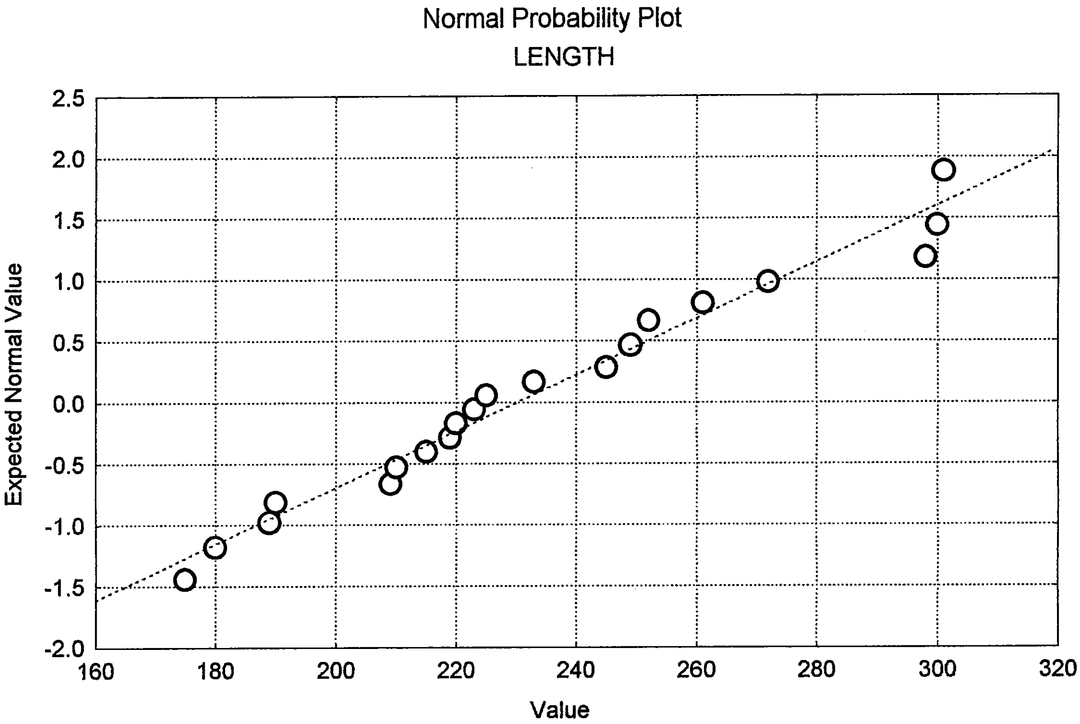


Figure III.4.12: Normal probility plot of the length of whiting in the sample.

The plot clearly suggests a normal distribution of the length in the sample.

The concentrations of VOCs, CBs and OCPs were then correlated with the length of the fish using, at the first instance, a non parametric Spearman correlation analysis. The results of the correlation analysis are given in table III.4.12 and illustrated in figures III.4.13 and III.4.14 Only in four cases a significant correlation at the 95 % level could be observed, namely for Toluene, Tetrachloroethylene, CB 105 and CB 156. For those cases concentrations are significantly higher in younger (shorter) fish. Although the correlation is only significant for toluene, the concentrations of benzene appear higher in younger fish as well (figure III.4.27) and the correlation is significant at the 90 % level. This is not the case for the other MAHs (figures III.4.13). For those contaminants the concentrations are independent of the length. For the CHCs other than tetrachloroethylene, where a negative correlation is observed, the variability is either too high or there is too little data to discern any patterns. The negative correlation of the tetrachloroethylene seems largely the result of the high value of one of the bigger fish and should therefore be interpreted with the necessary caution. For the two cases of CBs for which significant negative correlations are observed, the effect seems also at least for CB 156 caused by a set of outlying values. For all other CBs and OCPs no trends could be observed. A similar lack of correlation between the length and the CB concentration was already observed at the institute for CB concentrations in muscle tissue of cod (*Gadus morhua*) and flounder (*Platichtys flesus*) (Roose *et al.*, 1996). To exclude possible errors and in view of the possible normal distribution of both CB and the length the analysis was repeated using a parametric test. The results of this analysis are illustrated in table III.4.13.

Table III.4.12: Results of the Spearman correlation analysis between length and the concentrations of VOCs, CBs and OCPs.

Parameter	n	Spearman r	95% CI	P value (two-tailed)	P value summary
Benzene	13	-0.54	-0.85 to 0.03	0.0557	+
m&p-Xylene	20	-0.10	-0.53 to 0.37	0.6632	ns
Ethylbenzene	21	-0.09	-0.51 to 0.37	0.6930	ns
o-Xylene	21	-0.27	-0.64 to 0.20	0.2420	ns
Toluene	15	-0.68	-0.89 to -0.24	0.0055	*
Chloroform	10	0.50	0.14	na	ns
Tetrachloroethylene	9	0.70	0.04	na	*
Tetrachloromethane	4	-0.80	0.33	na	ns
Trichloroethane	12	0.29	-0.36 to 0.75	0.3663	ns
Trichloroethylene	20	-0.16	-0.58 to 0.31	0.4877	ns
CB101	22	-0.12	-0.52 to 0.33	0.6043	ns
CB105	22	-0.47	-0.750 to -0.049	0.0267	*
CB118	22	-0.17	-0.56 to 0.29	0.4525	ns
CB138	22	-0.14	-0.54 to 0.31	0.5391	ns
CB153	22	-0.15	-0.55 to 0.30	0.4997	ns
CB156	22	-0.61	-0.83 to -0.24	0.0026	*
CB180	22	-0.03	-0.46 to 0.41	0.9007	ns
CB28	22	0.25	-0.20 to 0.62	0.2559	ns
CB31	22	-0.22	-0.59 to 0.24	0.3336	ns
CB52	22	-0.20	-0.58 to 0.26	0.3834	ns
DDEPP	22	0.16	-0.29 to 0.56	0.4695	ns
HCB	22	0.17	-0.28 to 0.56	0.4509	ns

ns = not significant, * = significant at 95 % level, + = significant at 90 % level, na not available, CI = confidence interval, n = number of samples.

The outcome of the parametric correlation analysis is not different. Significant correlations are observed for the same compounds. The conclusions are in any case that in general there is no relation between the concentration of VOCs, CBs and OCPs and the length of the fish. At least for the length class under investigation no biomagnification could be observed. It would, however, be interesting to expand the length class and to reinvestigate the correlations.

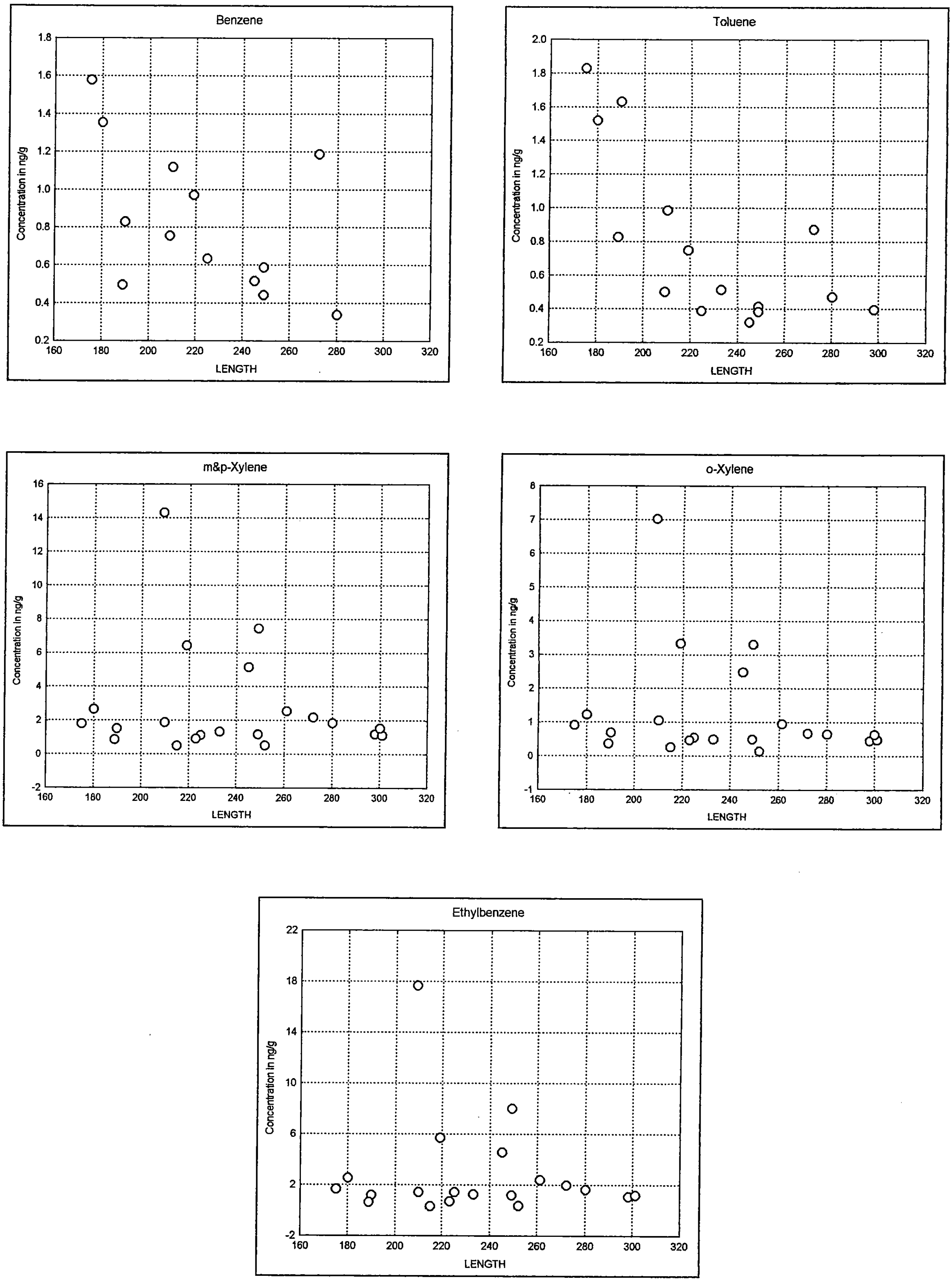


Figure III.4.13: Correlation between the length and benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in muscle tissue of whiting.

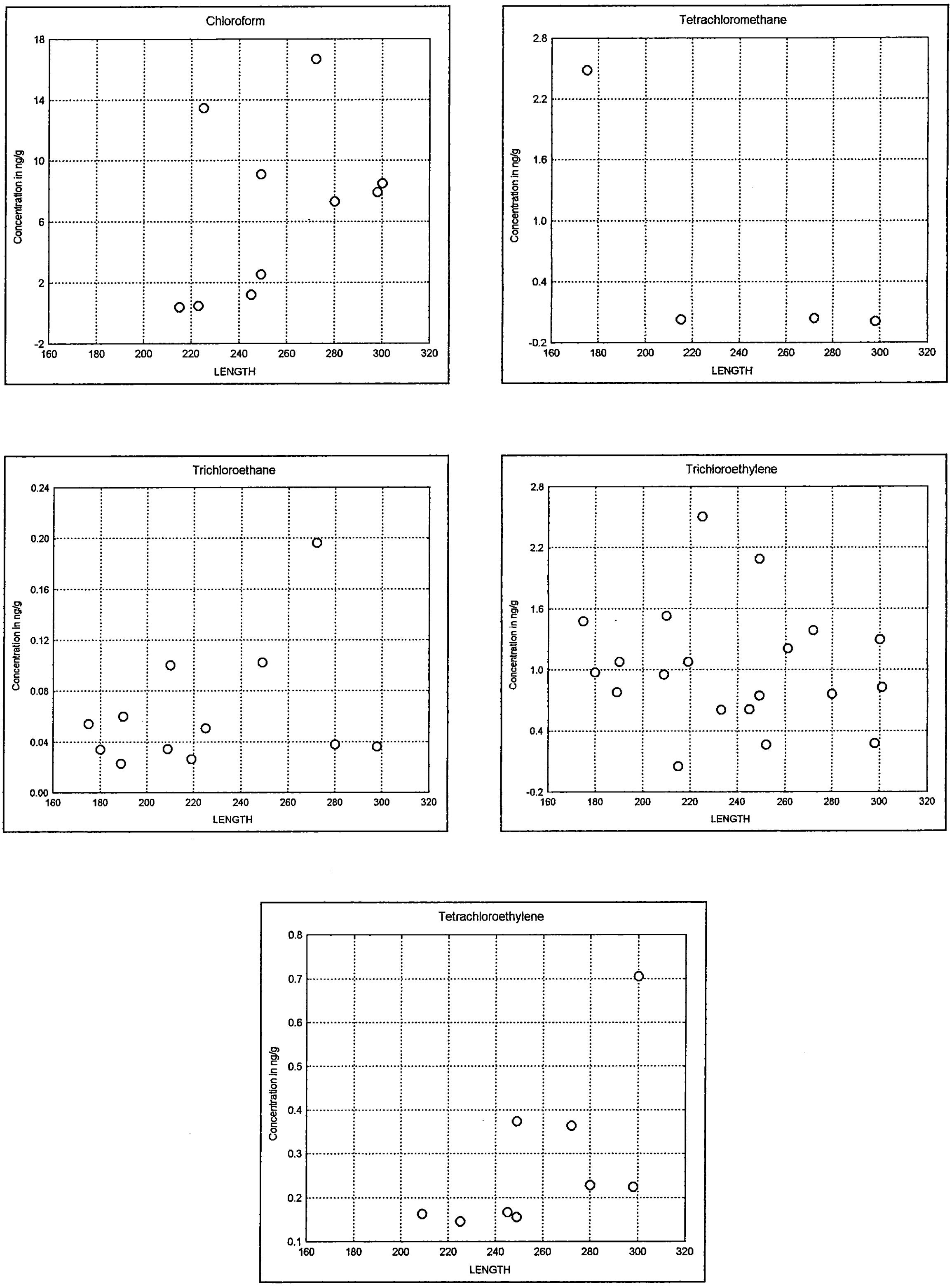


Figure III.4.14: Correlation between the length and chloroform (upper left), tetrachloromethane (upper right), trichloroethane (middle left), trichloroethylene (middle right) and tetrachloroethylene (bottom) in muscle tissue of whiting.

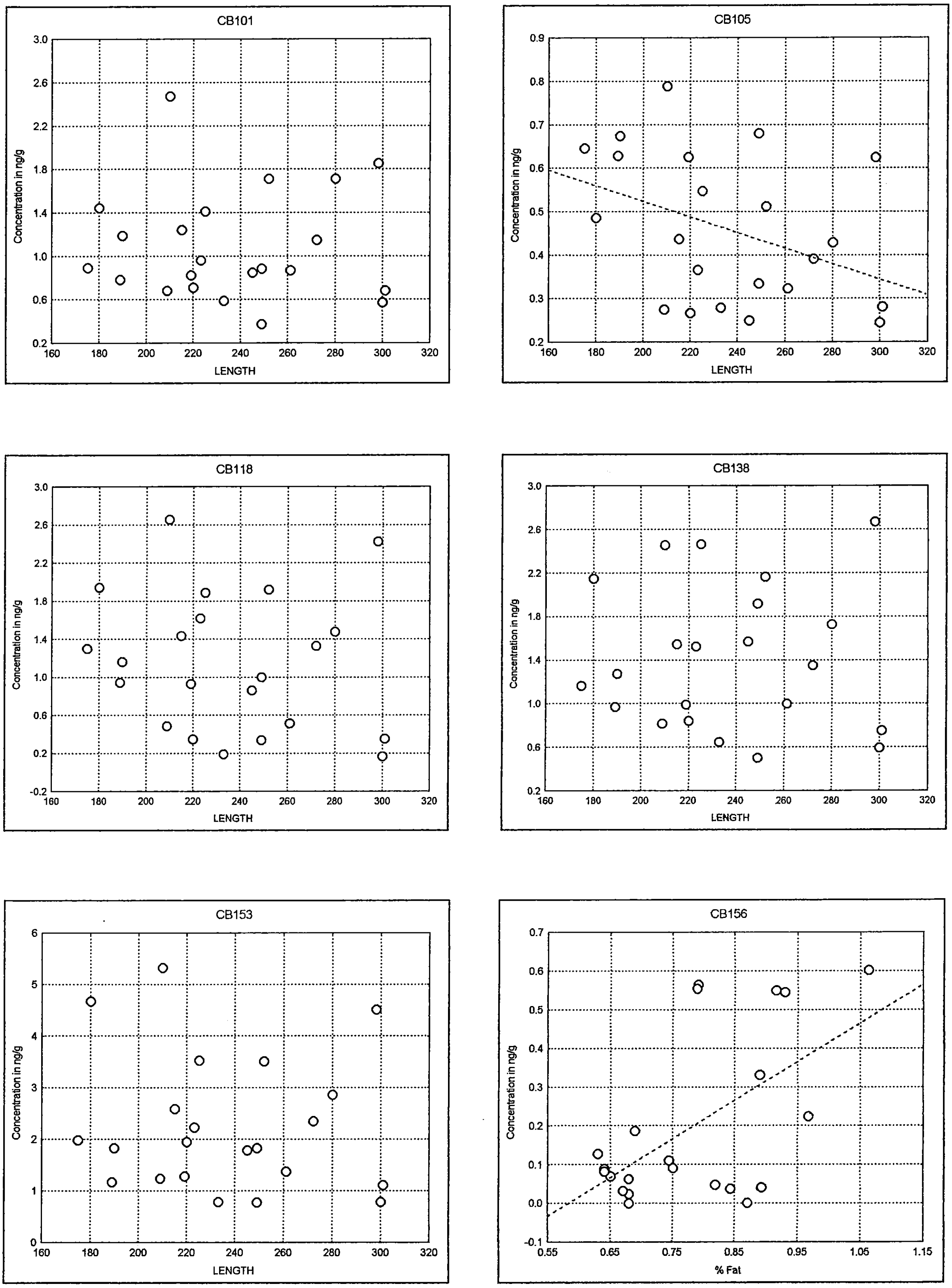


Figure III.4.15: Correlation between the length and CB 101 (upper left), CB 105 (upper right), CB 118 (middle left), CB 138 (middle right), CB 153 (bottom left) and CB 156 (bottom right) in muscle tissue of whiting.

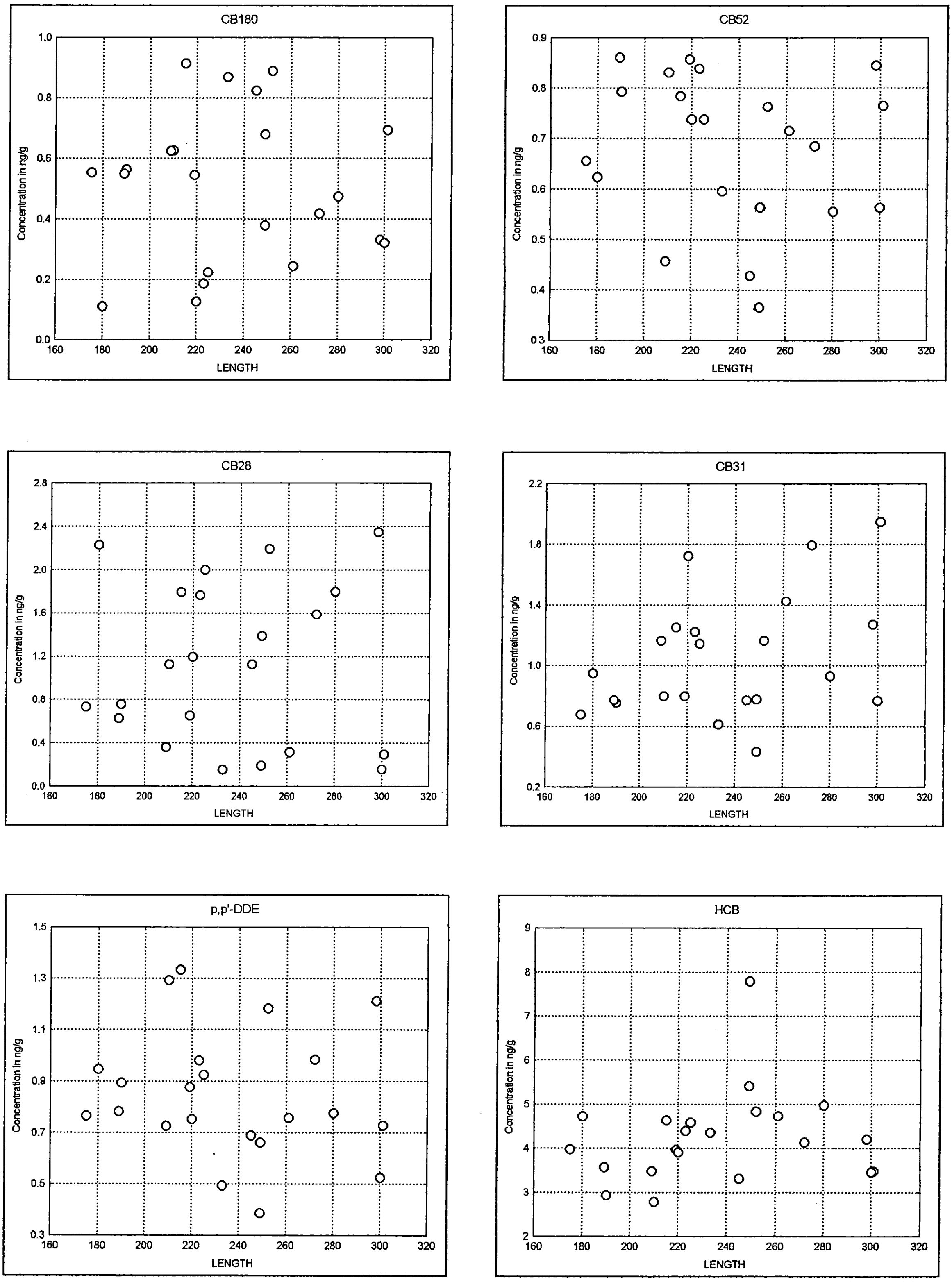


Figure III.4.16: Correlation between the length and CB 180 (upper left), CB 152 (upper right), CB 28 (middle left), CB 31 (middle right), p,p'-DDE (bottom left) and HCB (bottom right) in muscle tissue of whiting.

Table III.4.13: Results of the Pearson correlation analysis between length and the concentrations of CBs.

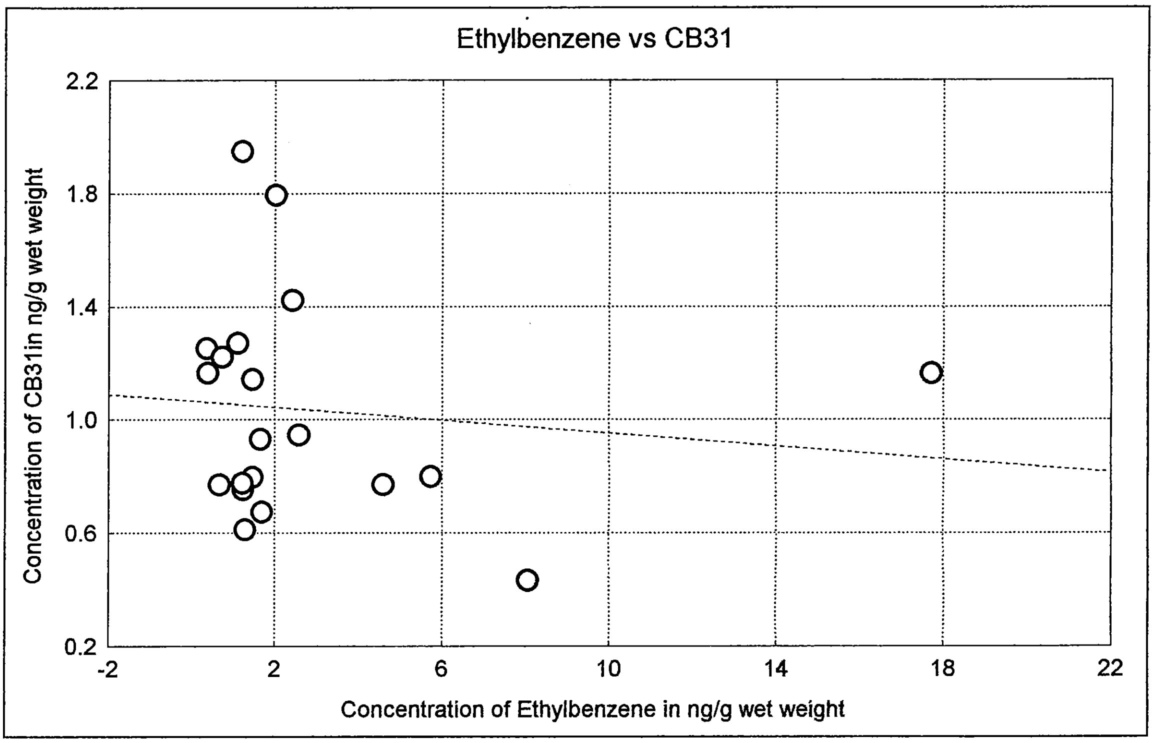
Parameter	n	Pearson r	95% CI	P value (two-tailed)	P value summary
CB101	22	-0.05	-0.46 to 0.38	0.8291	ns
CB105	22	-0.43	-0.72 to -0.01	0.0472	*
CB118	22	-0.11	-0.51 to 0.32	0.6117	ns
CB138	22	-0.06	-0.47 to 0.38	0.8061	ns
CB153	22	-0.10	-0.50 to 0.34	0.6593	ns
CB156	22	-0.54	-0.79 to -0.16	0.0091	*
CB180	22	-0.01	-0.43 to 0.42	0.9769	ns
CB28	22	0.24	-0.21to 0.60	0.2915	ns
CB31	22	-0.16	-0.54 to 0.29	0.491	ns
CB52	22	-0.13	-0.52 to 0.31	0.5721	ns
DDEPP	22	-0.11	-0.51 to 0.33	0.6208	ns
HCB	22	0.20	-0.24 to 0.57	0.3763	ns

ns = not significant, * = significant, CI = confidence interval, n = number of samples.

III.4.1.2.5 Correlation between the concentration of VOCs and CBs and OCPs

Concentrations of individual VOCs were correlated with those of CBs and OCPs. It was already mentioned that the concentrations of the different contaminants are of the same order of magnitude. The goal of this test was to determine whether any relation exists between the concentrations of VOCs and the CBs and OCPs. In view of the fact that a normal distribution could not be assumed for the concentration of most of the contaminants, a non parametric Spearman correlation analysis was performed. The results of the different analyses are given in tables III.4.14 to III.4.23.

On seven occasions a correlation was observed between VOCs and CBs. There is a positive correlation between benzene and CB 52, and toluene and CB 105 and CB 156. A negative correlation is observed between ethylbenzene and the CBs 31 and 28, between m&p-xylene and CB 31 and between o-xylene and CB 28. These correlations are illustrated in figures III.4.17 to III.4.19. The negative correlations, although significant, seem to be far more the result of a few outlying values than a real effect. The positive correlations, on the contrary, seem caused by a real effect. Higher values of the VOC result in higher values of CBs and vice versa. This could indicate that zones with a higher CB contamination are likely to have a higher VOC contamination. The latter is certainly possible for zones with industrial activities.



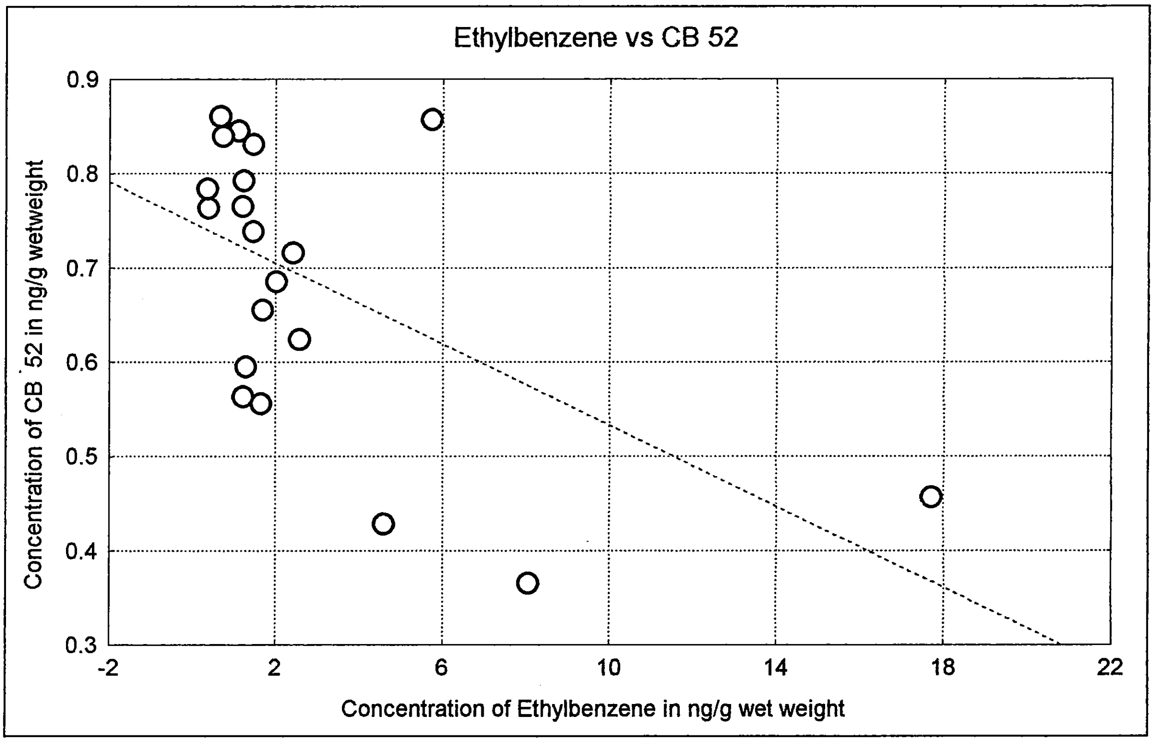
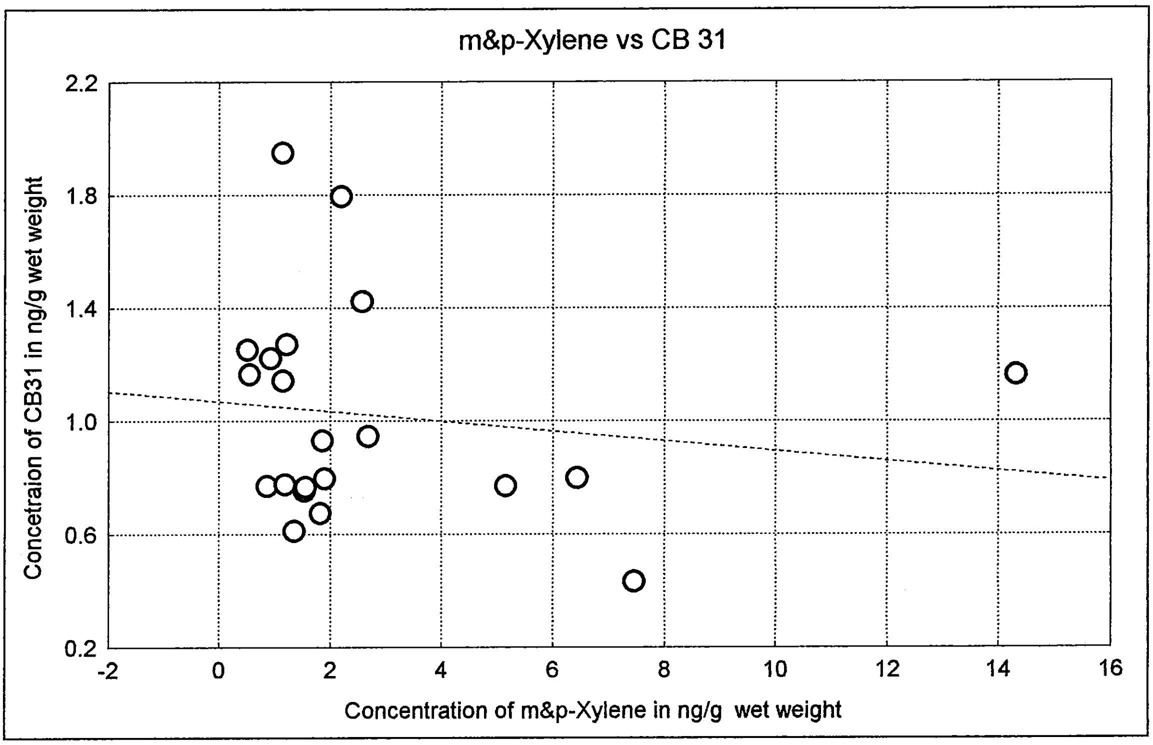


Figure III.4.17: Correlation between ethylbenzene and CB 31 (upper) and correlation between ethylbenzene and CB 52 (lower) in muscle tissue of whiting.



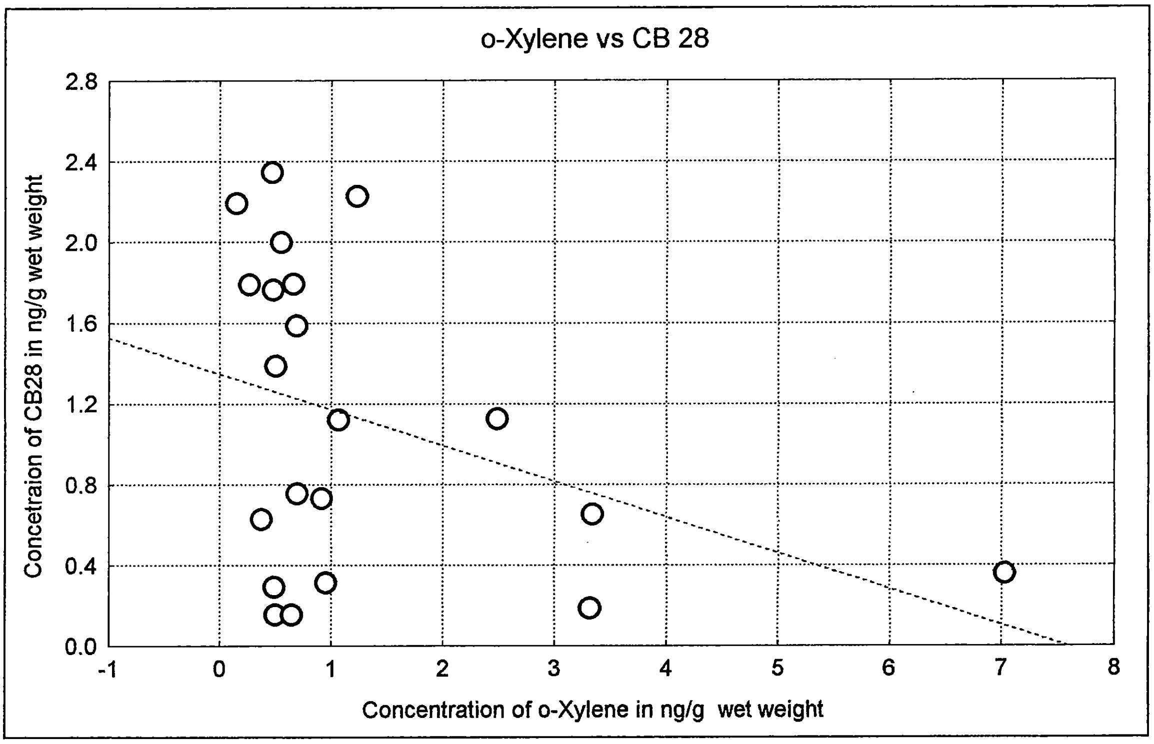
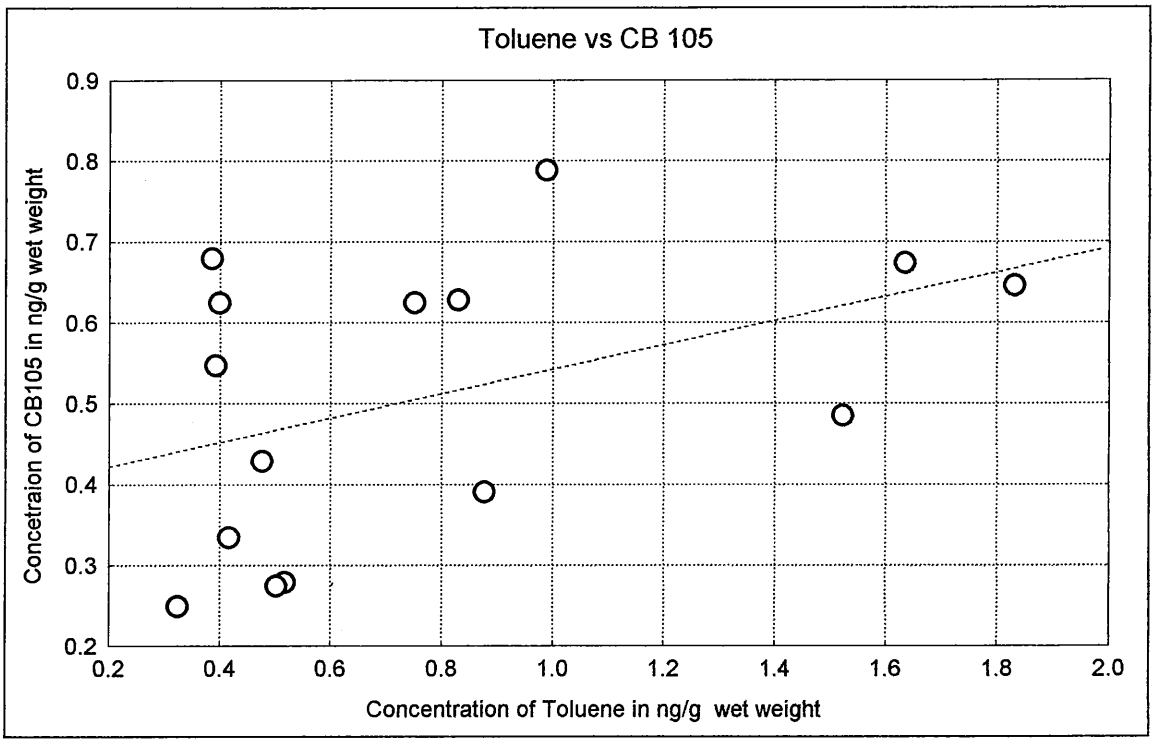


Figure III.4.18: Correlation between the m&p-Xylene and CB 31 (upper) and correlation between o-xylene and CB 28 (lower) in muscle tissue of whiting.



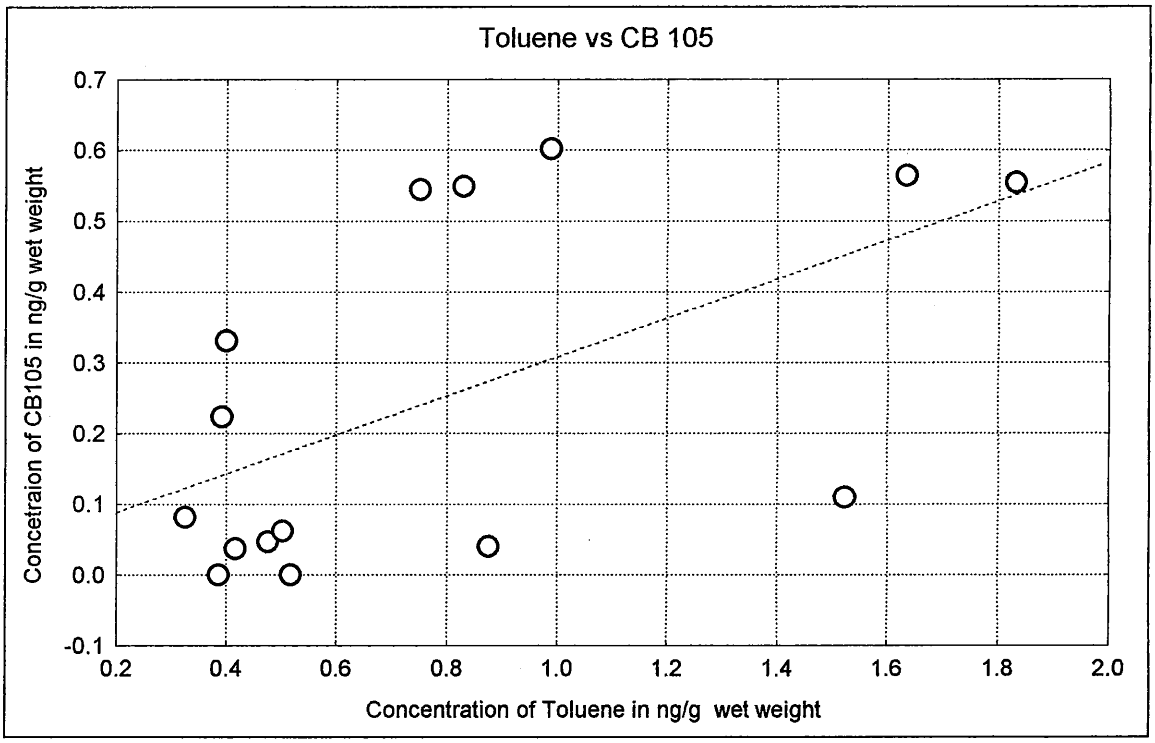


Figure III.4.19: Correlation between toluene and CB 105 (upper) and correlation between toluene and CB 156 (lower) in muscle tissue of whiting.

Table III.4.14: Results of the correlation analysis between the concentration of Benzene and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	13	0.40	-0.21 to 0.79	0.1744	ns
CB105	13	0.43	-0.18 to 0.80	0.1440	ns
CB118	13	0.34	-0.28 to 0.76	0.2629	ns
CB138	13	0.35	-0.27 to 0.76	0.2466	ns
CB153	13	0.40	-0.22 to 0.78	0.1809	ns
CB156	13	0.44	-0.17 to 0.80	0.1329	ns
CB180	13	0.08	-0.51 to 0.62	0.7890	ns
CB28	13	0.10	-0.49 to 0.63	0.7343	ns
CB31	13	0.36	-0.25 to 0.77	0.2233	ns
CB52	13	0.56	-0.01 to 0.85	0.0463	*
DDEPP	13	-0.03	-0.58 to 0.55	0.9290	ns
HCB	13	-0.07	-0.61 to 0.51	0.8166	ns

ns = not significant, * significant

Table III.4.15: Results of the correlation analysis between the concentration of Chloroform and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	11	0.20	-0.47 to 0.72	0.5554	ns
CB105	11	0.16	-0.50 to 0.71	0.6307	ns
CB118	11	0.17	-0.49 to 0.71	0.6115	ns
CB138	11	0.12	-0.53 to 0.68	0.7293	ns
CB153	11	0.20	-0.47 to 0.72	0.5554	ns
CB156	11	-0.20	-0.72 to 0.47	0.5554	ns
CB180	11	0.09	-0.55 to 0.67	0.7904	ns
CB28	11	-0.13	-0.69 to 0.53	0.7092	ns
CB31	11	-0.20	-0.72 to 0.47	0.5554	ns
CB52	11	-0.15	-0.70 to 0.51	0.6500	ns
DDEPP	11	0.06	-0.57 to 0.65	0.8525	ns
HCB	11	-0.20	-0.72 to 0.47	0.5554	ns

ns = not significant, * significant

Table III.4.16: Results of the correlation analysis between the concentration of Ethylbenzene and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	21	-0.41	-0.72 to 0.04	0.0619	+
CB105	21	-0.42	-0.73 to 0.03	0.0592	+
CB118	21	-0.41	-0.72 to 0.04	0.0637	+
CB138	21	-0.41	-0.7242 to 0.03495	0.0619	+
CB153	21	-0.32	-0.67 to 0.14	0.1580	ns
CB156	21	-0.25	-0.62 to 0.22	0.2757	ns
CB180	21	-0.35	-0.69 to 0.11	0.1162	ns
CB28	21	-0.41	-0.72 to 0.044	0.0675	ns
CB31	21	-0.52	-0.78 to -0.11	0.0149	*
CB52	21	-0.49	-0.77 to -0.058	0.0247	*
DDEPP	21	-0.08	-0.50 to 0.38	0.7456	ns
HCB	21	-0.29	-0.65 to 0.18	0.2029	ns

ns = not significant, * significant at 95 % level, + significant at 90 % level

Table III.4.17: Results of the correlation analysis between the concentration of m&p-Xylene and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	22	-0.33	-0.67 to 0.12	0.1305	ns
CB105	22	-0.34	-0.68 to 0.11	0.1197	ns
CB118	22	-0.32	-0.66 to 0.13	0.1463	ns
CB138	22	-0.33	-0.67 to 0.11	0.1277	ns
CB153	22	-0.26	-0.62 to 0.19	0.2420	ns
CB156	22	-0.20	-0.58 to 0.25	0.3711	ns
CB180	22	-0.30	-0.65 to 0.15	0.1718	ns
CB28	22	-0.39	-0.71 to 0.048	0.0708	+
CB31	22	-0.44	-0.73 to -0.01	0.0411	*
CB52	22	-0.38	-0.70 to 0.06	0.0811	+
DDEPP	22	-0.04	-0.47 to 0.40	0.8477	ns
HCB	22	-0.29	-0.64 to 0.17	0.1983	ns

ns = not significant, * significant at 95 % level, + significant at 90 % level

Table III.4.18: Results of the correlation analysis between the concentration of o-Xylene and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	22	-0.31	-0.66 to 0.14	0.1556	ns
CB105	22	-0.25	-0.61 to 0.21	0.2705	ns
CB118	22	-0.30	-0.65 to 0.15	0.1701	ns
CB138	22	-0.32	-0.66 to 0.13	0.1479	ns
CB153	22	-0.24	-0.61 to 0.22	0.2915	ns
CB156	22	-0.05	-0.47 to 0.39	0.8165	ns
CB180	22	-0.32	-0.67 to 0.14	0.1524	ns
CB28	22	-0.43	-0.73 to 0.01	0.0447	*
CB31	22	-0.37	-0.69 to 0.08	0.0935	+
CB52	22	-0.36	-0.69 to 0.09	0.1001	ns
DDEPP	22	-0.07	-0.49 to 0.37	0.7473	ns
HCB	22	-0.36	-0.68 to 0.09	0.1048	ns

ns = not significant, * significant at 95 % level, + significant at 90 % level

Table III.4.19: Results of the correlation analysis between the concentration of tetrachloroethylene and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	9	-0.43	0.2499	na	ns
CB105	9	-0.47	0.2125	na	ns
CB118	9	-0.47	0.2054	na	ns
CB138	9	-0.45	0.2242	na	ns
CB153	9	-0.45	0.2242	na	ns
CB156	9	-0.60	0.0876	na	ns
CB180	9	-0.47	0.2054	na	ns
CB28	9	-0.48	0.1875	na	ns
CB31	9	-0.17	0.6682	na	ns
CB52	9	-0.30	0.4328	na	ns
DDEPP	9	-0.05	0.8984	na	ns
HCB	9	-0.18	0.6368	na	ns

ns = not significant, * significant, na = not applicable

Table III.4.20: Results of the correlation analysis between the concentration of tetrachloromethane and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	5	-0.80	0.1333	na	ns
CB105	5	0.10	0.95	na	ns
CB118	5	-0.80	0.1333	na	ns
CB138	5	-0.60	0.35	na	ns
CB153	5	-0.80	0.1333	na	ns
CB156	5	0.60	0.35	na	ns
CB180	5	-0.70	0.2333	na	ns
CB28	5	-0.70	0.2333	na	ns
CB31	5	-0.30	0.6833	na	ns
CB52	5	-0.60	0.35	na	ns
DDEPP	5	-0.60	0.35	na	ns
HCB	5	-0.40	0.5167	na	ns

ns = not significant, * significant, na = not applicable

Table III.4.21: Results of the correlation analysis between the concentration of tetrachloromethane and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	15	0.26	-0.31to 0.69	0.3480	ns
CB105	15	0.68	0.25 to 0.89	0.0051	*
CB118	15	0.26	-0.31 to 0.69	0.3549	ns
CB138	15	0.21	-0.35 to 0.66	0.4431	ns
CB153	15	0.27	-0.30 to 0.70	0.3344	ns
CB156	15	0.56	0.05 to 0.84	0.0297	*
CB180	15	-0.05	-0.56 to 0.49	0.8595	ns
CB28	15	-0.11	-0.60 to 0.44	0.6851	ns
CB31	15	0.49	-0.05 to 0.81	0.0642	ns
CB52	15	0.40	-0.15 to 0.77	0.1358	ns
DDEPP	15	-0.19	-0.65 to 0.37	0.4910	ns
HCB	15	-0.26	-0.69 to 0.31	0.3480	ns

ns = not significant, * significant

Table III.4.22: Results of the correlation analysis between the concentration of trichloroethane and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	12	0.34	-0.31 to 0.78	0.2756	ns
CB105	12	-0.03	-0.61 to 0.56	0.9141	ns
CB118	12	0.26	-0.39 to 0.73	0.4168	ns
CB138	12	0.27	-0.38 to 0.74	0.4038	ns
CB153	12	0.30	-0.35 to 0.75	0.3423	ns
CB156	12	-0.15	-0.68 to 0.48	0.6331	ns
CB180	12	0.22	-0.42 to 0.72	0.4845	ns
CB28	12	-0.09	-0.64 to 0.52	0.7787	ns
CB31	12	-0.17	-0.69 to 0.47	0.6021	ns
CB52	12	0.13	-0.50 to 0.66	0.6967	ns
DDEPP	12	0.43	-0.21 to 0.81	0.1591	ns
HCB	12	-0.22	-0.71 to 0.42	0.4986	ns

ns = not significant, * significant

Table III.4.23: Results of the correlation analysis between the concentration of trichloroethylene and the concentration of CBs and OCPs.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
CB101	20	0.07	-0.39 to 0.51	0.7575	ns
CB105	20	0.21	-0.27 to 0.61	0.3695	ns
CB118	20	0.03	-0.43 to 0.48	0.8849	ns
CB138	20	0.02	-0.44 to 0.47	0.9248	ns
CB153	20	0.12	-0.35 to 0.54	0.6179	ns
CB156	20	0.16	-0.32 to 0.57	0.5061	ns
CB180	20	-0.05	-0.4935 to 0.41	0.8305	ns
CB28	20	-0.18	-0.59 to 0.30	0.4503	ns
CB31	20	0.03	-0.46 to 0.48	0.8849	ns
CB52	20	-0.02	-0.47 to 0.44	0.9248	ns
DDEPP	20	0.06	-0.41 to 0.50	0.8109	ns
HCB	20	-0.32	-0.68 to 0.15	0.1644	ns

ns = not significant, * significant

III.4.1.2.6 Distribution of VOCs in liver tissue of whiting

At the first instance, the minimum, maximum, 25% percentile, 75% percentile, median, mean, standard deviation (SDs), standard error, coefficient of variation and the geometric mean was determined for VOCs in liver tissue of whiting originating from one sample. Although, 25 individual samples were initially analysed, the results of two had to be discarded for reasons of quality assurance. VOCs could be determined in all the other samples.

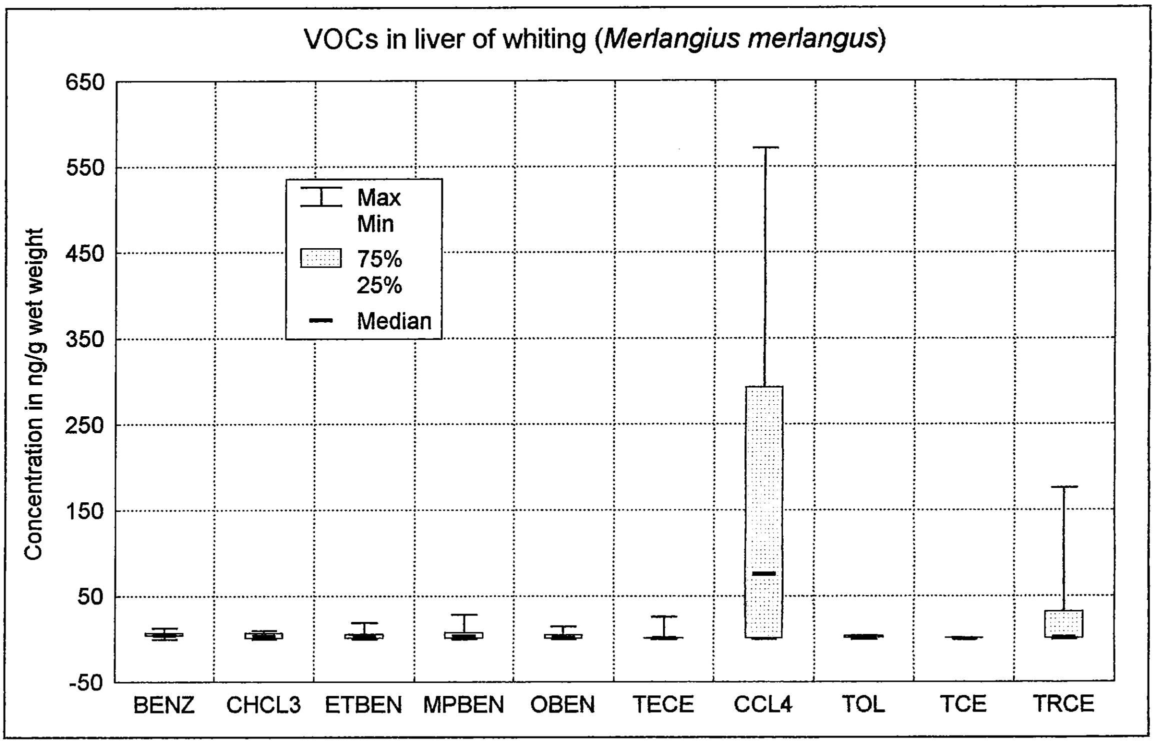
The results of the analyses are given in table III.4.24. The first observation is the occurrence of some extremely high concentrations of tetrachloromethane (more than 550 ng/g) and trichloroethylene (more than 150 ng/g). These high values could not be attributed to the analytical methodology. The concentrations of the other VOCs are in the same concentration range as those for muscle tissue.

The results of the statistical analyses are given in table III.4.25. The large variability of the concentrations is again evident with a coefficient of variation between 70 and 200 %. The discrepancy between the mean and the median suggests again that the values are not normally distributed. The variability and the distribution of the VOCs is illustrated in figure III.4.20.

Table III.4.24: Concentrations in ng/g wet weight of VOCs in liver of whiting (*Merlangius merlangus*) of one sampling location.

Sample	Benzene	Chloroform	Ethylbenzene	m&p-Xylene	o-Xylene	Tetrachloro-ethylene	Tetrachloro-methane	Toluene	Trichloro-ethane	Trichloro-ethylene
Whiting 1	5.14	nd	1.45	nd	4.67	nd	nd	nd	0.45	5.67
Whiting 2	nd	nd	1.44	0.80	1.67	8.81	181.34	nd	0.55	3.15
Whiting 3	4.59	nd	11.32	13.76	4.77	0.89	293.36	1.55	1.73	57.49
Whiting 4	4.62	nd	4.26	3.37	1.76	nd	342.66	1.39	0.22	65.83
Whiting 5	12.78	nd	16.17	11.39	6.14	nd	571.87	nd	0.80	175.83
Whiting 6	8.85	nd	4.20	4.55	2.54	nd	151.39	nd	0.18	154.44
Whiting 7	0.97	0.70	0.48	0.38	0.28	0.12	0.88	0.24	0.14	0.12
Whiting 8	3.36	7.55	4.76	5.66	2.26	0.52	nd	nd	0.32	0.30
Whiting 9	4.19	5.15	3.46	3.14	1.94	nd	0.66	0.94	0.22	1.87
Whiting 10	3.79	0.53	2.26	1.17	1.25	26.24	nd	0.55	0.23	0.23
Whiting 11	6.17	9.76	5.45	7.55	5.75	nd	nd	4.53	1.54	nd
Whiting 12	nd	nd	0.21	nd	0.33	nd	nd	nd	nd	nd
Whiting 13	0.12	nd	0.92	0.57	0.12	nd	nd	nd	0.69	nd
Whiting 14	0.32	nd	0.28	0.25	0.23	nd	nd	nd	0.36	nd
Whiting 15	nd	nd	0.24	0.24	0.18	nd	nd	nd	0.18	nd
Whiting 16	nd	nd	0.17	nd	nd	nd	nd	nd	nd	nd
Whiting 17	nd	nd	0.16	nd	nd	nd	nd	nd	nd	nd
Whiting 18	4.25	0.17	0.74	0.54	0.48	0.20	nd	1.43	0.24	0.16
Whiting 19	1.78	6.57	19.33	28.80	11.44	0.95	0.85	2.83	1.23	1.79
Whiting 20	12.92	1.62	2.53	3.56	14.65	1.12	0.14	3.97	1.28	1.24
Whiting 21	12.70	3.52	6.99	9.90	3.79	0.58	0.65	4.66	0.72	0.55
Whiting 22	6.79	3.77	3.84	3.92	2.20	nd	nd	2.89	0.21	0.25
Whiting 23	6.50	3.66	5.31	1.81	1.47	nd	nd	**1.70**	0.45	0.43

nd = not detected



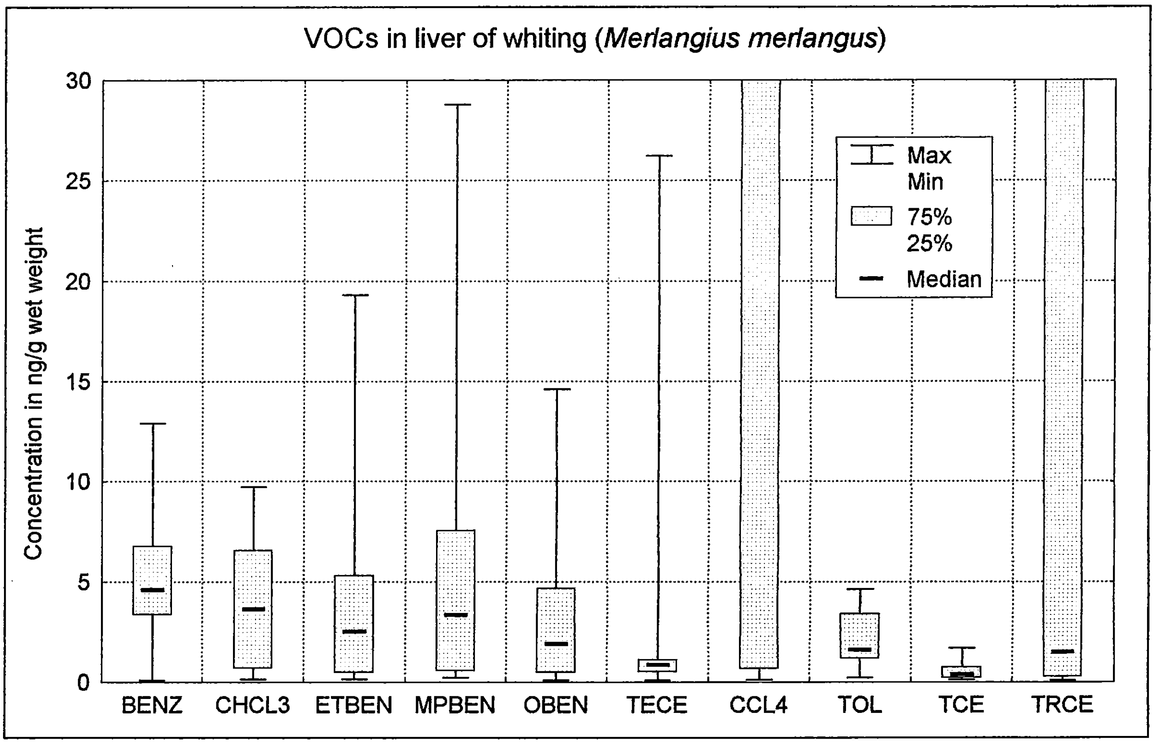


Figure III.4.20: Box and whisker plot of VOCs in liver tissue of whiting. Overview (upper graph) and detail (lower graph) with BENZ = benzene, CHCL3 = chloroform, ETBEN = ethylbenzene, MPBEN = m&p-xylene, OBEN = o-xylene, TECE = tetrachloroethylene, CCL4 = tetrachloromethane, TOL = toluene, TCE = trichloroethane, TRCE = trichloroethylene.

Table III.4.25: Basic statistics of VOCs in liver of whiting from one sample. The calculations were based on the concentrations expressed as ng/g wet weight.

Compound	n	Minimum	25% Percentile	Median	75% Percentile	Maximum	Mean	SD	SEM	CV	Geometric mean
Benzene	18	0.03	3.99	4.86	7.82	12.90	5.96	4.07	0.96	68 %	3.42
Chloroform	11	0.17	1.89	3.66	7.06	10.62	4.66	3.63	1.09	78 %	2.75
m&p-Xylene	23	0.02	0.36	3.46	5.38	20.53	4.90	6.16	1.29	126 %	1.49
Ethylbenzene	19	0.02	0.67	3.37	8.73	30.56	6.67	8.96	2.06	134 %	2.09
o-Xylene	21	0.02	0.47	2.20	4.07	14.65	3.60	4.11	0.90	114 %	1.36
Tetrachloroethylene	9	0.05	0.20	0.89	0.95	26.24	4.25	8.62	2.87	203 %	0.81
Tetrachloromethane	10	0.01	0.08	75.77	237.30	571.90	154.10	196.90	62.26	128 %	3.86
Toluene	12	0.24	1.17	1.63	3.40	4.54	2.10	1.42	0.41	68 %	1.60
Trichloroethane	20	0.04	0.18	0.22	0.75	1.73	0.51	0.53	0.12	103 %	0.30
Trichloroethylene	16	0.12	0.27	1.16	31.58	175.80	29.29	57.00	14.25	195 %	2.20

n = number of samples, SD = standard deviation, SEM = standard error of the mean, CV = coefficient of variation

A Kolmogorov-Smirnov test was again used to determine whether the distribution of VOCs in liver of whiting is Gaussian. The results of these tests are given in table III.4.25. The distribution was, as above, further investigated, as above, by means of normal probability plots. The plots for the various VOCs are given in figures III.4.21 and III.4.22.

Table III.4.25: Results of the Kolmogorov-Smirnov test for VOCs in muscle of whiting.

Compound	KS distance	P value	Passed normality test (*=0.05)?
Benzene	0.146	P > 0.10	Yes
Chloroform	0.155	P > 0.10	Yes
m&p-Xylene	0.247	P > 0.10	Yes
Ethylbenzene	0.232	P > 0.10	Yes
o-Xylene	0.220	P > 0.10	Yes
Tetrachloroethylene	0.420	0.0839	Yes
Tetrachloromethane	0.283	P > 0.10	Yes
Toluene	0.195	P > 0.10	Yes
Trichloroethane	0.256	P > 0.10	Yes
Trichloroethylene	0.411	0.0091	No

Although the results of the Kolomogorov-Smirnov test suggest a normal distribution for all VOCs with the exception of trichloroethylene, the contrary is suggested by the normal probability plots. For nearly all cases a s shaped pattern, not unlike the one for the concentrations in muscle tissue, can be observed around the expected straight line. The sample size is again small so firm conclusions concerning the distribution are not possible. As for muscle, it was therefore assumed that the concentrations of VOCs in liver are not normally distributed and non parametric statistical tests were used.

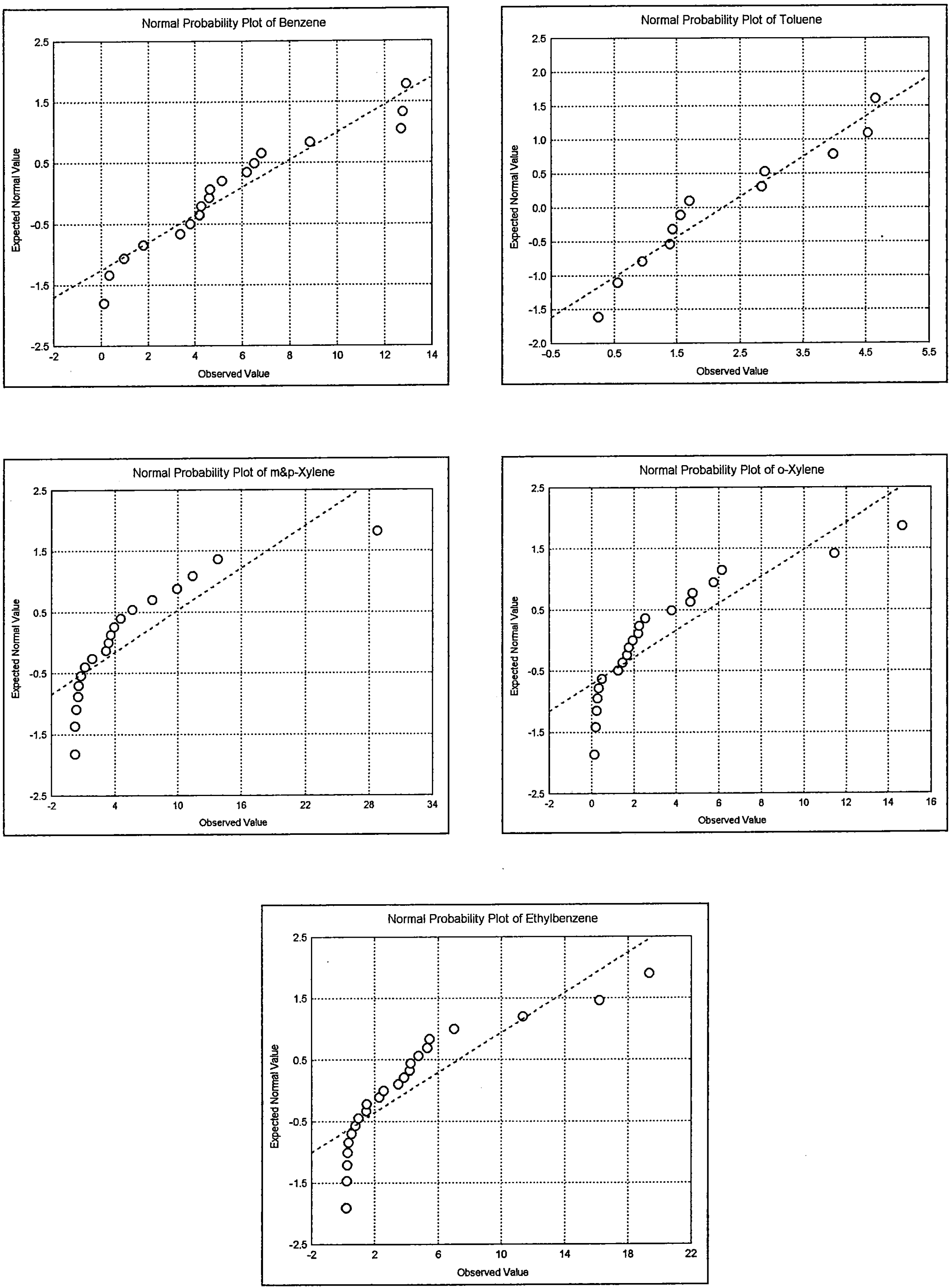


Figure III.4.21: Normal probability plot of benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in liver tissue of whiting.

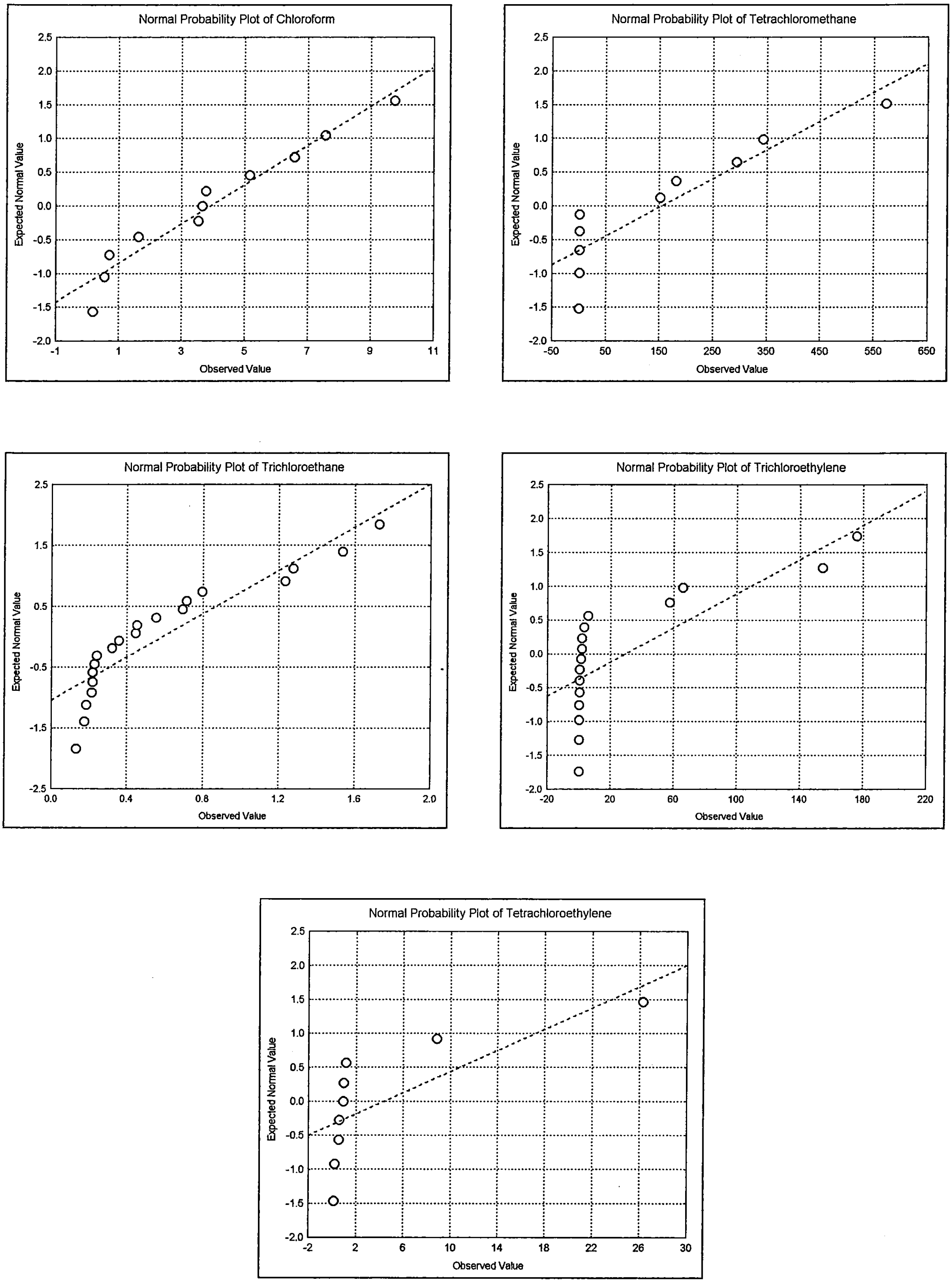


Figure III.4.22: Normal probability plot of chloroform (upper left), tetrachloromethane (upper right), trichloroethane (middle left), trichloroethylene (middle right) and tetrachloroethylene (bottom) in liver tissue of whiting.

III.4.1.2.7 Correlation between the concentration of VOCs in the liver of whiting and size of the fish

The concentrations of VOCs in liver of whiting were correlated with the size (length). As was mentioned before, increasing concentrations with the increasing size indicates the possibility of biomagnification. Such increases are reported in literature for CBs (de Boer, 1994) and OCPs (Kruse and Krüger, 1981) in the liver of cod.

In view of the supposed absence of a normal distribution the correlation analysis was performed using the non parametric Spearman correlation test. The results of this test are given in table III.4.26 and in figures III.4.23 and III.4.24.

Table III.2.26: Results of the correlation analysis between the length and the concentration of VOCs in liver of whiting.

Parameter	Number of XY Pairs	Spearman r	95% CI	P value (two-tailed)	P value summary
Benzene	17	-0.67	-0.88 to -0.27	0.003	*
Chloroform	10	-0.35	0.3304	na	ns
m&p-Xylene	22	-0.57	-0.80 to -0.18	0.0061	*
Ethylbenzene	18	-0.57	-0.82 to -0.12	0.0138	*
o-Xylene	20	-0.67	-0.86 to -0.30	0.0014	*
Tetrachloroethylene	9	-0.45	0.23	na	ns
Tetrachloromethane	10	-0.72	0.02	na	*
Toluene	11	-0.33	-0.78 to 0.36	0.3269	ns
Trichloroethane	19	-0.24	-0.63 to 0.26	0.3289	ns
Trichloroethylene	15	-0.80	-0.93 to -0.48	0.0003	*

ns = not significant, * = significant, na = not applicable, CI = confidence interval, r = correlation coefficient

On six occasions a negative correlation is found between the concentration of VOCs in liver and the size of the fish. This is quite in contrast with the findings for CBs and OCPs and with the finding for muscle tissue. Looking at the graphs indeed suggests that for the MAHs this correlation is real, meaning that smaller fish have higher concentrations in their liver. The significant correlations for the CHCs should be interpreted with more caution, as the correlation seems more the result of high outlying values. The only sensible explanation for this phenomenon that comes to mind is a higher metabolic activity of the taller fishes. There is, however, no proof for this assumption. It would certainly be worthwhile to investigate this phenomenon in a larger sample.

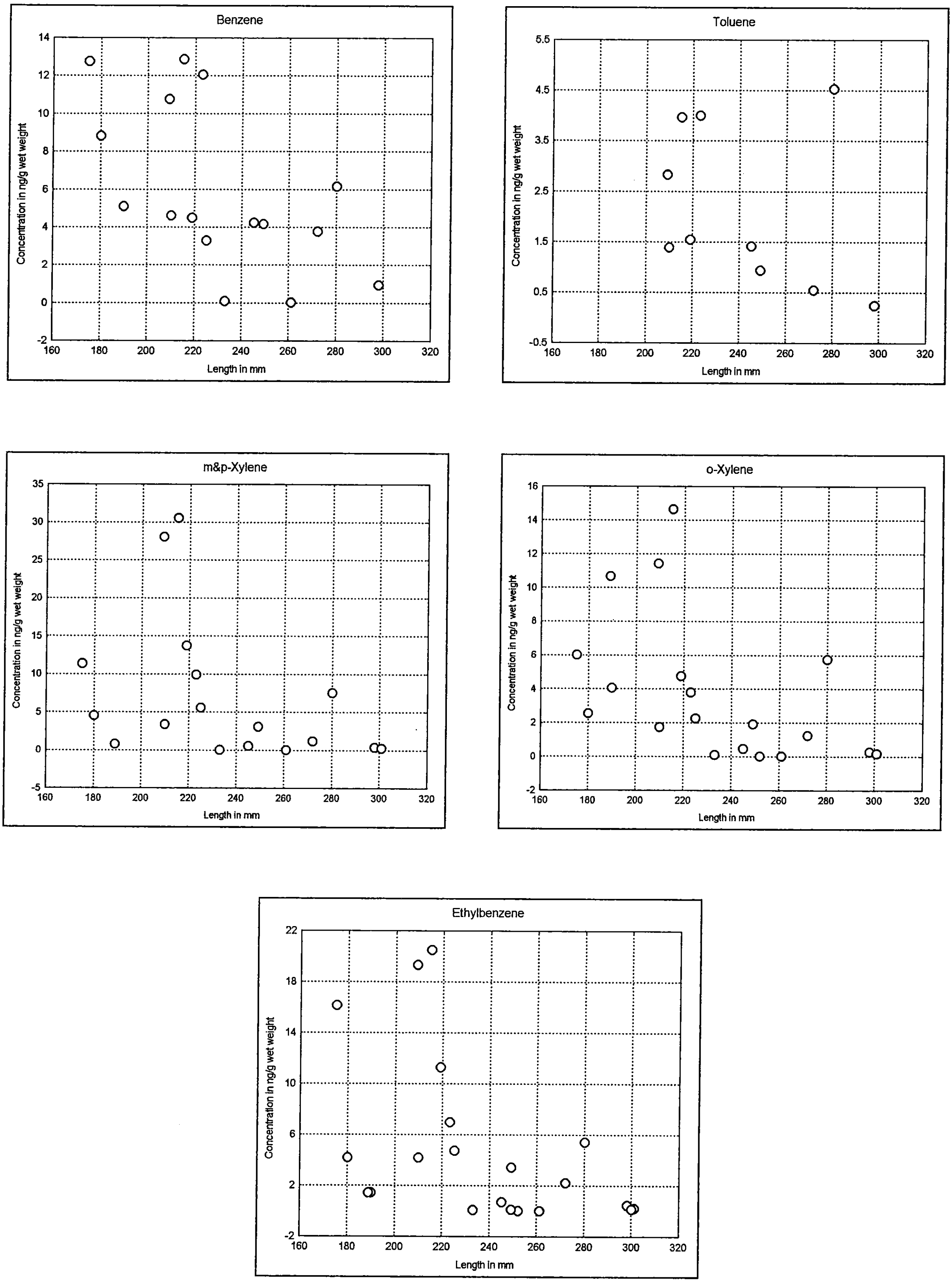


Figure III.4.23: Correlation between the length and benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in liver tissue of whiting.

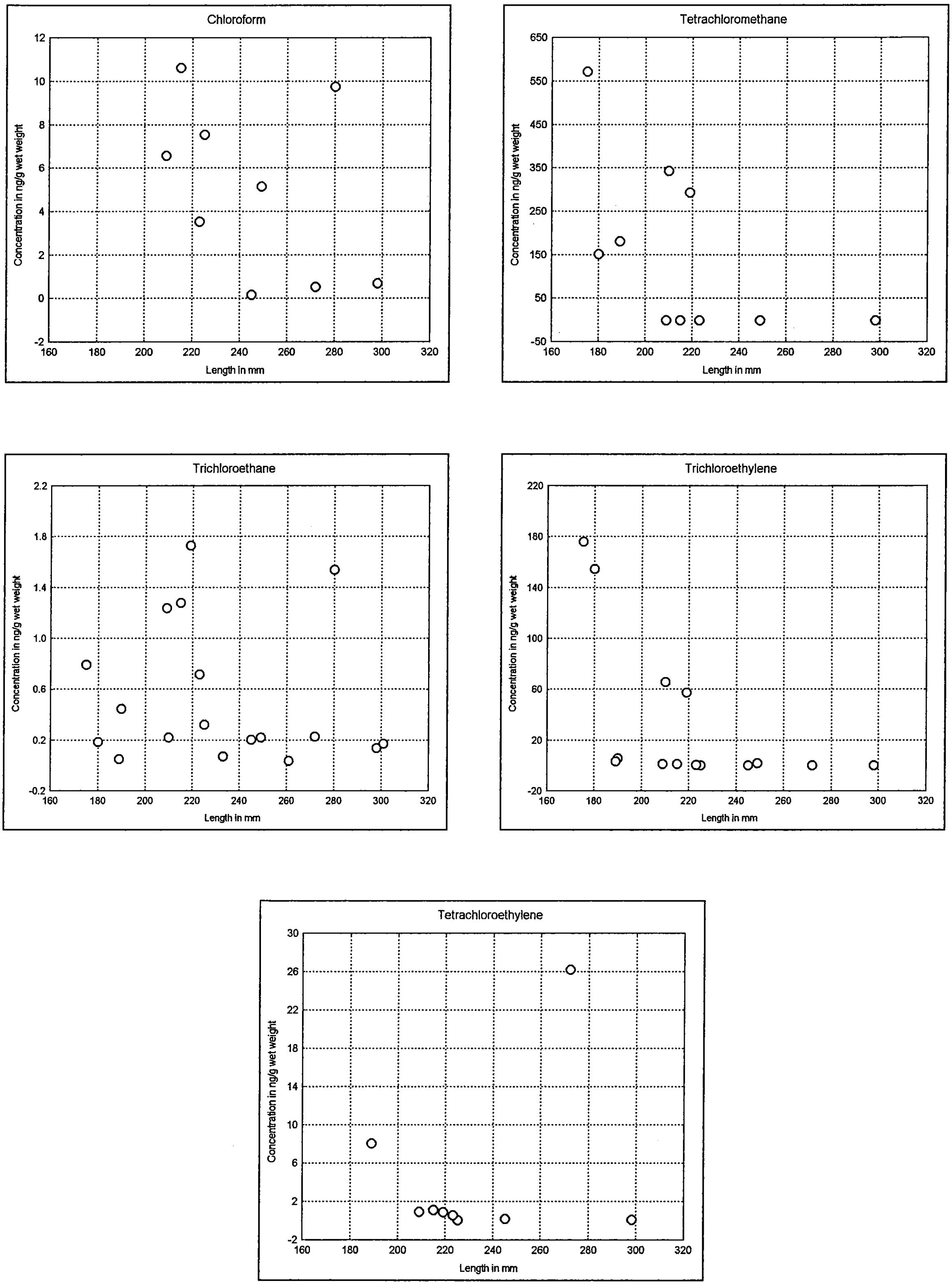


Figure III.4.24: Correlation between the length and chloroform (upper left), tetrachloromethane (upper right), trichloroethane (middle left), trichloroethylene (middle right) and tetrachloroethylene (bottom) in liver tissue of whiting.

III.4.1.2.8 Comparison of the concentrations of VOCs in liver and muscle tissue of whiting

The interspecimen distribution of VOCs in whiting was investigated by comparing the concentrations in liver and muscle tissue. The rationale behind these test was to determine whether differences occur within the same specimen, as a result of differences in uptake, metabolisation or storage.

Concentrations in liver and muscle tissue were first compared with the Mann-Whitney test. The results of this comparison are given in table III.4.26.

Table III.4.26: Results of the comparison of VOC concentrations in liver and muscle.

Compound	P value	Mann-Whitney U	P value summary
Benzene	0.0033	116	*
Ethylbenzene	0.4809	211	ns
m&p-Xylene	0.8142	231	ns
o-Xylene	0.2594	193	ns
Toluene	0.8504	233	ns
Chloroform	0.8064	299	ns
Tetrachloromethane	0.0894	170.5	ns
Trichloroethane	P<0.0001	69.5	*
Trichloroethylene	0.2957	196.5	ns
Tetrachloroethylene	0.8675	234	ns

ns = not significant, * = significant.

On general, concentrations in liver are not significantly different from the concentrations in muscle tissue, with two exceptions. Concentrations of benzene and trichloroethane are significantly higher in liver than in muscle tissue. The concentrations in liver and muscle are further illustrated in figure III.4.25. The graph shows that the concentrations are indeed more or less equal for both tissues. The extreme values for tetrachloromethane, trichloroethane and even tetrachloroethylene in liver are, however, quite peculiar and deserve further attention.

Concentrations in liver and muscle were further correlated with each other to determine if some sort of relationship exists between them. The results of the non parametric Spearman correlation analysis are given in table III.4.27. The relation between liver and muscle tissue concentrations in illustrated in figures III.4.26 to III.4.27.

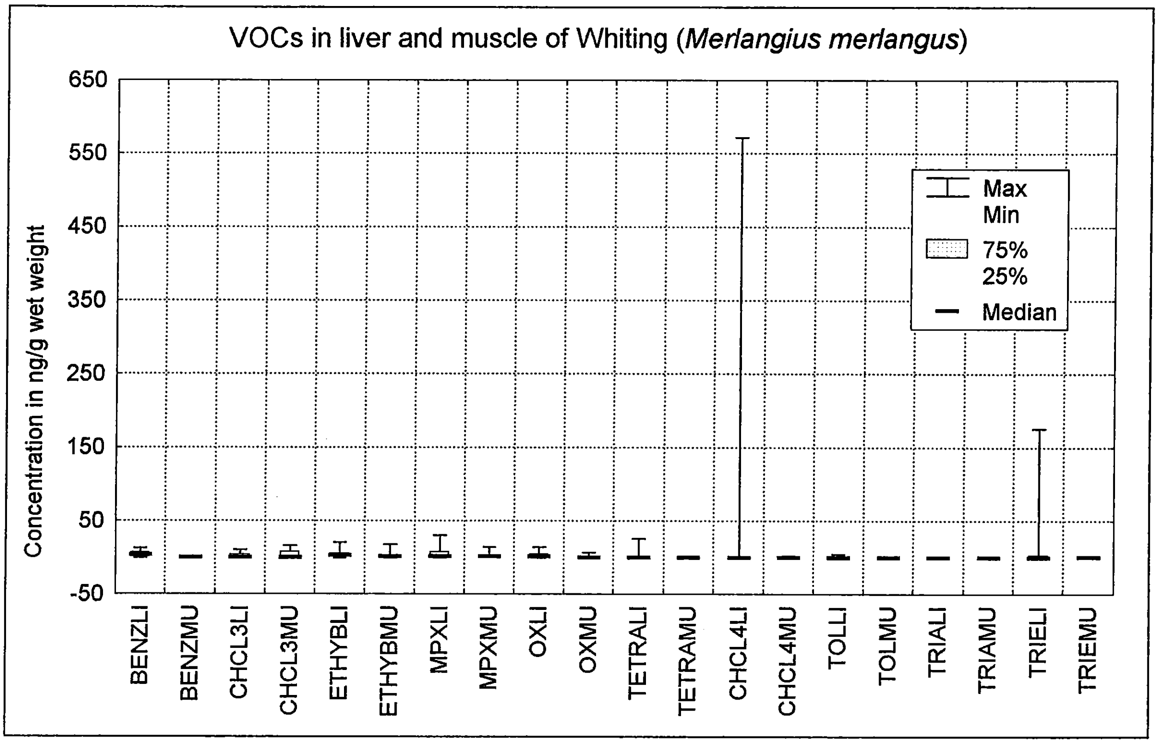
In only one of the cases a significant relation between concentrations in liver and muscle tissue could be observed. Higher concentrations of benzene in the liver are related to higher concentrations in muscle tissue. For the other VOCs this could not be observed. In contrast, a significant linear relation has already been observed by Roose *et al.* (1996) for CBs in muscle and liver of cod (*Gadus morhua*) and flounder (*Platichtys flesus*).

Table III.4.27: Results of the correlation analysis of concentrations in liver and muscle in whiting.

Parameter	Number of XY Pairs	Spearman r	P value (two-tailed)	P value summary
Benzene	12	0.50	0.1006	+
Chloroform	11	-0.23	0.5015	ns
Ethylbenzene	20	0.12	0.6045	ns
m&p-Xylene	17	0.05	0.8591	ns
o-Xylene	19	0.13	0.5913	ns
Tetrachloroethylene	5	0.60	na	ns
Tetrachloromethane	4	0.40	na	ns
Toluene	8	0.07	na	ns
Trichloroethane	12	0.02	0.9484	ns
Trichloroethylene	13	0.34	0.2547	ns

ns = not significant, na = not applicable, r = correlation coefficient, + significant at the 90 % level

The conclusion is that there are on general no significant differences between the concentrations in liver and muscle tissue of whiting and the concentrations in both tissues are not related, with the likely exception of benzene. This does, however , not mean that different pathways are responsible for the concentrations observed in both tissues. The matter should be further investigated.



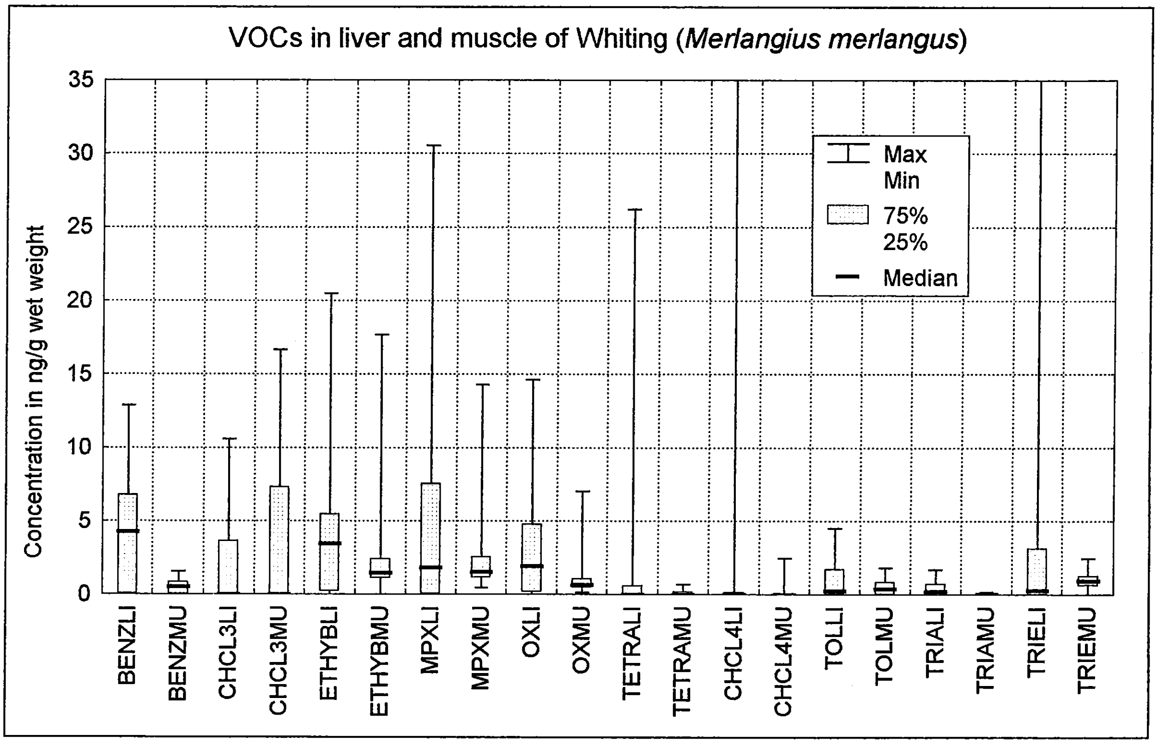


Figure III.4.25: Comparison of the concentrations of VOCs in liver and muscle tissue of whiting. Overview (upper) and detail (lower) with BENZ = benzene, CHCL3 = chloroform, ETHYB = ethylbenzene, MPX = m&p-xylene, OX = o-xylene, TETRA = tetrachloroethylene, CHCL4 = tetrachloromethane, TOL = toluene, TRIA = trichloroethane, TRIE = trichloroethylene, LI = liver and MU = muscle tissue.

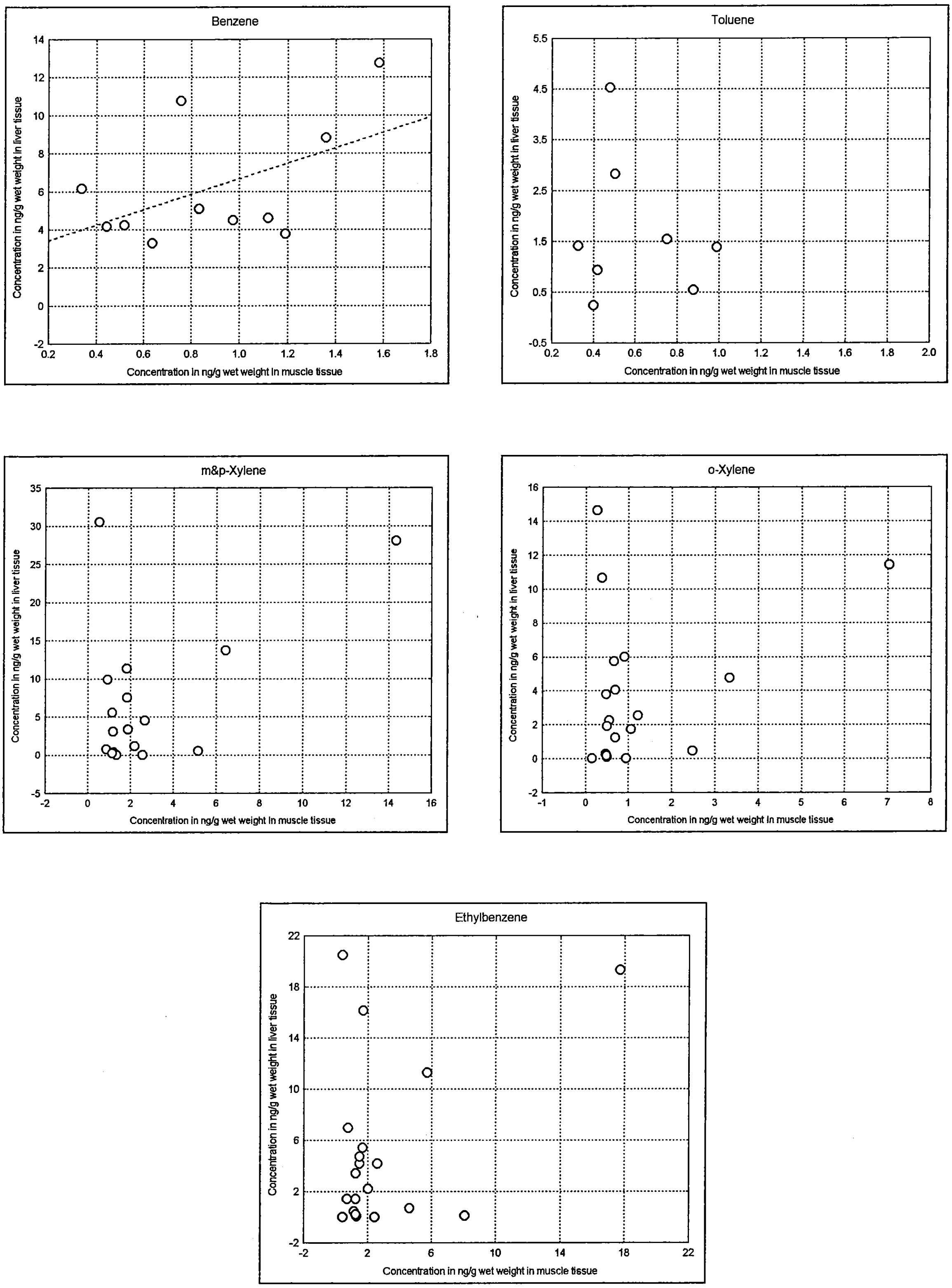


Figure III.4.26: Correlation between concentrations in muscle tissue and liver of whiting for benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom).

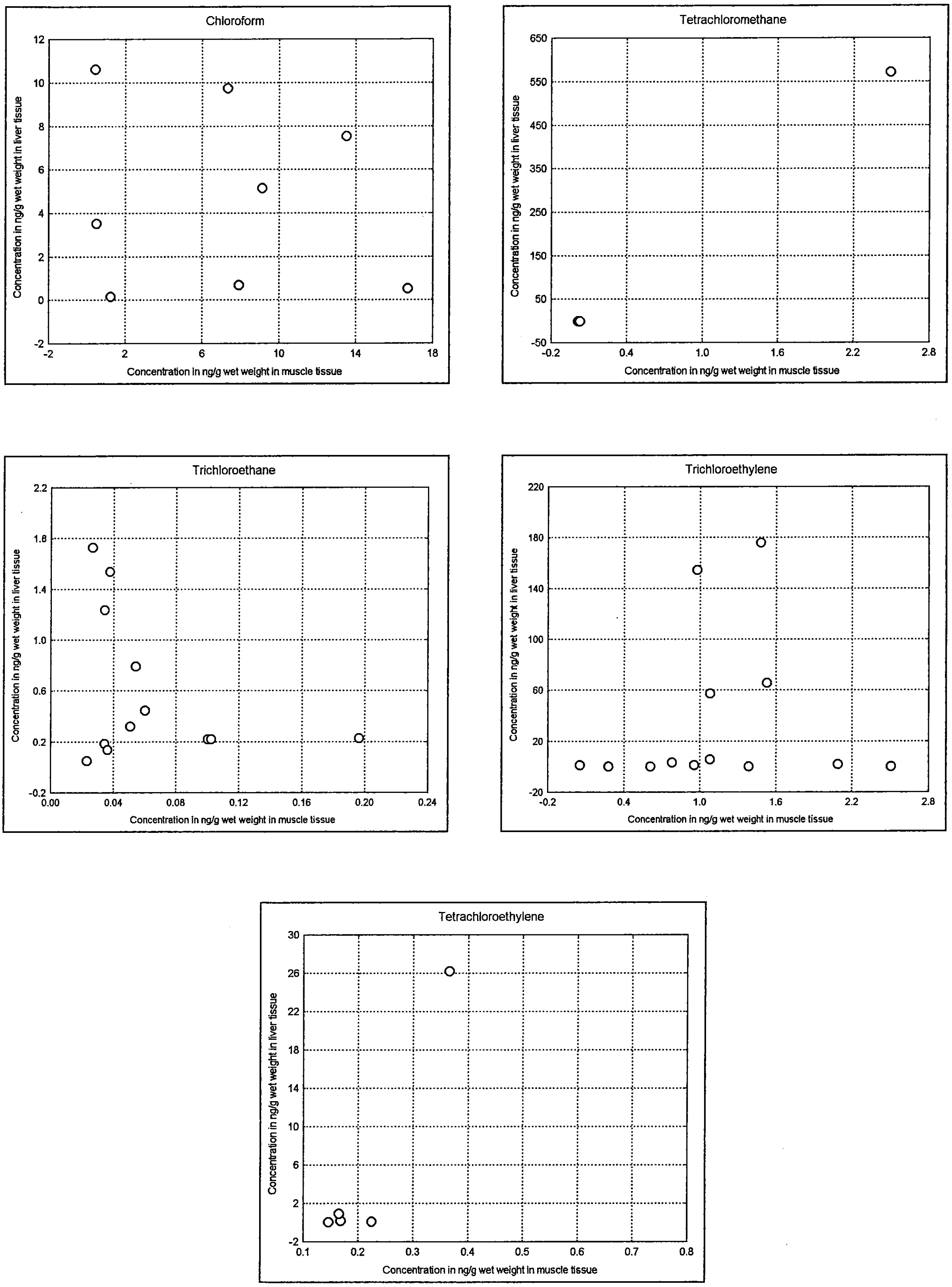


Figure III.4.27: Correlation between concentrations in muscle tissue and liver of whiting for chloroform (upper left), tetrachloromethane (upper right), trichloroethane (middle left), trichloroethylene (middle right) and tetrachloroethylene (bottom).

III.4.1.3 INTERSPECIES AND INTERSPECIMEN DISTRIBUTION IN DAB

III.4.1.3.1 Distribution of VOCs in muscle tissue of dab

As for whiting, the minimum, maximum, 25% percentile, 75% percentile, median, mean, standard deviation (SDs), standard error, lower 95% confidence interval, coefficient of variation and the geometric mean was determined for VOCs in muscle of dab originating from one sample. Although 25 individual samples were initially analysed, the results of four had to be discarded for reasons of quality assurance. VOCs could be determined in all the other samples.

The results of the analyses are given in table III.4.28. For certain compounds such as trichloroethane the data set is small as only few concentrations were above the detection limit.

The results of the statistical analysis are given in table II.4.29. The variability of the concentrations is high but a lot smaller than observed for muscle of whiting. The discrepancy between the mean and the median is, on general smaller as well. This suggests that the values are perhaps normally distributed. The variability and the distribution of the VOCs is illustrated in figure III.4.28. Some rather high values, which could not be attributed to the analytical method, are in this case noted for chloroform. The values for the other VOCs are in the same order of magnitude as those found in muscle tissue of whiting.

A Kolmogorov-Smirnov test, as described earlier, was therefore executed to determine whether the distribution is normal. The results of these tests are given in table III.4.30.

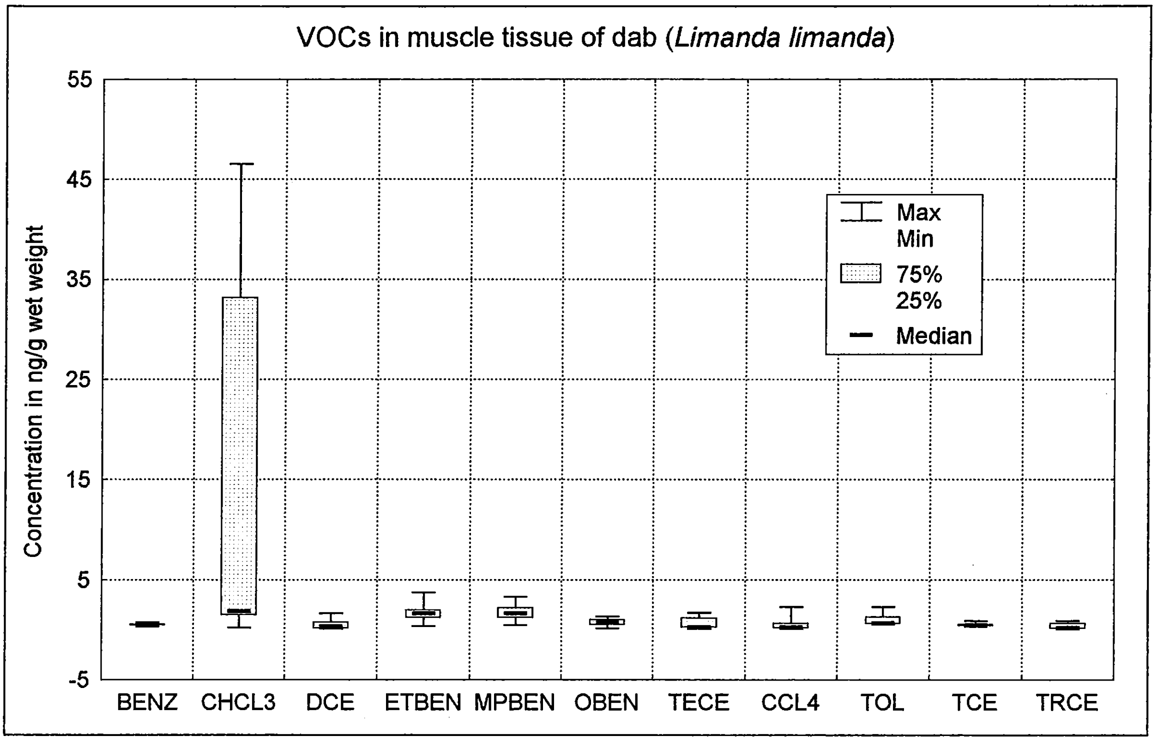
The tests indicate that concentrations of all the VOCs under investigation are normally distributed in muscle tissue of dab. This does however not mean that for the other cases a normal distribution can be assumed as the sample size is generally small (see earlier). The test only indicates that the P values in those cases, are not inconsistent with a Gaussian population. To further investigate the distribution of the

VOCs in muscle tissue of dab, a normal probability plot was made for each compound.

Table III.4.28: Concentrations in ng/g wet weight of VOCs in muscle of dab (*Limanda limanda*) of one sampling location.

Sample	Benzene	Chloroform	1,2-Dichloro-ethane	Ethyl-benzene	m&p-Xylene	o-Xylene	Tetrachloro-ethylene	Tetrachloro-methane	Toluene	Trichloro-ethane	Trichloro-ethylene
Dab 1	0.41	1.90	1.13	1.33	1.76	0.92	0.28	0.23	2.35	0.54	0.11
Dab 2	nd	nd	nd	3.77	nd	nd	nd	nd	nd	nd	nd
Dab 3	nd	1.46	nd	3.12	3.34	nd	nd	nd	nd	nd	nd
Dab 4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dab 5	nd	nd	nd	nd	nd	nd	0.30	0.15	nd	nd	nd
Dab 6	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.51	nd
Dab 7	0.51	1.66	0.84	0.97	1.12	0.49	nd	nd	0.70	0.45	0.41
Dab 8	0.52	1.63	0.69	1.88	1.45	0.84	nd	nd	0.62	0.35	0.48
Dab 9	0.39	1.51	0.47	1.35	1.26	0.64	nd	nd	0.62	nd	0.31
Dab 10	0.38	0.46	0.96	0.41	0.53	0.22	0.24	nd	0.58	0.39	0.71
Dab 11	0.67	0.26	0.15	2.27	2.53	1.38	0.32	0.78	0.82	nd	nd
Dab 12	0.52	0.25	0.14	1.98	1.96	1.13	0.19	0.18	0.60	nd	0.74
Dab 13	0.58	0.54	0.12	1.54	1.67	0.92	0.22	0.74	0.75	nd	0.65
Dab 14	0.57	3.85	0.14	0.92	0.94	0.42	0.15	0.51	0.55	nd	0.92
Dab 15	0.56	5.75	0.18	1.55	1.15	0.56	0.18	0.54	0.67	nd	0.12
Dab 16	0.76	28.22	1.67	1.87	1.69	0.86	1.37	2.33	1.28	0.92	0.24
Dab 17	0.44	36.48	0.58	1.18	1.64	0.75	1.18	0.35	1.17	nd	0.15
Dab 18	0.53	33.47	0.43	2.12	2.42	1.14	1.75	0.23	1.33	nd	0.15
Dab 19	0.70	33.16	0.38	1.85	2.94	1.13	1.39	0.24	1.58	nd	0.15
Dab 20	0.50	46.58	0.15	0.83	nd	0.33	nd	nd	nd	nd	0.13
Dab 21	0.52	46.50	0.24	1.76	1.58	0.68	0.51	0.16	nd	nd	0.11

nd = not detected



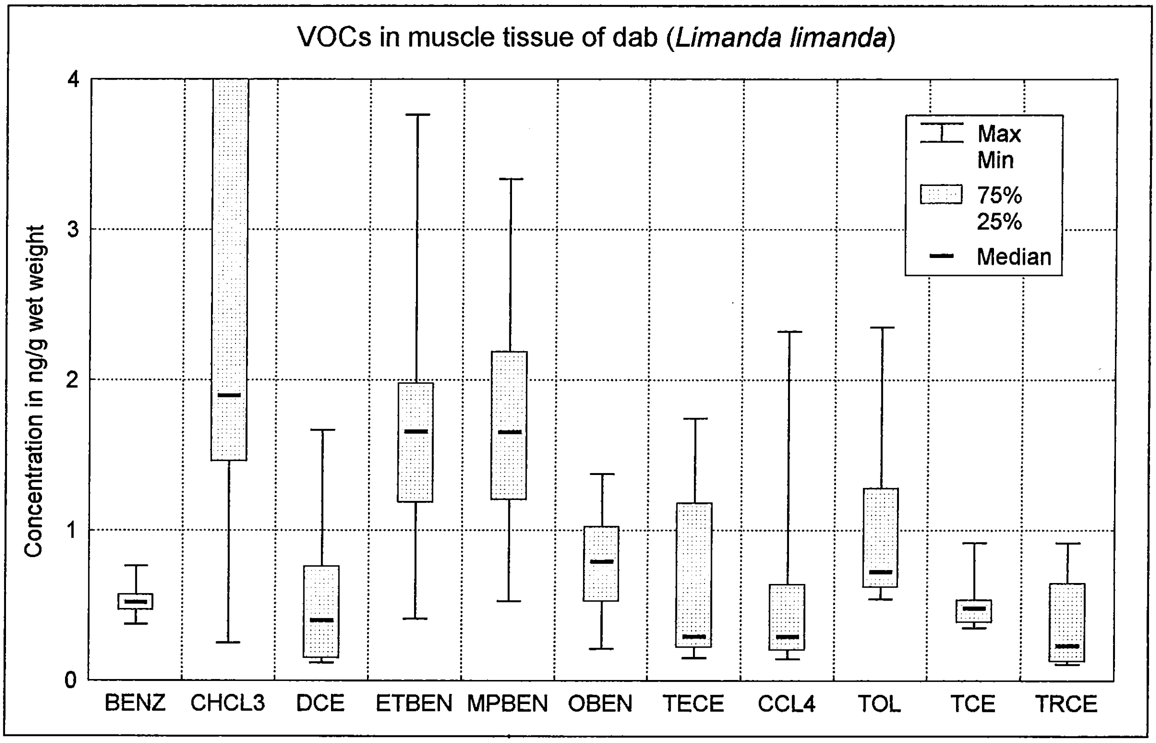


Figure III.4.28: Box and whisker plot of VOCs in muscle tissue of dab. Overview (upper graph) and detail (lower graph) with BENZ = benzene, CHCL3 = chloroform, DCE = 1,2-dichloroethane, ETBEN = ethylbenzene, MPBEN = m&p-xylene, OBEN = o-xylene, TECE = tetrachloroethylene, CCL4 = tetrachloromethane, TOL = toluene, TCE = trichloroethane, TRCE = trichloroethylene.

Table III.4.29: Basic statistics of VOCs in muscle of dab from one sample. The calculations were based on the concentrations expressed as ng/g wet weight.

Compound	n	Minimum	25% Percentile	Median	75% Percentile	Maximum	Mean	SD	SEM	Lower 95% CI	Upper 95% CI	CV	Geometric mean
Benzene	16	0.38	0.47	0.52	0.58	0.76	0.54	0.11	0.03	0.48	0.59	20%	0.53
Chloroform	17	0.25	1.46	1.90	28.22	46.58	14.33	18.11	4.39	5.02	23.65	126%	3.88
1,2-Dichloroethane	16	0.12	0.15	0.40	0.76	1.67	0.52	0.45	0.11	0.28	0.75	86%	0.37
m&p-Xylene	18	0.41	1.26	1.66	1.93	3.77	1.71	0.81	0.19	1.30	2.11	47%	1.52
Ethylbenzene	16	0.53	1.20	1.66	2.19	3.34	1.75	0.74	0.19	1.35	2.15	43%	1.60
o-Xylene	16	0.22	0.53	0.79	1.02	1.38	0.77	0.33	0.08	0.60	0.95	42%	0.70
Tetrachloroethylene	13	0.16	0.22	0.30	0.51	1.75	0.62	0.58	0.16	0.28	0.97	92%	0.43
Tetrachloromethane	12	0.15	0.20	0.30	0.64	2.33	0.54	0.61	0.17	0.15	0.92	113%	0.37
Toluene	14	0.55	0.62	0.73	1.23	2.35	0.97	0.52	0.14	0.67	1.27	53%	0.88
Trichloroethane	6	0.35	0.42	0.48	0.53	0.92	0.53	0.20	0.08	0.31	0.74	39%	0.50
Trichloroethylene	15	0.11	0.14	0.24	0.56	0.92	0.36	0.28	0.07	0.21	0.51	77%	0.27

n = number of samples, SD = standard deviation, SEM = standard error of the mean, CI = confidence interval, CV = coefficient of variation

Table III.4.30: Results of the Kolmogorov-Smirnov test for VOCs in muscle of dab.

Compound	KS distance	P value	Passed normality test (P>0.05)?
Benzene	0.1578	P > 0.10	Yes
Chloroform	0.3292	0.0502	Yes
1,2-Dichloroethane	0.1874	P > 0.10	Yes
m&p-Xylene	0.1449	P > 0.10	Yes
Ethylbenzene	0.1805	P > 0.10	Yes
o-Xylene	0.1108	P > 0.10	Yes
Tetrachloroethylene	0.3148	P > 0.10	Yes
Tetrachloromethane	0.2609	P > 0.10	Yes
Toluene	0.2601	P > 0.10	Yes
Trichloroethane	0.3129	P > 0.10	Yes
Trichloroethylene	0.2384	P > 0.10	Yes

The results of these plots is given in figures III.4.29 to III.4.30 for the different VOCs. Most of the plots, with the exception of o-xylene, show an s shaped pattern around the expected straight line not unlike the earlier observations for muscle tissue whiting. The plot for o-xylene, however, shows a remarkable good fit to the expected straight line. This can either mean that the plot for o-xylene is the most representative for the It seemed advisable to consider the contrary as the number of data was limited. It was therefore concluded that both the MAHs and the CHCs are not normally distributed in muscle tissue of whiting. Ensuing statistical comparisons should as a result be made with non parametric tests.

III.4.1.3.2 Correlation between size and the concentration of VOCs in muscle tissue of dab

As for whiting, concentrations of VOCs in muscle tissue of dab were correlated with the length of the fish. In contrast to whiting, the length of dab is less representative for the age of the fish. In the case of a length effect the results should therefore not be interpreted in terms of biomagnification. Length is, however, an important biological parameter and a correlation analysis is highly justified.

Prior to performing a correlation analysis, the distribution of the length in the sample was investigated. The results of the analyses are given in table III.4.31.

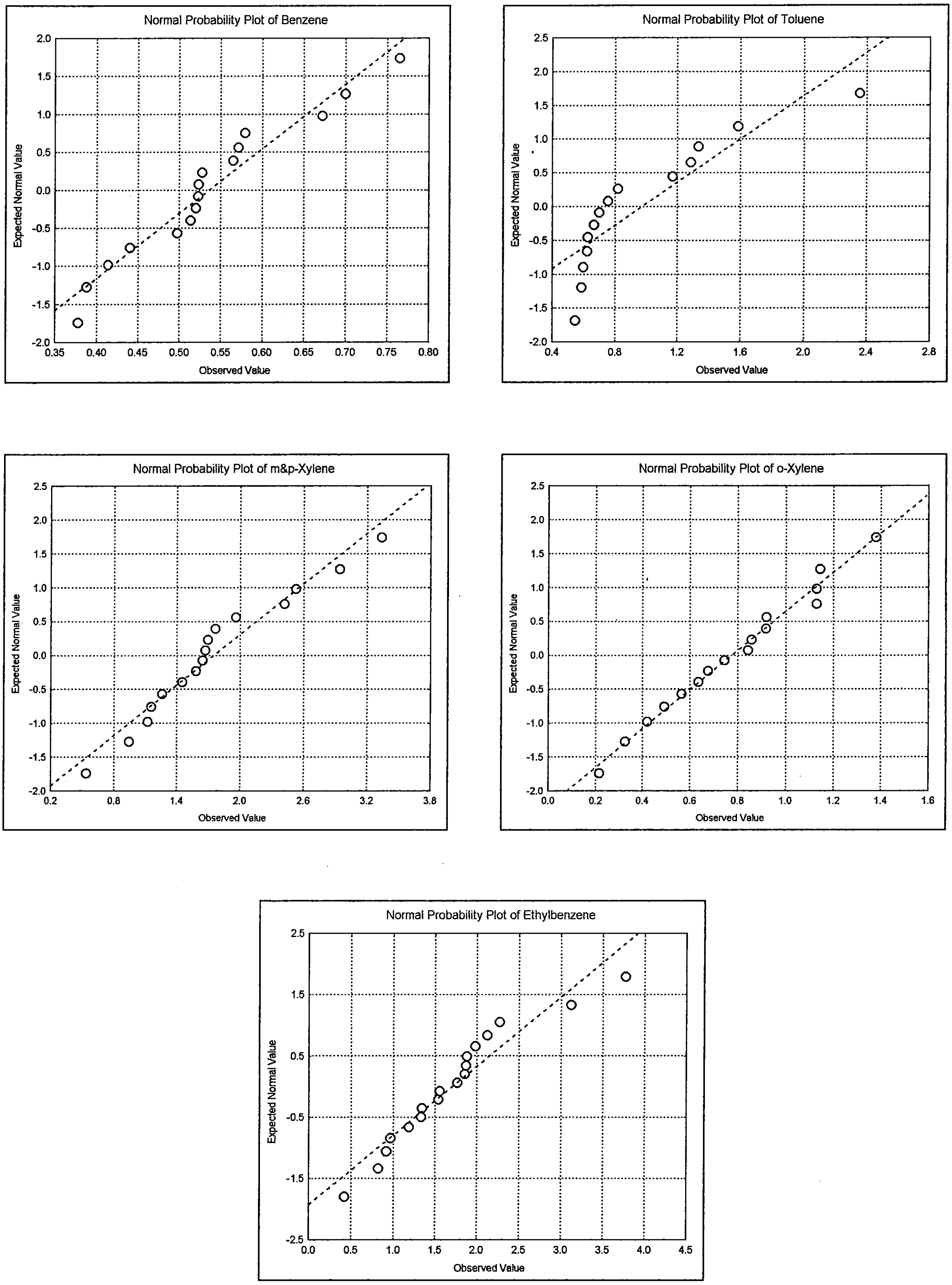


Figure III.4.29: Normal probability plot of benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in muscle tissue of dab.

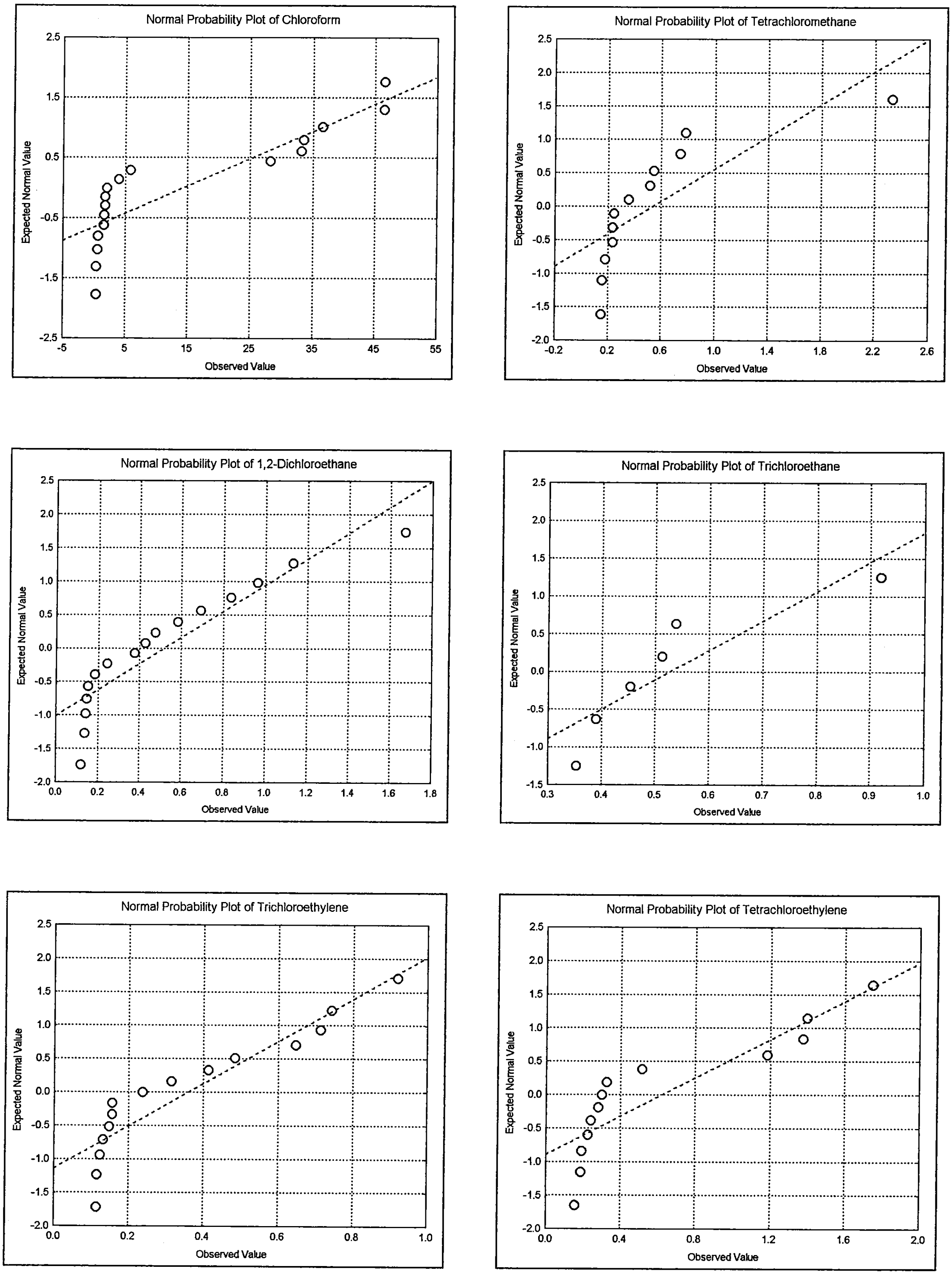


Figure III.4.30: Normal probability plot of chloroform (upper left), tetrachloromethane (upper right), 1,2-dichloroethane (middle left), trichloroethane (middle right), trichloroethylene (bottom left) and tetrachloroethylene (bottom right) in muscle tissue of dab.

Table III.4.31: Statistical analysis of the length of the fish

Parameter	Value
Number of values	21
Minimum	165
25% Percentile	181
Median	185
75% Percentile	190
Maximum	257
Mean	190.8
Standard Deviation	22.3
Standard error of the mean	4.9
Lower 95% CI	180.7
Upper 95% CI	201
Coefficient of variation	12%
Geometric mean	189.7
Normality Test	
KS distance	0.2288
P value	P > 0.10
Passed normality test (P>0.05)?	Yes

CI = confidence interval

The results indicate that there is little variability in the length of the fishes for the selected class and the length in normally distributed.

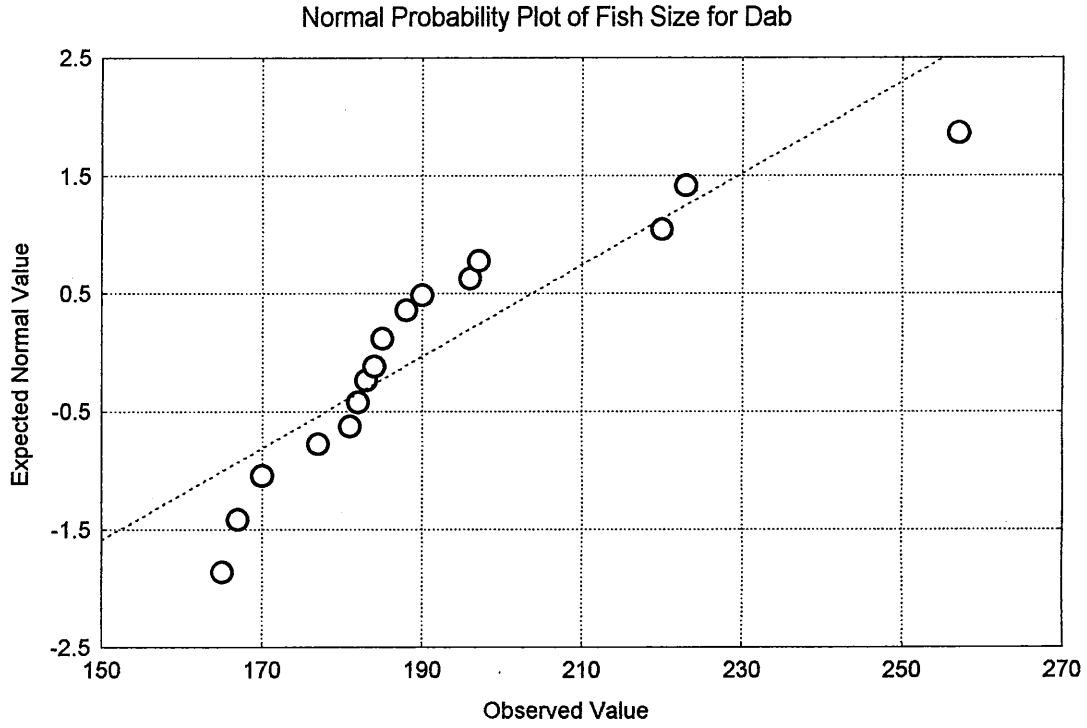


Figure III.31: Normal probability plot of the size of dab in the selected length class.

The latter was once again further investigated using a normal probability plot. The result of this analysis is given in figure III.4.31.

The plot indicates a substantial deviation of the normal distribution. It was therefore assumed that the sizes of the fishes, used for this study, are not normally distributed.

For the correlation analysis the non parametric test of Spearman was used, as it was assumed that the concentration of VOCs are not normally distributed in muscle tissue of whiting. The results of the analyses are given in table III.4.31 and illustrated in figures III.4.32. to III.4.33.

Table III.4.32: Results of the correlation analysis between fish size and the VOC concentration in muscle of dab.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
Benzene	16	0.24	-0.30 to 0.67	0.3645	ns
Chloroform	17	-0.27	-0.67 to 0.26	0.3016	ns
1,2-Dichloroethane	16	-0.41	-0.76 to 0.13	0.1167	ns
m&p-Xylene	18	0.20	-0.31 to 0.62	0.4196	ns
Ethylbenzene	16	0.33	-0.21 to 0.72	0.2078	ns
o-Xylene	16	0.38	-0.16 to 0.75	0.1432	ns
Tetrachloroethylene	13	0.14	-0.46 to 0.65	0.6475	ns
Tetrachloromethane	12	0.09	-0.53 to 0.64	0.7867	ns
Toluene	14	0.07	-0.50 to 0.59	0.8108	ns
Trichloroethane	6	-0.66	0.16	na	ns
Trichloroethylene	15	0.37	-0.19 to 0.75	0.1720	ns

r = correlation coefficient, ns = not significant, na = not applicable

In none of the cases a significant relation between the length and the VOC concentration could be established. The conclusion is therefore that the concentration of VOCs in muscle of dab is independent of the size of the fish.

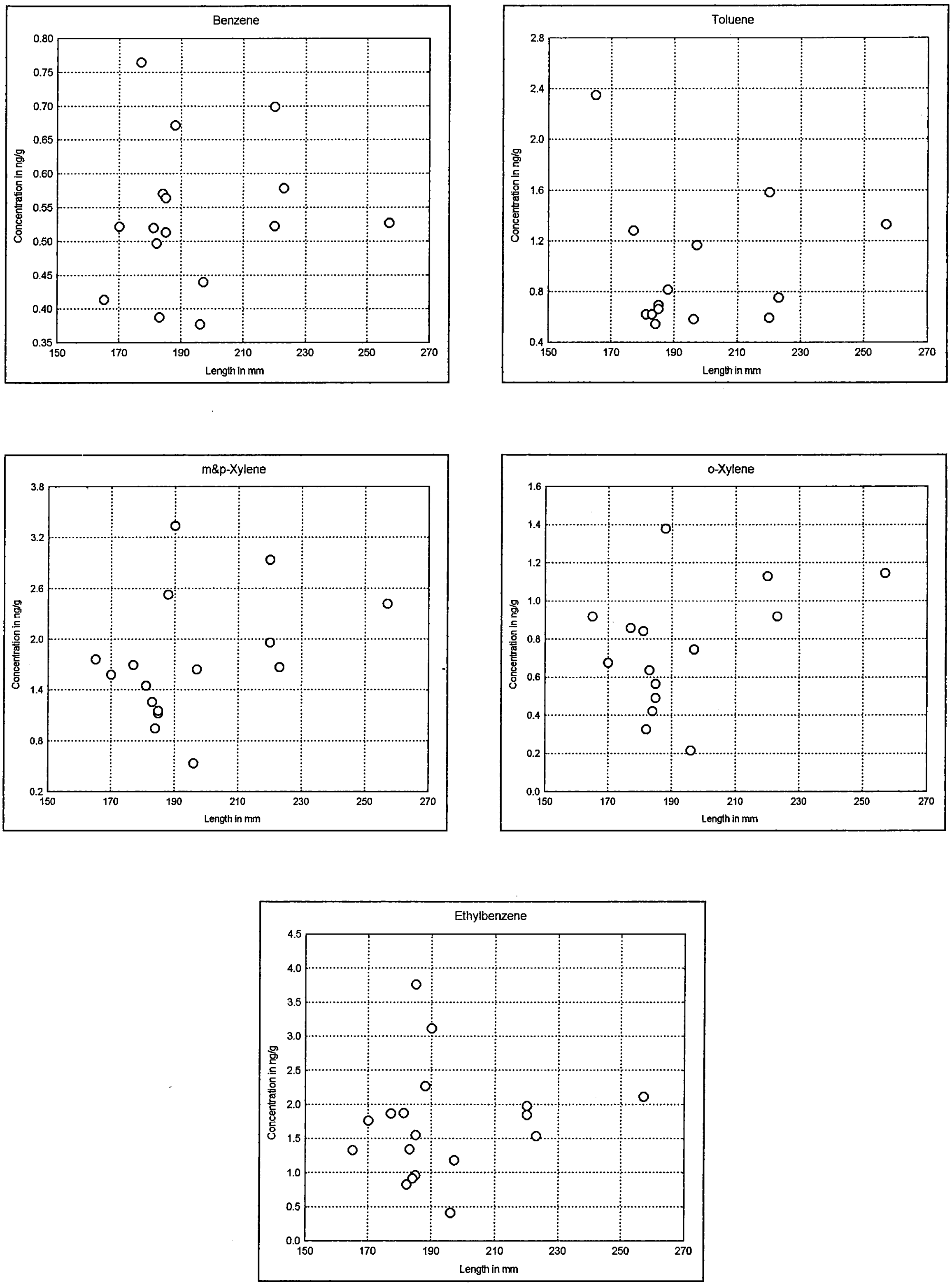


Figure III.4.32: Correlation between the length and benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in muscle tissue of dab.

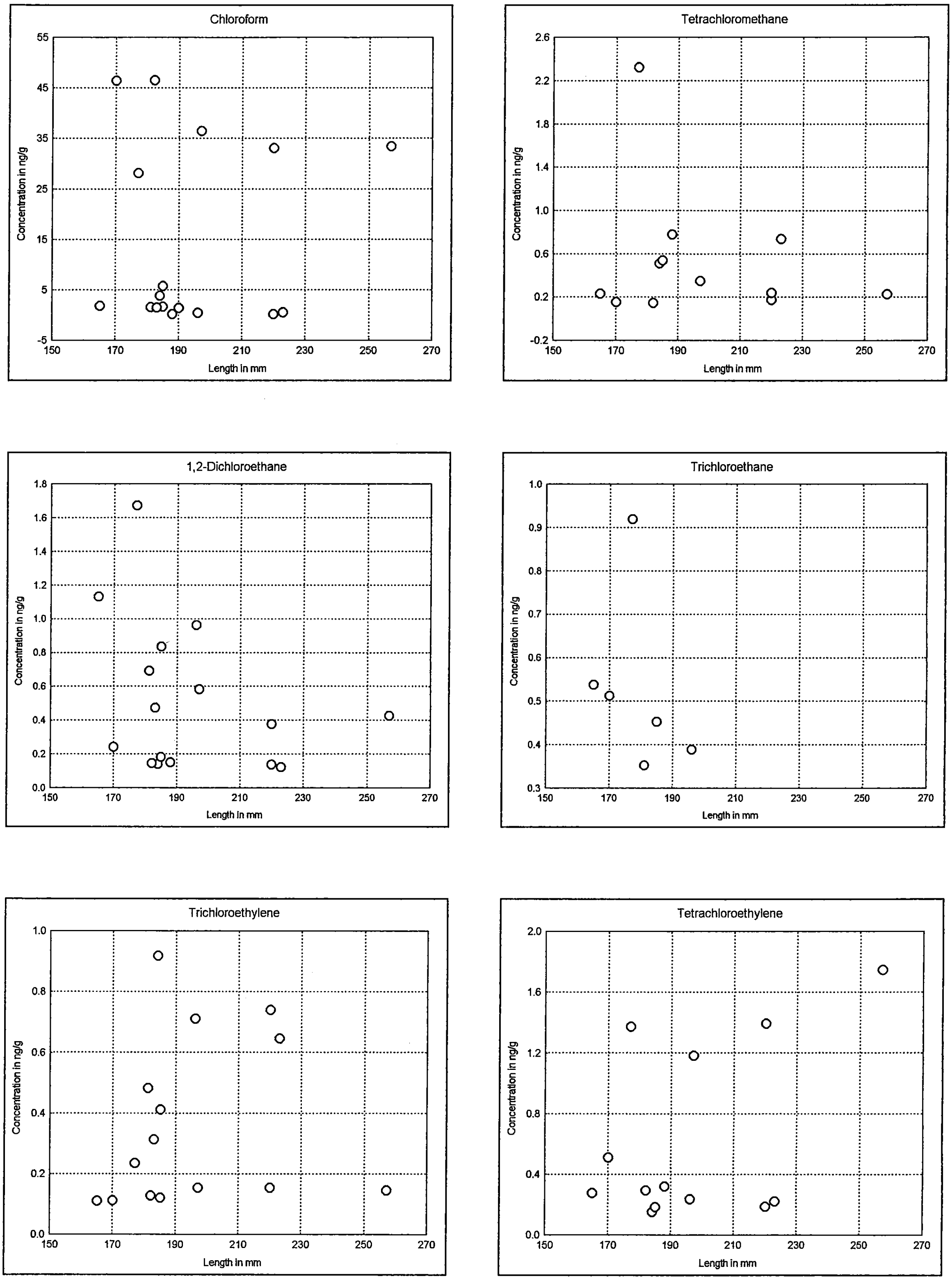


Figure III.4.33: Correlation between the length and chloroform (upper left), tetrachloromethane (upper right), 1,2-dichloroethane (middle left), trichloroethane (middle right), trichloroethylene (bottom left) and tetrachloroethylene (bottom right) in muscle tissue of dab.

III.4.1.3.3 Distribution of VOCs in liver tissue of dab

As above, the minimum, maximum, 25% percentile, 75% percentile, median, mean, standard deviation (SDs), standard error, coefficient of variation and the geometric mean was determined for VOCs in liver of dab originating from one sample. Although, 25 individual samples were initially analysed, the results of four had to be discarded for reasons of quality assurance. VOCs could be determined in all the other samples.

The results of the analyses are given in table II.4.33. The data set is again small for certain compounds such as tetrachloromethane.

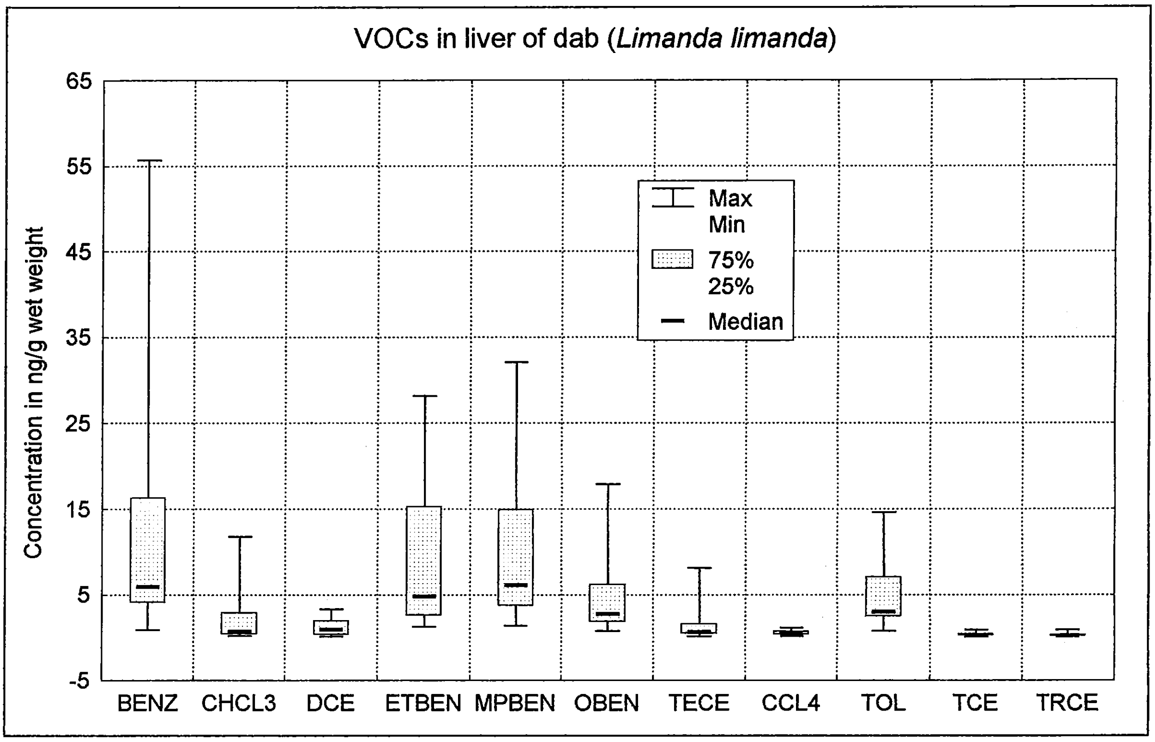
The results of the statistical analyses are given in table III.4.34. The variability of the concentrations is high and in the same order of magnitude as for muscle tissue. The discrepancy between the mean and the median is again high. This suggests that the values are not normally distributed. The variability and the distribution of the VOCs is illustrated in figure III.4.34.

Some rather high values, which could not be attributed to the analytical method, are in this case noted for benzene. The values for the most of the CHCs is in the same order of magnitude as those found in muscle tissue and in whiting. The values of the MAHs are however, considerably higher compared to those for muscle tissue and for whiting.

Table III.4.33: Concentrations in ng/g wet weight of VOCs in liver of dab (*Limanda limanda*) of one sampling location.

Sample	Benzene	Chloroform	1,2-Dichloro-ethane	Ethyl-benzene	m&p-Xylene	o-Xylene	Tetrachloro-ethylene	Tetrachloro-methane	Toluene	Trichloro-ethane	Trichloro-ethylene
Dab 1	26.92	nd	0.34	2.87	2.40	2.33	0.75	nd	8.53	0.22	0.26
Dab 2	15.24	1.78	2.13	24.80	3.57	11.88	0.73	nd	6.48	0.29	0.29
Dab 3	4.76	0.32	1.38	2.33	2.33	1.93	0.19	0.44	1.23	0.92	0.93
Dab 4	12.57	0.59	0.21	28.23	32.12	12.66	0.57	nd	3.81	0.23	0.30
Dab 5	55.74	1.49	1.12	19.33	19.74	1.99	0.72	nd	14.62	nd	0.28
Dab 6	0.95	0.53	2.87	3.42	3.89	1.74	0.36	nd	1.86	0.95	0.13
Dab 7	2.64	0.22	0.33	16.76	18.21	1.29	1.24	nd	7.75	0.32	0.42
Dab 8	1.93	0.75	2.14	11.77	11.64	7.42	0.55	nd	2.66	0.13	nd
Dab 9	25.84	0.78	0.87	1.38	8.67	5.84	0.48	nd	5.83	0.20	0.23
Dab 10	5.64	0.55	1.82	5.16	5.70	2.75	0.56	0.59	2.80	0.25	0.23
Dab 11	4.16	3.91	0.69	5.94	6.67	3.35	0.53	0.29	2.62	0.19	0.19
Dab 12	2.51	0.57	0.52	1.47	1.45	0.79	0.27	nd	0.83	nd	0.15
Dab 13	5.35	0.29	0.30	3.79	4.54	2.29	0.37	nd	2.35	nd	0.25
Dab 14	34.47	0.34	0.42	1.28	9.75	6.23	0.61	nd	9.92	0.30	0.32
Dab 15	7.44	0.30	3.36	4.58	4.97	3.29	1.81	nd	3.18	0.23	0.18
Dab 16	12.82	3.00	1.71	13.87	18.18	1.37	1.53	0.58	2.89	0.53	0.49
Dab 17	3.97	7.67	nd	1.97	2.36	1.41	1.72	0.21	1.54	0.25	0.14
Dab 18	5.17	1.85	nd	4.46	4.33	2.86	1.84	0.41	2.77	0.14	0.16
Dab 19	17.39	2.85	nd	24.95	29.18	17.91	8.15	1.17	11.53	0.58	0.76
Dab 20	6.29	11.85	nd	8.84	9.96	6.21	2.49	0.82	4.62	0.41	0.27
Dab 21	nd	9.44	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd = not detected



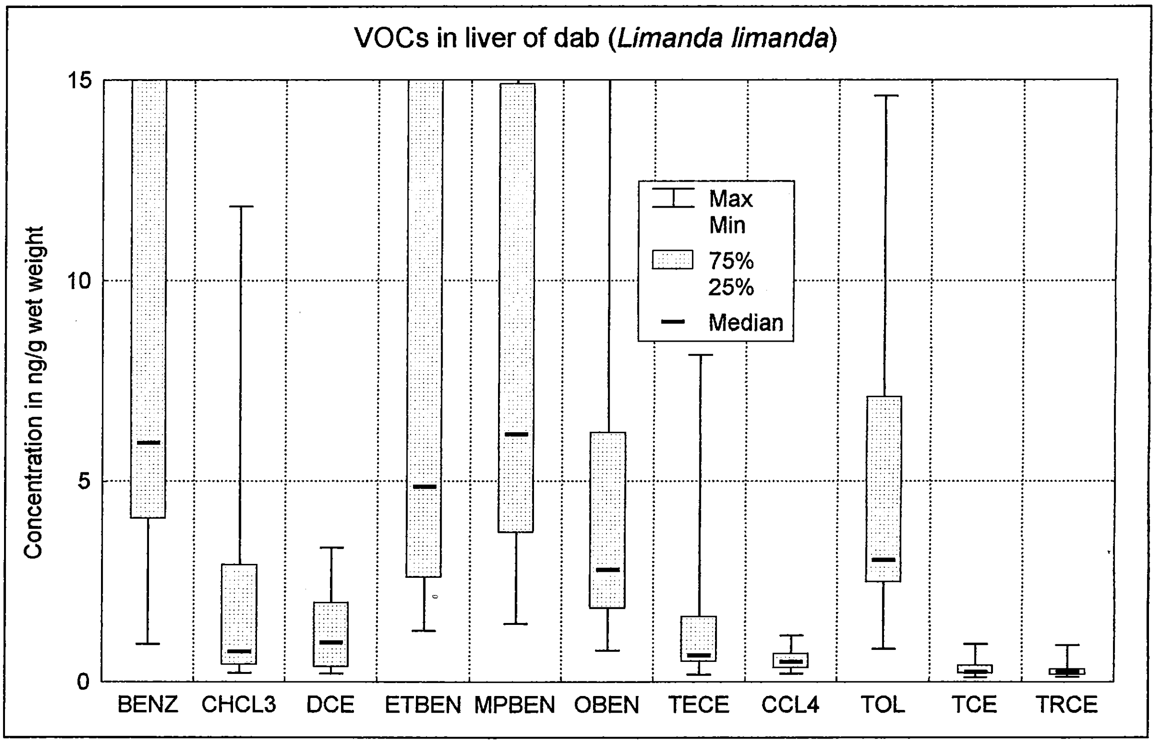


Figure III.4.34: Box and whisker plot of VOCs in liver tissue of dab. Overview (upper graph) and detail (lower graph) with BENZ = benzene, CHCL3 = chloroform, DCE = 1,2-dichloroethane, ETBEN = ethylbenzene, MPBEN = m&p-xylene, OBEN = o-xylene, TECE = tetrachloroethylene, CCL4 = tetrachloromethane, TOL = toluene, TCE = trichloroethane, TRCE = trichloroethylene.

Table III.4.34: Basic statistics of VOCs in liver of dab from one sample. The calculations were based on the concentrations expressed as ng/g wet weight.

Compound	n	Minimum	25% Percentile	Median	75% Percentile	Maximum	Mean	SD	SEM	CV	Geometric mean
Benzene	19	0.95	4.07	5.64	14.03	55.74	11.84	13.77	3.16	116%	7.10
Chloroform	20	0.22	0.43	0.76	2.92	11.85	2.45	3.34	0.75	136%	1.15
1,2-Dichloroethane	16	0.21	0.38	0.99	1.97	3.36	1.26	0.98	0.25	78%	0.90
m&p-Xylene	20	1.28	2.60	4.87	15.31	28.23	9.36	8.88	1.99	95%	5.86
Ethylbenzene	20	1.45	3.73	6.19	14.91	32.12	9.98	8.99	2.01	90%	6.90
o-Xylene	20	0.79	1.83	2.81	6.22	17.91	4.78	4.58	1.02	96%	3.33
Tetrachloroethylene	20	0.19	0.50	0.66	1.63	8.15	1.27	1.74	0.39	137%	0.81
Tetrachloromethane	8	0.21	0.35	0.51	0.71	1.17	0.57	0.31	0.11	55%	0.50
Toluene	20	0.83	2.49	3.04	7.12	14.62	4.89	3.79	0.85	77%	3.72
Trichloroethane	17	0.13	0.22	0.25	0.32	0.95	0.36	0.25	0.06	69%	0.30
Trichloroethylene	19	0.13	0.18	0.26	0.31	0.93	0.31	0.21	0.05	67%	0.27

n = number of samples, SD = standard deviation, SEM = standard error of the mean, CV = coefficient of variation

A Kolmogorov-Smirnov test was again used to determine whether the distribution is normal. The results of these tests are given in table III.4.35.

Table III.4.35: Results of the Kolmogorov-Smirnov test for VOCs in liver of dab.

Compound	KS distance	P value	Passed normality test (*=0.05)?
Benzene	0.2567	P > 0.10	Yes
Chloroform	0.2722	P > 0.10	Yes
1,2-Dichloroethane	0.1572	P > 0.10	Yes
m&p-Xylene	0.25	P > 0.10	Yes
Ethylbenzene	0.2012	P > 0.10	Yes
o-Xylene	0.2725	P > 0.10	Yes
Tetrachloroethylene	0.2725	P > 0.10	Yes
Tetrachloromethane	0.2148	P > 0.10	Yes
Toluene	0.224	P > 0.10	Yes
Trichloroethane	0.2687	P > 0.10	Yes
Trichloroethylene	0.2799	P > 0.10	Yes

The tests indicate that concentrations of all the VOCs under investigation are normally distributed in liver tissue of dab. This does however not mean that a normal distribution can be assumed as the sample size is generally small (see earlier). The test only indicates that the P values, those cases, are not inconsistent with a Gaussian population. To further investigate the distribution of the VOCs in muscle tissue of dab, a normal probability plot was made for each compound. The results of these test are given in figures III.4.35 to III.4.36.

The plots indicate a considerable deviation of the expected straight line with perhaps the exception of tetrachloromethane (only 8 values!). It was therefore assumed that the concentrations of VOCs in liver of dab are not normally distributed and statistical comparisons were made accordingly.

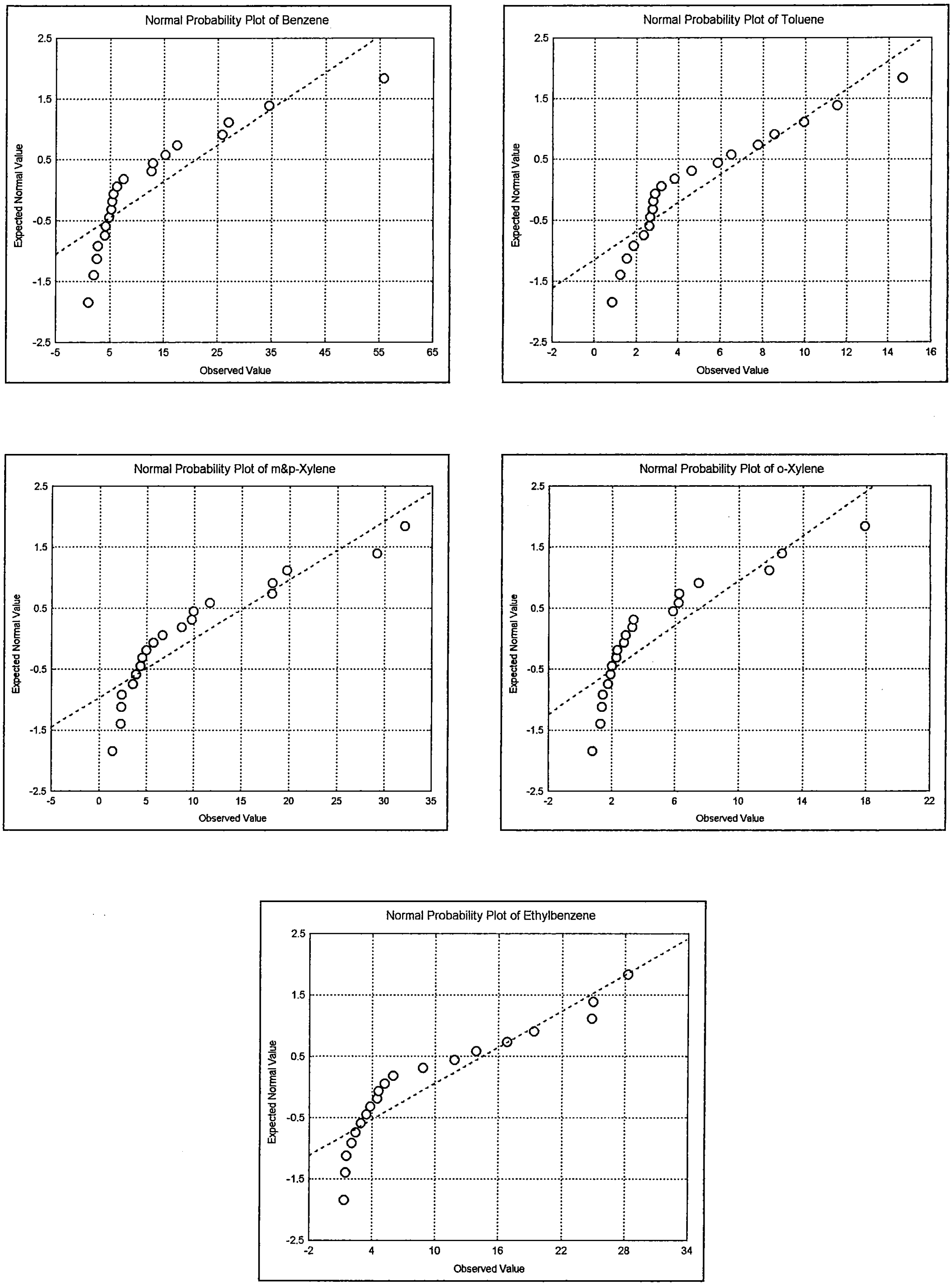


Figure III.4.35: Normal probability plot of benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in liver tissue of dab.

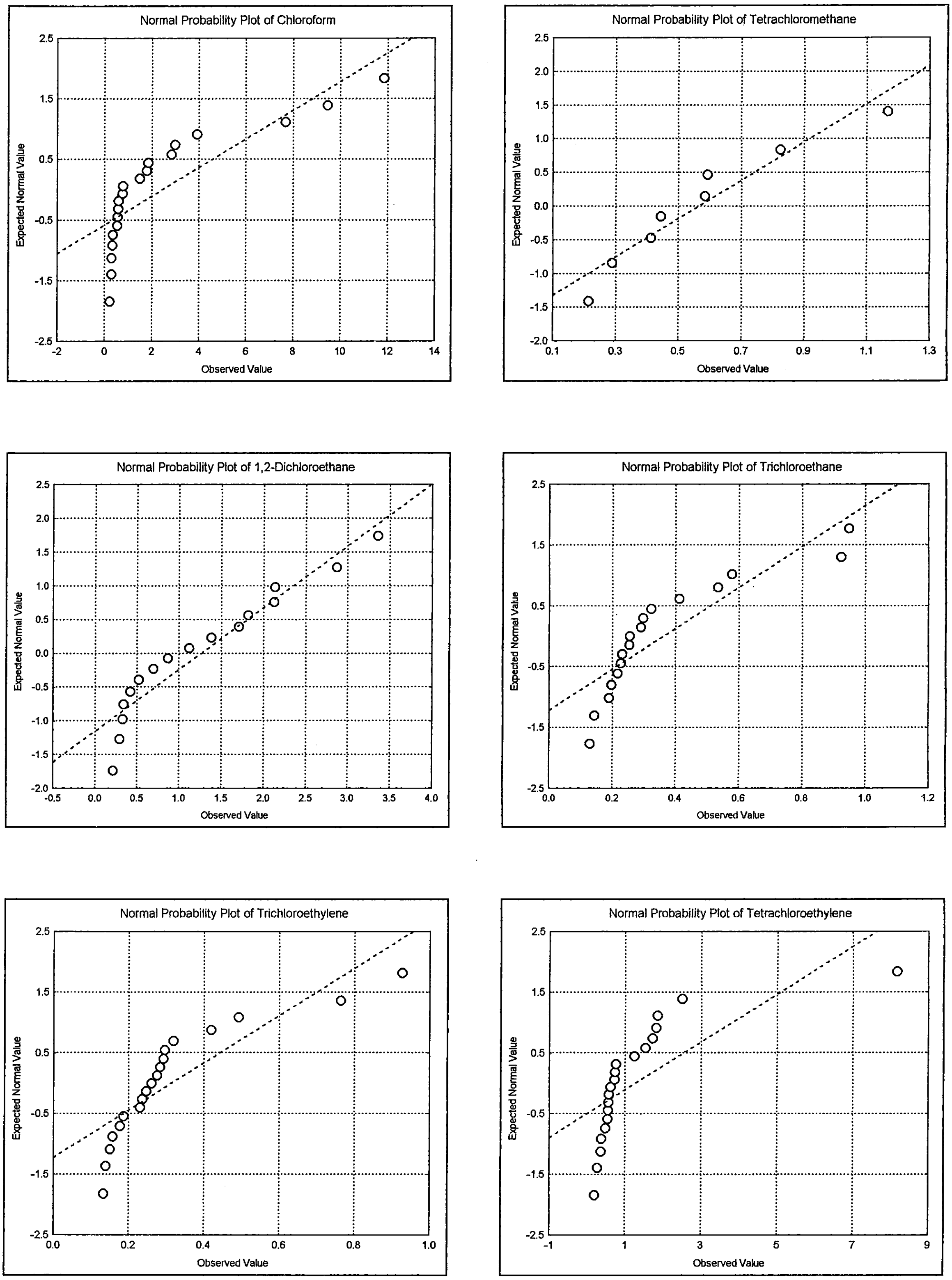


Figure III.4.36: Normal probability plot of chloroform (upper left), tetrachloromethane (upper right), 1,2-dichloroethane (middle left), trichloroethane (middle right), trichloroethylene (bottom left) and tetrachloroethylene (bottom right) in liver tissue of dab.

III.4.1.3.4 Correlation between size and the concentration of VOCs in liver tissue of dab

As for muscle tissue, the concentration of VOCs were correlated with the length of the fish. The non parametric test of Spearman was again used, in view of the assumed non Gaussian distribution of the concentration of VOCs in liver. The results of the analyses are given in table III.4.36 and illustrated in figures III.4.37. to III.4.38.

Table III.4.36: Results of the correlation analysis between fish size and the VOC concentration in liver of dab.

Parameter	Number of XY Pairs	Spearman r	95% confidence interval	P value (two-tailed)	P value summary
Benzene	20	-0.26	-0.64 to 0.22	0.2669	ns
Chloroform	20	-0.15	-0.57 to 0.32	0.5216	ns
1,2-Dichloroethane	16	-0.05	-0.54 to 0.47	0.8537	ns
m&p-Xylene	20	-0.20	-0.60 to 0.28	0.4004	ns
Ethylbenzene	20	-0.35	-0.69to 0.13	0.1325	ns
o-Xylene	20	-0.13	-0.55 to 0.34	0.5751	ns
Tetrachloroethylene	20	0.03	-0.43 to 0.47	0.9146	ns
Tetrachloromethane	8	-0.12	0.79	na	ns
Toluene	20	-0.35	-0.69 to 0.12	0.1298	ns
Trichloroethane	17	0.00	-0.49 to 0.49	1	ns
Trichloroethylene	19	-0.19	-0.61 to 0.30	0.4274	ns

ns = not significant, na = not applicable, r = correlation coefficient

In none of the cases a significant relation between the length and the VOC concentration could be established. The conclusion is therefore that the concentration of VOCs in liver of dab is independent of the size of the fish.

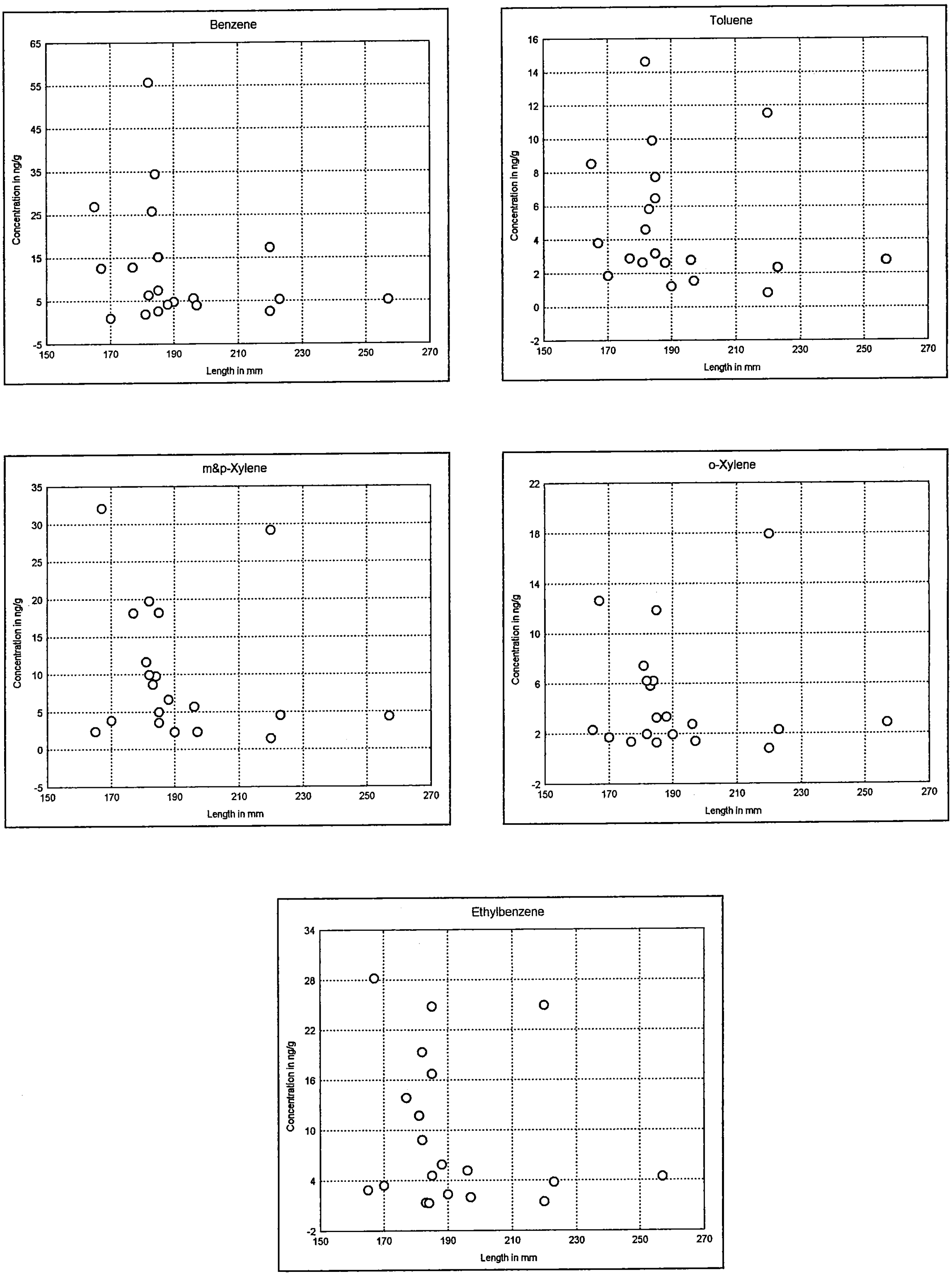


Figure III.4.37: Correlation between the length and benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom) in liver tissue of dab.

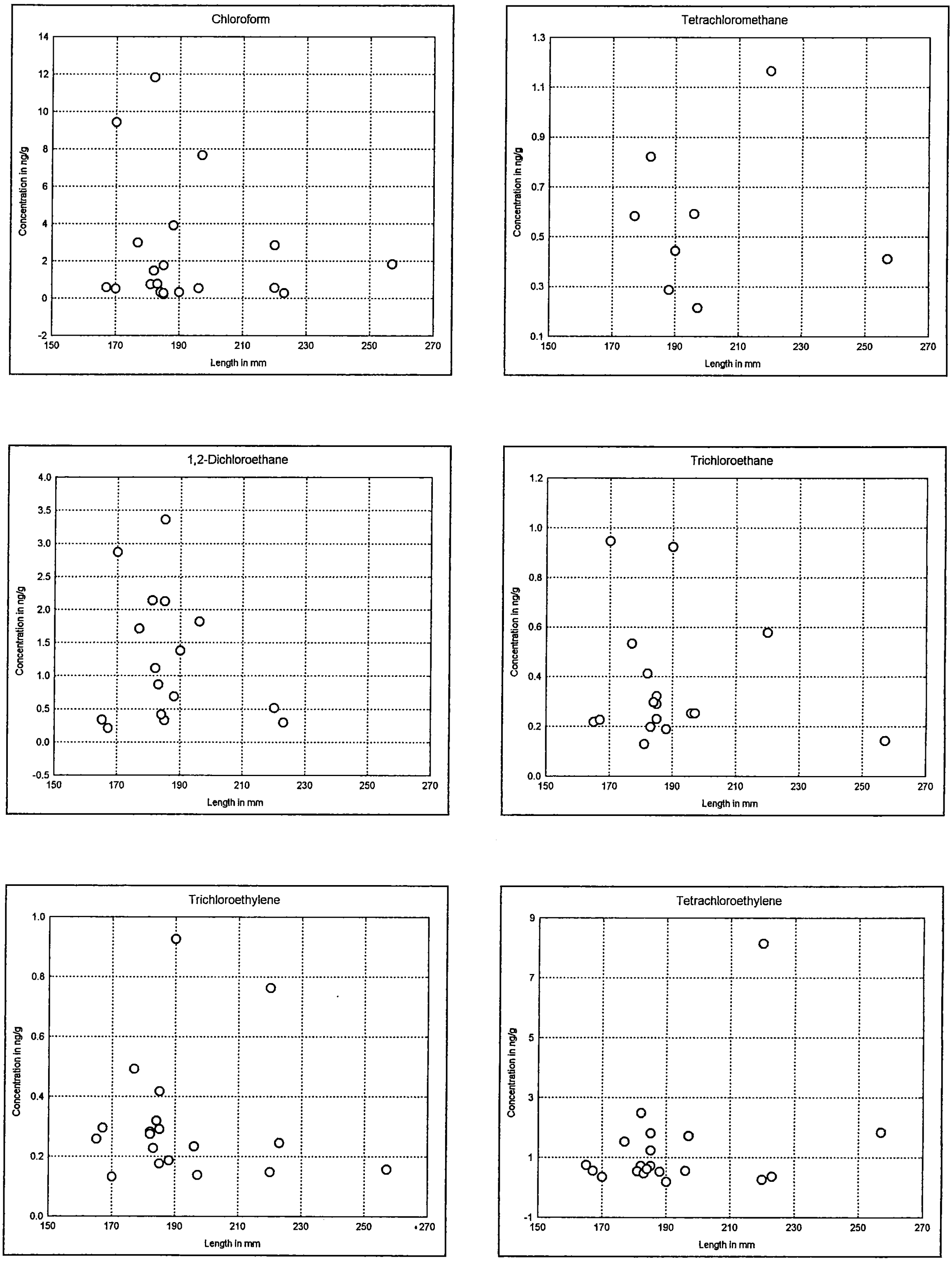


Figure III.4.38: Correlation between the length and chloroform (upper left), tetrachloromethane (upper right), 1,2-dichloroethane (middle left), trichloroethane (middle right), trichloroethylene (bottom left) and tetrachloroethylene (bottom right) in liver tissue of dab.

III.4.1.3.5 Comparison of the concentrations of VOCs in liver and muscle tissue of dab

The interspecimen distribution of VOCs in dab was investigated by comparing the concentrations in liver and muscle tissue. The rationale behind these test was, as for whiting, to determine whether differences occur within the same specimen, as a result of differences in uptake, metabolisation or storage.

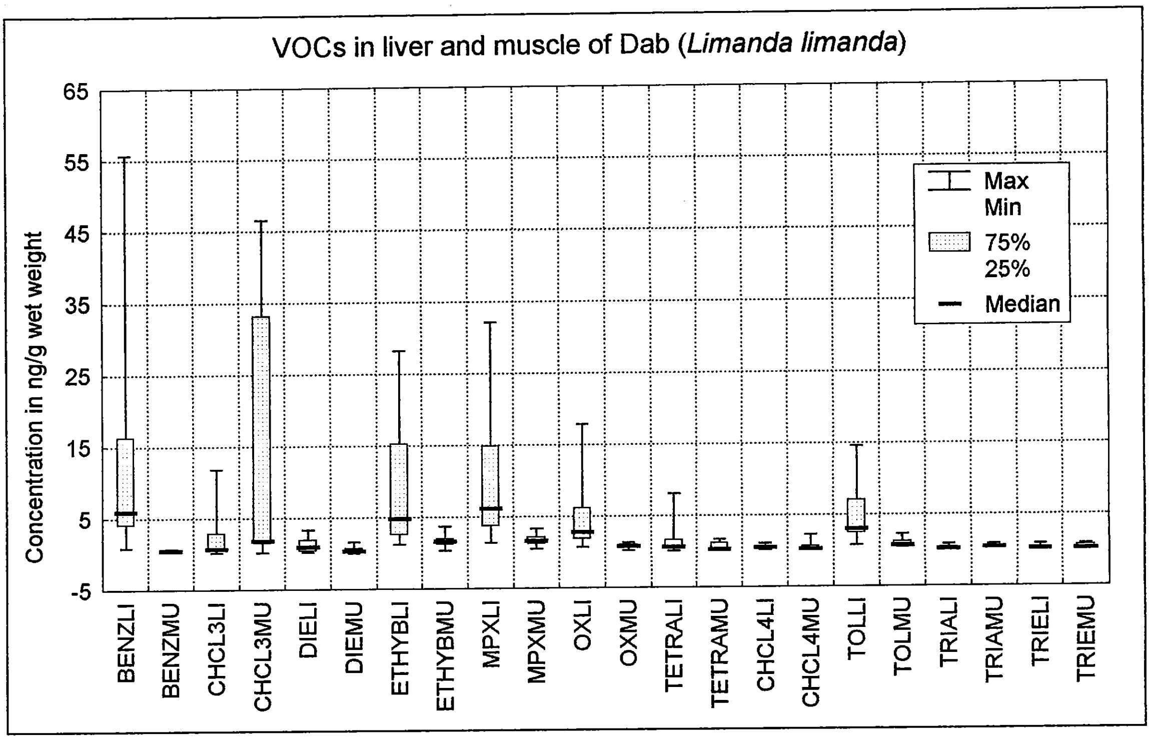
Concentrations in liver and muscle tissue were first compared with the Mann-Whitney test. The results of this comparison is given in table III.4.37. The concentration differences between liver and muscle tissue are further illustrated in figure III.4.39.

Table III.4.37: Results of the comparison of VOC concentrations in liver and muscle.

Mann Whitney test	Mann-Whitney U	P value	P value summary
Benzene	0	P<0.0001	**
Ethylbenzene	0	P<0.0001	**
m&p-Xylene	22	P<0.0001	**
o-Xylene	10	P<0.0001	**
Toluene	13	P<0.0001	**
Chloroform	113	0.0851	*
Tetrachloromethane	33	0.2633	ns
1,2-Dichloroethane	62	0.0136	**
Trichloroethane	33	0.2633	ns
Trichloroethylene	130	0.6773	ns
Tetrachloroethylene	71	0.0312	**

ns not significant, * significant at 90 % level, ** significant at 95 %level

On seven occasions concentrations were significantly different at the 95 % level in muscle tissue compared to liver tissue. Especially the concentrations of MAHs are a lot higher in the liver than in muscle tissue. As the liver is the main organ for metabolisation of exogenic compounds, the observed difference could well be related to metabolisation. For the CHCs significantly higher concentrations in the liver are only found for tetrachloroethylene and 1,2-dichloroethane. Contrarily, the concentration of chloroform is significantly higher in muscle tissue when the significancy level is set at 90 %. These finding can be readily observed in figure III.4.85.



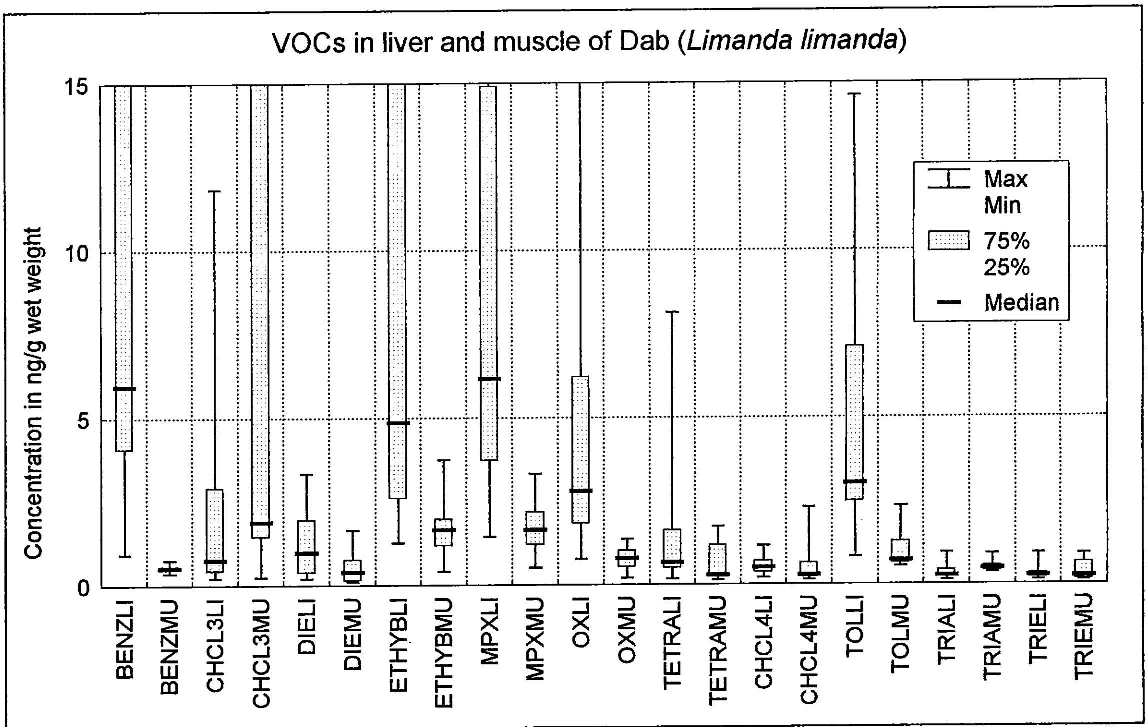


Figure III.4.39: Comparison of the concentrations of VOCs in liver and muscle tissue of dab. Overview (upper) and detail (lower) with BENZ = benzene, CHCL3 = chloroform, DIE = 1,2-dichloroethane, ETHYB = ethylbenzene, MPX = m&p-xylene, OX = o-xylene, TETRA = tetrachloroethylene, CHCL4 = tetrachloromethane, TOL = toluene, TRIA = trichloroethane, TRIE = trichloroethylene, LI = liver and MU = muscle tissue.

Correlation in liver and muscle were further correlated with each other to determine if a relation exists between them. The results of the non parametric Spearman correlation analysis are given in table III.4.38. The relation between the concentration in both tissue types is further illustrated in figures III.4.40 and III.4.41.

Table 4.III.38: Results of the correlation analyses between the concentrations of VOCs in muscle and liver tissue in dab.

Parameter	Number of XY Pairs	Spearman r	P value (two-tailed)	P value summary
Benzene	15	0.07	0.8101	ns
Chloroform	16	0.55	0.0273	**
1,2-Dichloroethane	11	0.30	0.3701	ns
m&p-Xylene	15	-0.30	0.2773	ns
Ethylbenzene	17	0.18	0.48	ns
o-Xylene	15	-0.07	0.8003	ns
Tetrachloroethylene	12	0.57	0.0513	*
Tetrachloromethane	5	-0.10	na	ns
Toluene	14	0.15	0.6154	ns
Trichloroethane	6	0.54	na	ns
Trichloroethylene	13	0.08	0.8028	ns

ns = not significant, ** significant at the 95 % level, significant at the 90 % level, na = not applicable

On two occasions a significant positive correlation was observed, namely for chloroform (at the 95 % level) and for tetrachloroethylene (at the 90 % level). This would indicate, at least for those compounds, that higher concentrations in one tissue result in higher concentrations in another or that tissue are equally affected by the contamination. Similar observations have already been made for CBs (Roose, unpublished results). The CB concentrations in cod (*Gadus morhua*) liver and muscle tissue and flounder (*Platichtys flesus*) liver and muscle tissue are also positively correlated. The significance of these observations requires further study, but it could be assumed that this is the result of identical uptake mechanisms for both tissue types. Looking at the plot for the MAHs leads to the observation that for increased concentration in muscle tissue, there is no similar increase in the concentration in the liver.

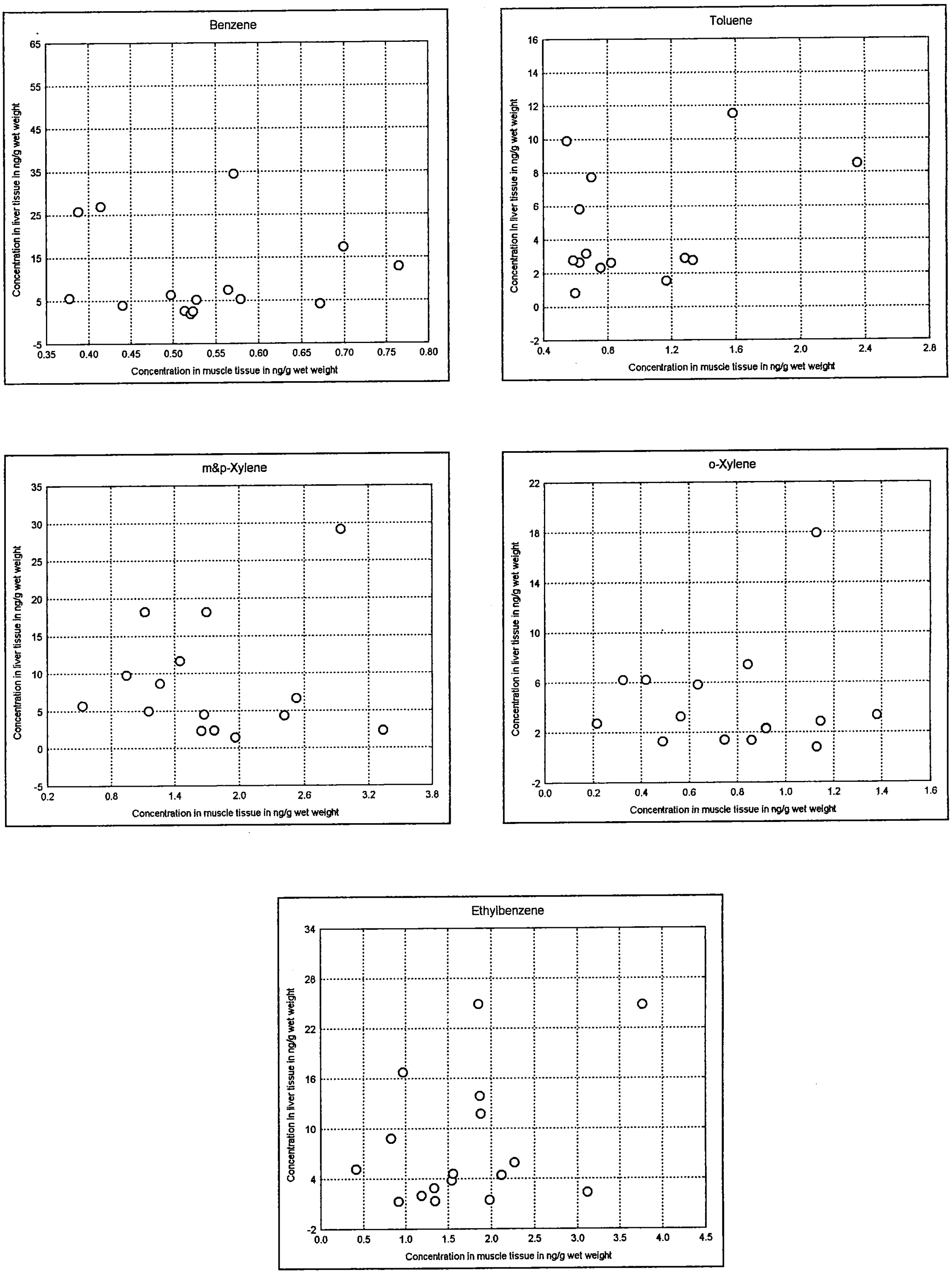


Figure III.4.40: Correlation between the concentrations in muscle tissue and liver of dab for benzene (upper left), toluene (upper right), m&p-xylene (middle left), o-xylene (middle right) and ethylbenzene (bottom).

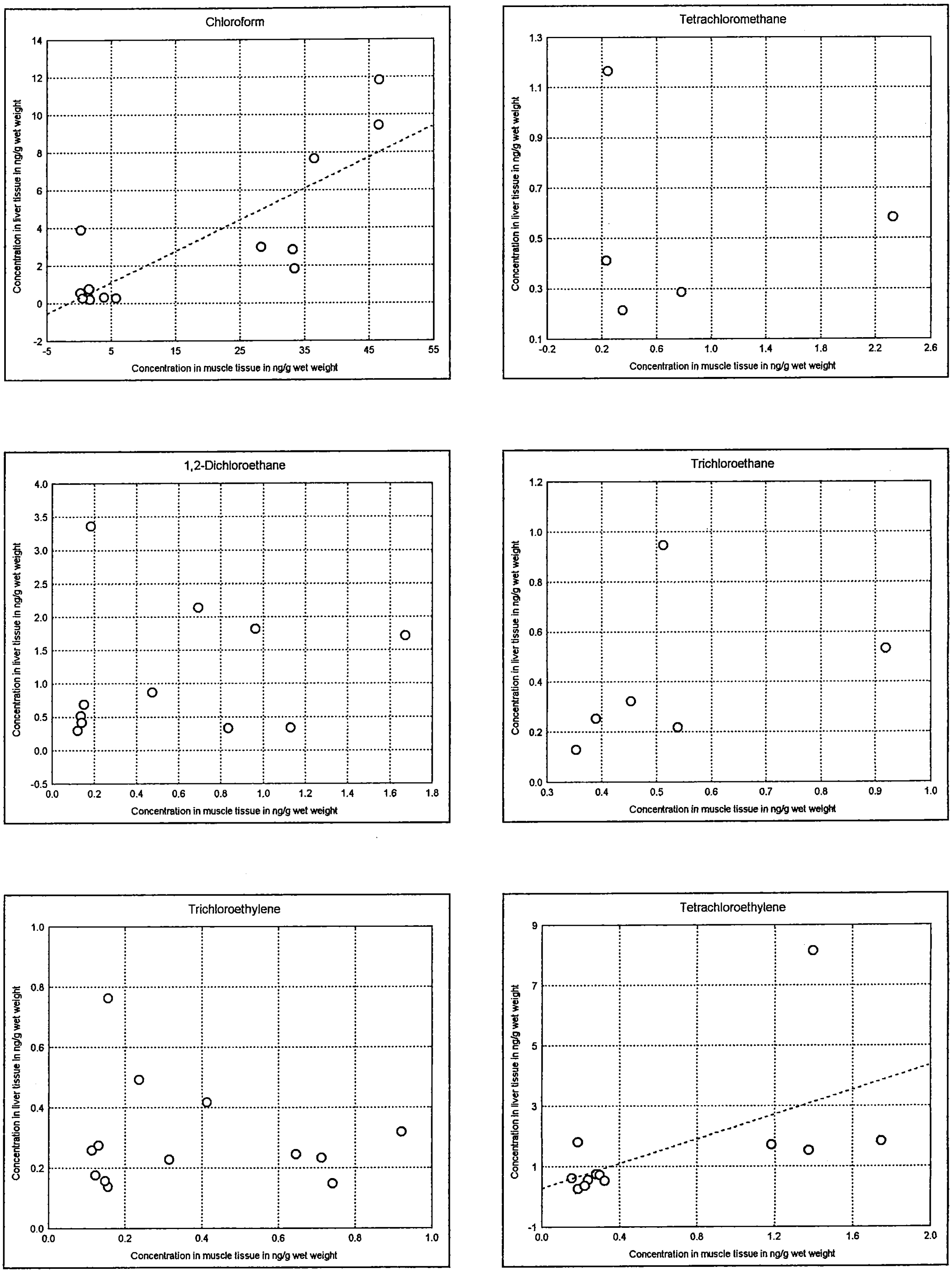


Figure III.4.41: Correlation between the concentrations in muscle tissue and liver of dab for chloroform (upper left), tetrachloromethane (upper right), 1,2-dichloroethane (middle left), trichloroethane (middle right), trichloroethylene (bottom left) and tetrachloroethylene (bottom right).

III.4.2. RESULTS OF THE MONITORING CAMPAIGN

III.4.2.1 INTRODUCTION

Although a analytical method was developed that allowed the determination of VOCs in marine biota with sufficient sensitivity, reproducibility and recovery, the method was still hampered by substantial practical problems. Frequent leaks, system contamination due to high concentrations, severe background concentrations caused frequent system cleaning and system downtime. A system of QA allowed proper action but this resulted in a slow sample processing and frequent discards of analysis results. Moreover, when taking into account that an average analysis step takes about 2 hours, it becomes obvious that the number of samples that is likely to be processed during a day is small. In view of future monitoring robustness of methodology and speed of sample processing should in any case be considerably improved. A lot of effort is currently undertaken to realise both. As a result it proved impossible to comply with the quantity of samples set forth at the onset of the programme. The choice was therefore made to consider more time to the study of the interspecies and specimen distribution and to give priority to study a selected number of situations rather than trying to deal with a lot of issues incompletely. The monitoring campaign was used to consider the following questions of primary importance. In the first instance the seasonal variability of the concentrations of VOCs in fish from selected monitoring stations. Secondly, the importance of spatial distribution of the concentrations for a given season was considered. Finally, concentrations in different organisms were compared with each other and with the concentrations reported preciously in literature. The entire list of analysis results is in annex.

III.4.2.2 SEASONAL VARIATION OF VOCS IN MARINE BIOTA

III.4.2.2.1 Introduction

To determine the seasonal variability, the analysis results of the samples that were collected on five occasions in 1995, roughly representing the four seasons, at the five sampling stations (figure III.4.42) were selected. A total of 4 species could be considered, namely shrimp (*Crangon crangon*), whiting (*Merlangius merlangus*), dab

(*Limanda limanda*) and the bivalve *Spisula subtruncata*. When available liver and muscle tissue of the fish were processed separately. For the fish, 5 samples were individually analysed. For shrimp a pooled sampled of about 100 individuals was analysed. For the bivalve, a pooled sample of about 10 specimens was analysed. The results allowed to compare the seasonal variation at three different sampling stations namely 120, 780 and B07 which represent respectively the west coast, the east coast and the Scheldt estuary.

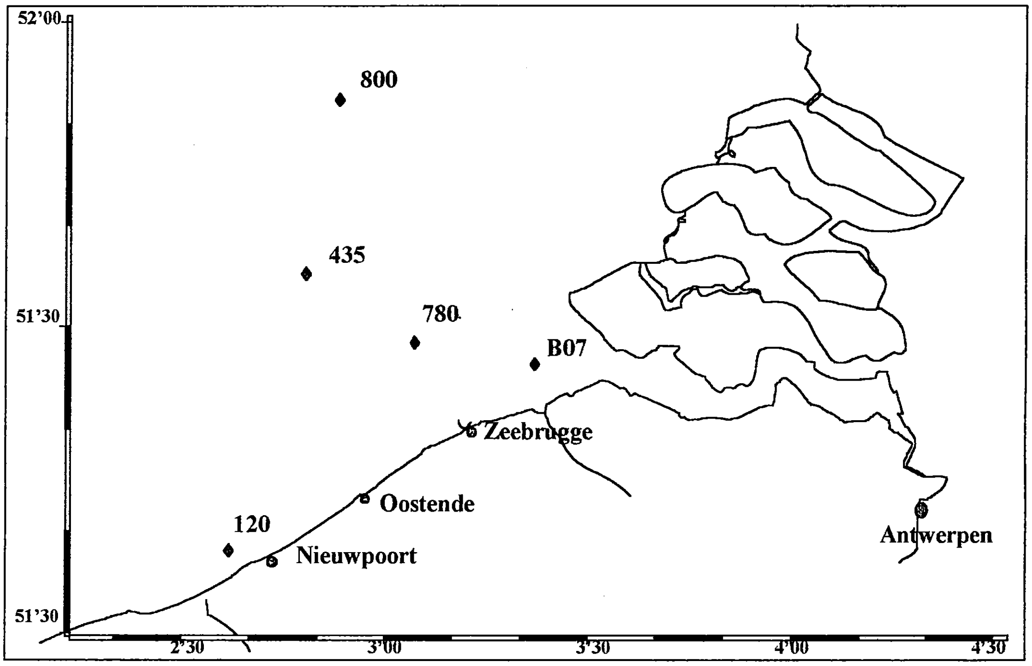
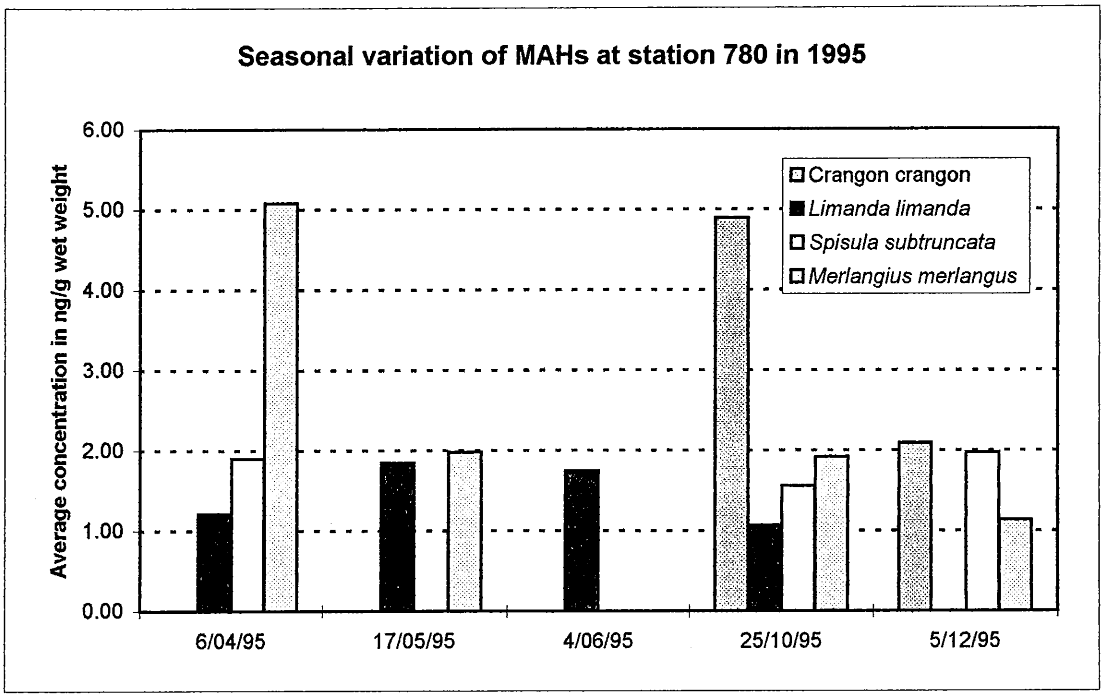


Figure 4.III.42: Sampling locations on the Belgian continental shelf (BCP).

III.4.2.2.2 Results and discussion

The seasonal variability of the different sampling stations is illustrated in figures III.4.43 to III.4.45. No sound statistical comparisons were possible because of the limited data set and the large interspecies variability (see earlier).



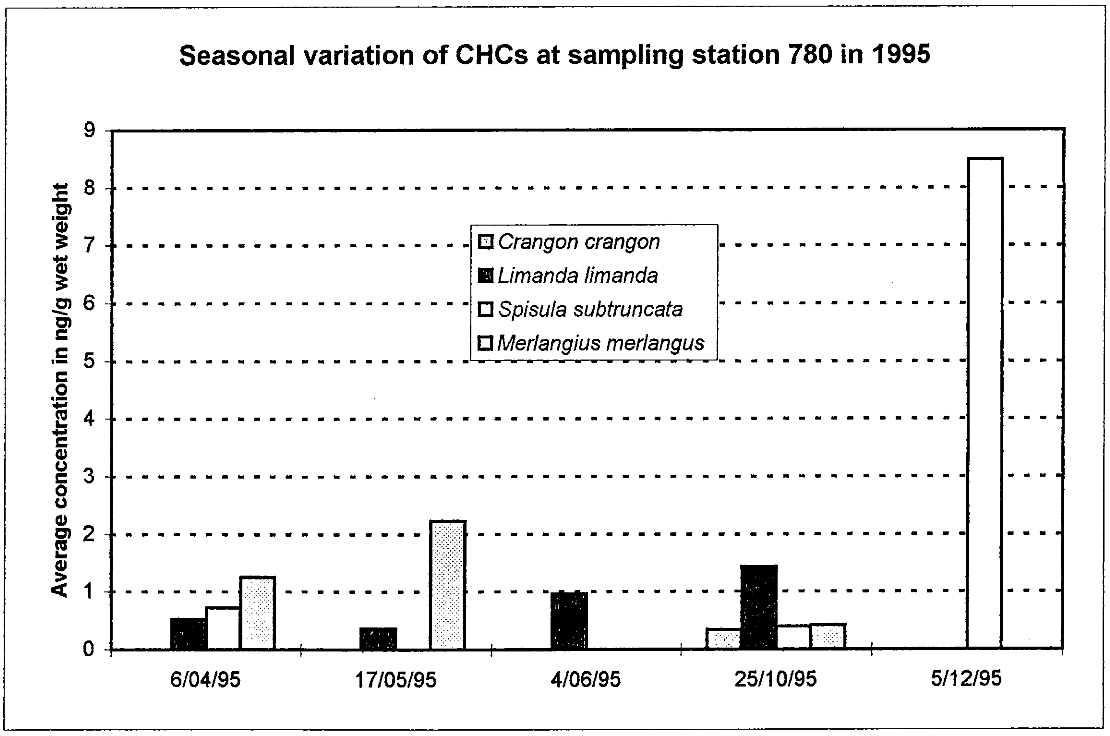
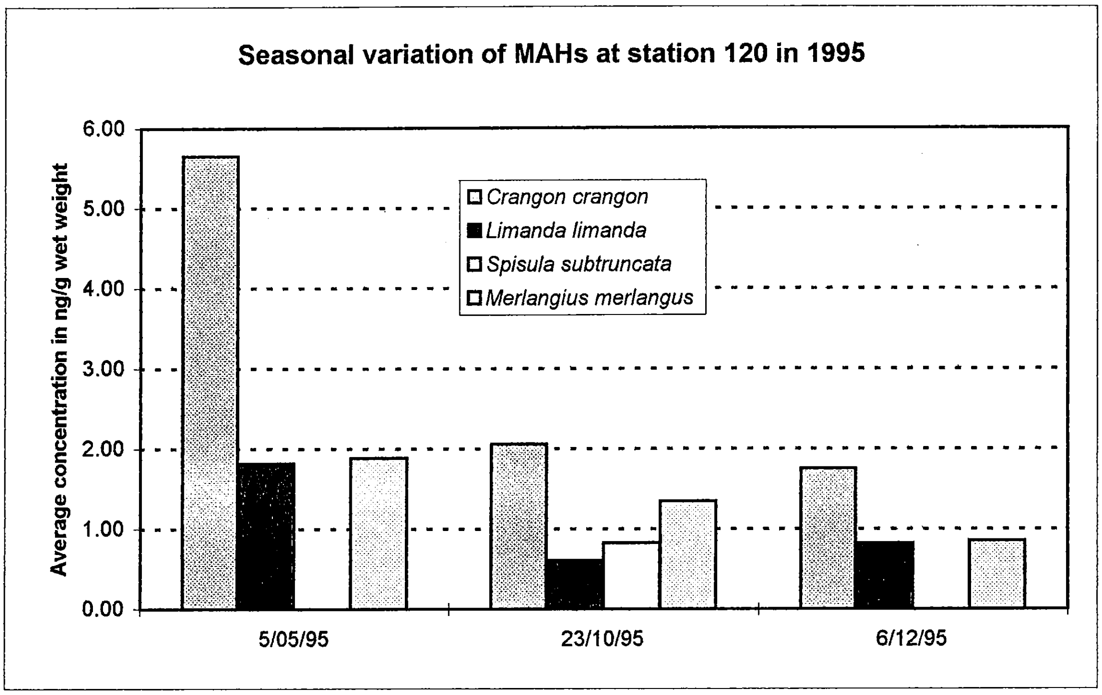


Figure III.4.43: Seasonal variation of MAHs (upper) and CHCs (lower) in the *species Crangon crangon, Limanda limanda, Spisula subtruncata* and *Merlangius merlangus* at station 780 in 1995.



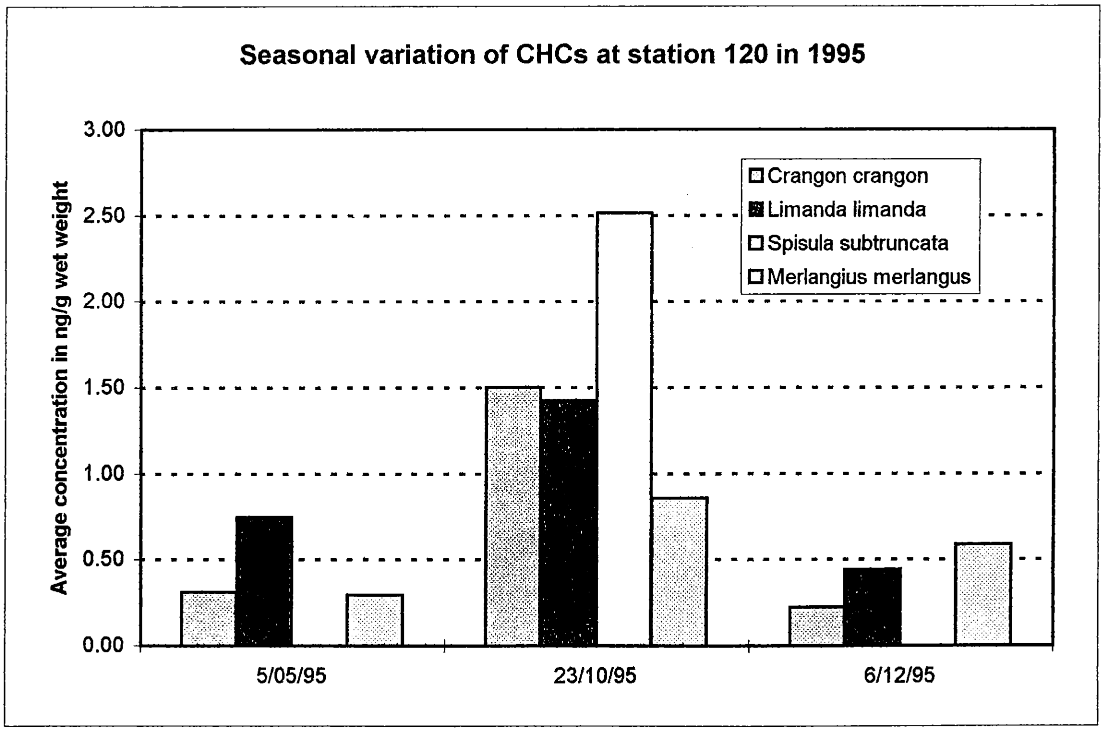
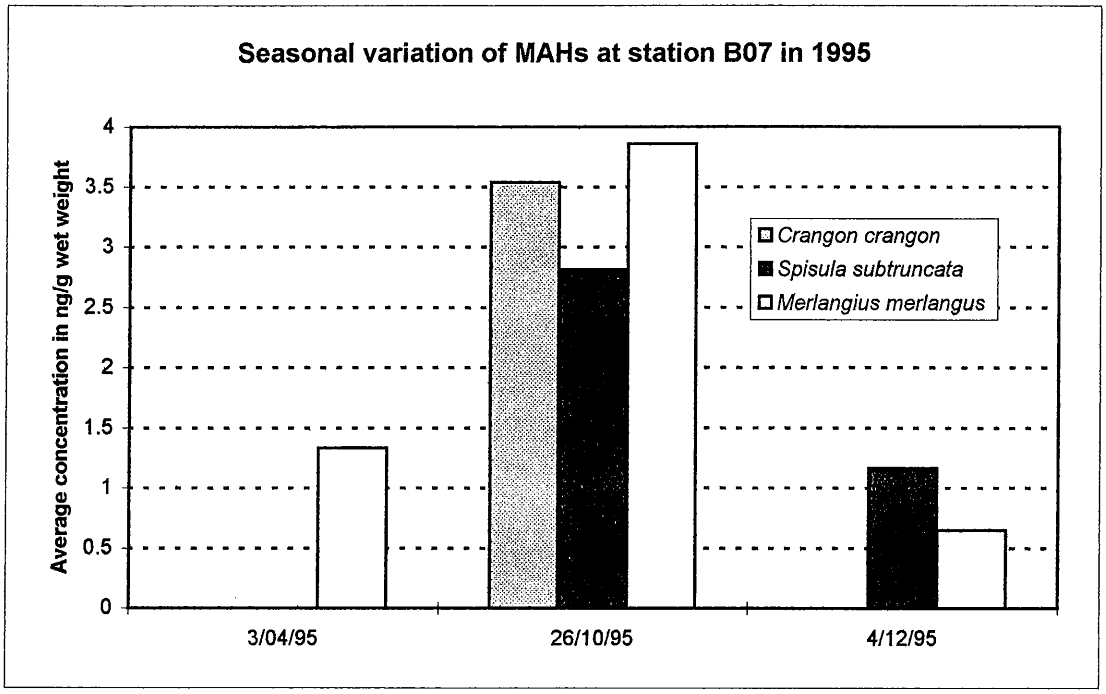


Figure III.4.44: Seasonal variation of MAHs (upper) and CHCs (lower) in the *species Crangon crangon, Limanda limanda, Spisula subtruncata* and *Merlangius merlangus* at station 120 in 1995.



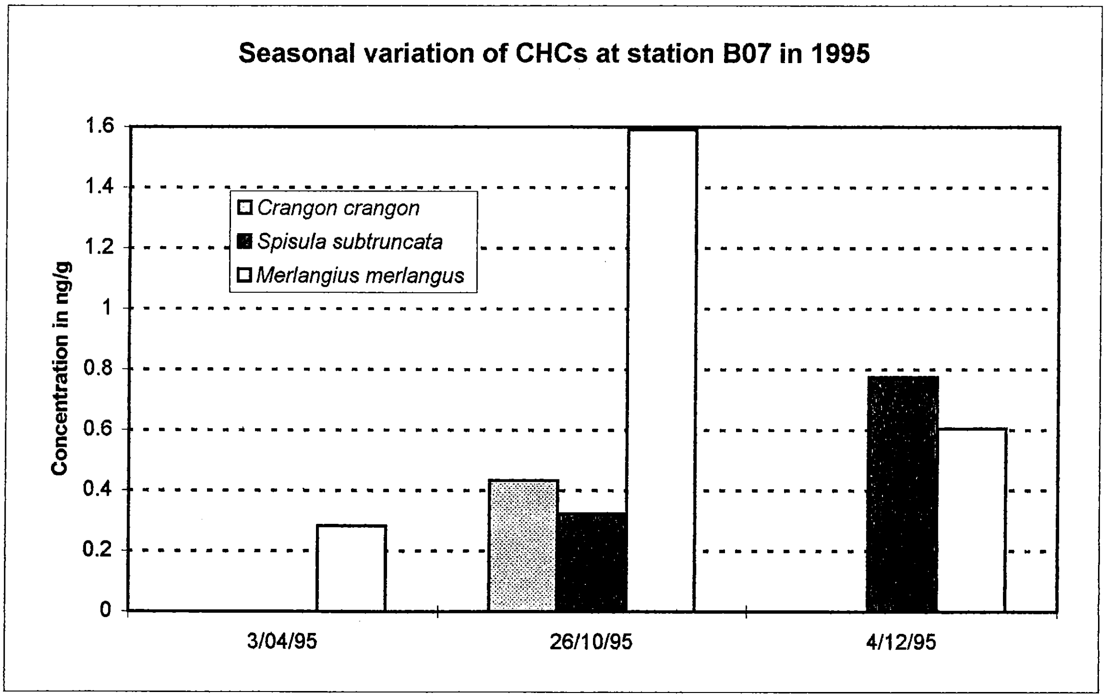


Figure III.4.45: Seasonal variation of MAHs (upper) and CHCs (lower) in the *species Crangon crangon, Limanda limanda, Spisula subtruncata* and *Merlangius merlangus* at station B07 in 1995.

For reasons of availability of data, the different VOCs were not considered individually but grouped into MAHs and CHCs. The results for station 780 (figure III.4.93) show that for both fish species and the bivalve, no significant variability can be observed for MAHs. For shrimp, however, there is a noticeable difference between the beginning of the year, when no detectable levels are observed, and the end of the year were relatively high concentrations are observed. This pattern is not present when the concentrations of CHCs are considered. No seasonal variability can again be observed for the concentrations of the CHCs in fish. A distinct variation is at first glance observed for the bivalve with much higher concentrations in winter. These observations should however be treated with considerable caution. In the previous section it was already demonstrated that the natural variability is high, with CVs of up to 200%. It is therefore quite possible that the observed differences are solely caused by this natural variability.

III.4.2.3 SPATIAL DISTRIBUTION OF VOCS DURING ONE SAMPLING PERIOD

III.4.2.3.1 Introduction

To determine the spatial distribution, the samples collected at the five locations (figure III.4.92) during the winter period of 1995 were selected. For this period detectable levels were available for nearly all species at all stations. Shrimp (*Crangon crangon*), whiting (*Merlangius merlangus*), dab (*Limanda limanda*) and the bivalve *Spisula subtuncata* were again selected as the species of choice. When available liver and muscle tissue of the fish were processed separately. For the fish, 5 samples were individually analysed. For shrimp a pooled sample of about 100 individuals was analysed. For the bivalve, a pooled sample of about 10 specimens was analysed. The different VOCs were again not treated as individual concentrations but grouped into MAHs and CHCs.

III.4.2.3.2 Results and discussion

The average concentrations of MAHs and CHCs for different sampling locations during one season are illustrated in figure III.4.46 and III.4.47.

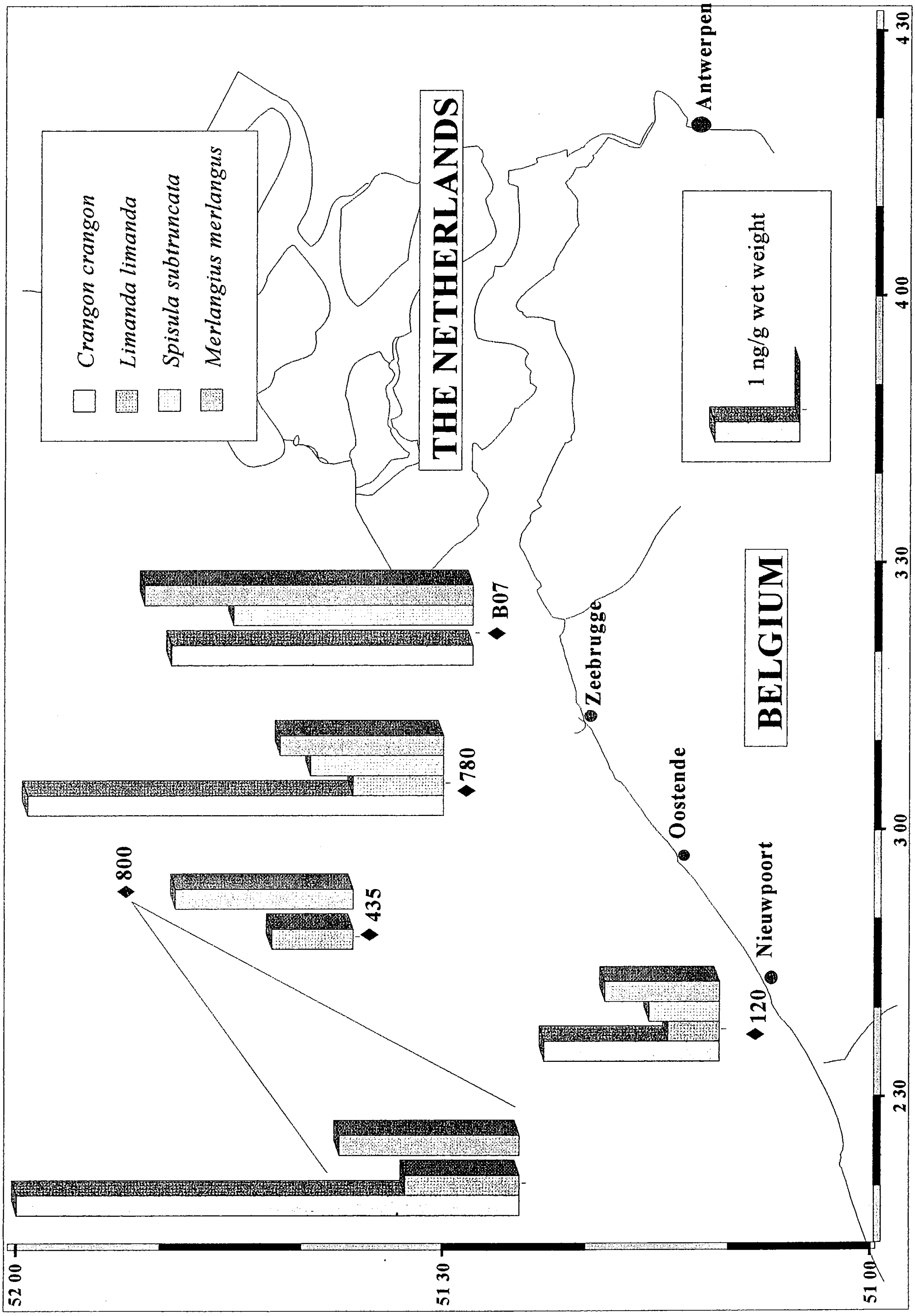


Figure III.4.46: Spatial distribution of MAHs in the *species Crangon crangon, Limanda limanda, Spisula subtruncata* and *Merlangius merlangus* at station 780 in the winter of 1995.

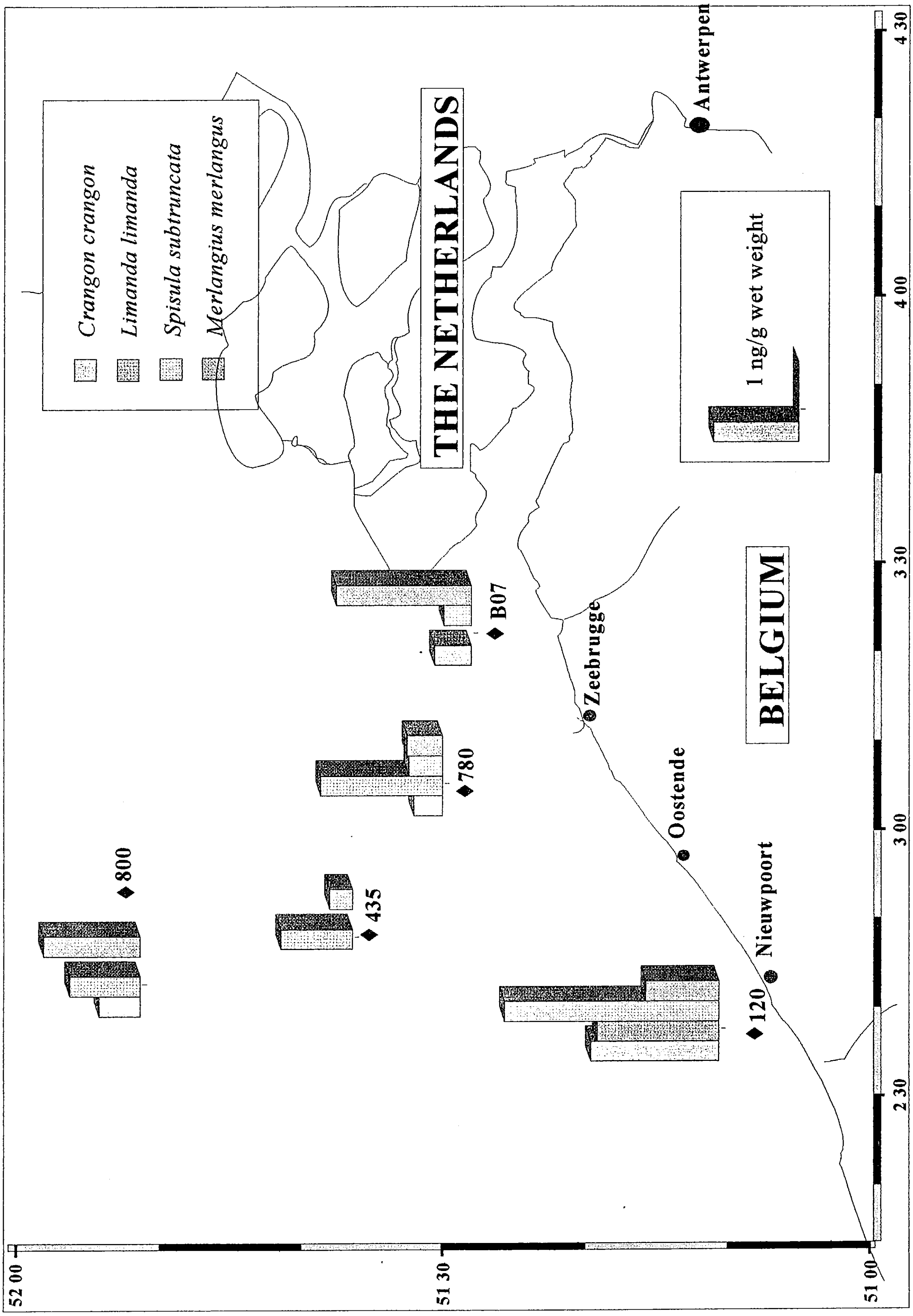


Figure III.4.47: Spatial distribution of CHCs (in the *species Crangon crangon, Limanda limanda, Spisula subtruncata* and *Merlangius merlangus* at station 780 in the winter of 1995.

Little spatial variation can be observed from the graphs, with perhaps the exception of slightly elevated MAHs concentrations in the Scheldt estuary, north of the harbour entrance of Zeebrugge (station 780, figure III.4.96) and surprisingly at station 800. CHC concentrations appear also higher on the west coast (point 120). The significance of if these differences should be considered with the necessary caution as the natural variability is high. For all practical purposes, the Belgian Continental Shelf (BCP) could be considered as one zone. It would therefore be interesting to analyse samples from other regions of the North Sea and to compare the values with those found on the BCP.

III.4.2.4 COMPARISON OF THE VOC CONCENTRATIONS IN THE DIFFERENT SPECIES

III.4.2.4.1 Introduction

From the previous paragraph it can be concluded that there is no marked seasonal and spatial distribution of VOCs in marine organisms. The observed variability would therefore only be the result of the natural variability of the concentration of these compounds in fish. This should, however, again be treated with the appropriate caution. Accepting the facts mentioned above, the concentrations of the different VOCs observed for one year could be averaged and the differences between the species could be investigated with a lot more data. This was done for the 1995 and 1993 data for all the species and tissues under investigation.

III.4.2.4.2 Results and discussion

The average concentrations for the different species and tissues in 1995 are illustrated in figure III.4.98. An overview of the average concentrations for the different species and tissues in 1993 is given in figure III.4.99 and in detail in figure III.4.100. One of the most remarkable observations is the fact that on average the concentrations of ethylbenzene, m&p-xylene and o-xylene are the highest in shrimp, both in 1993 and 1995. These compounds seem further the most important as far as their concentration is concerned. Record concentrations of tetrachloromethane and trichloroethylene were further found in the liver of whiting (see earlier) and of toluene in the bivalve *Mactra corralina.*

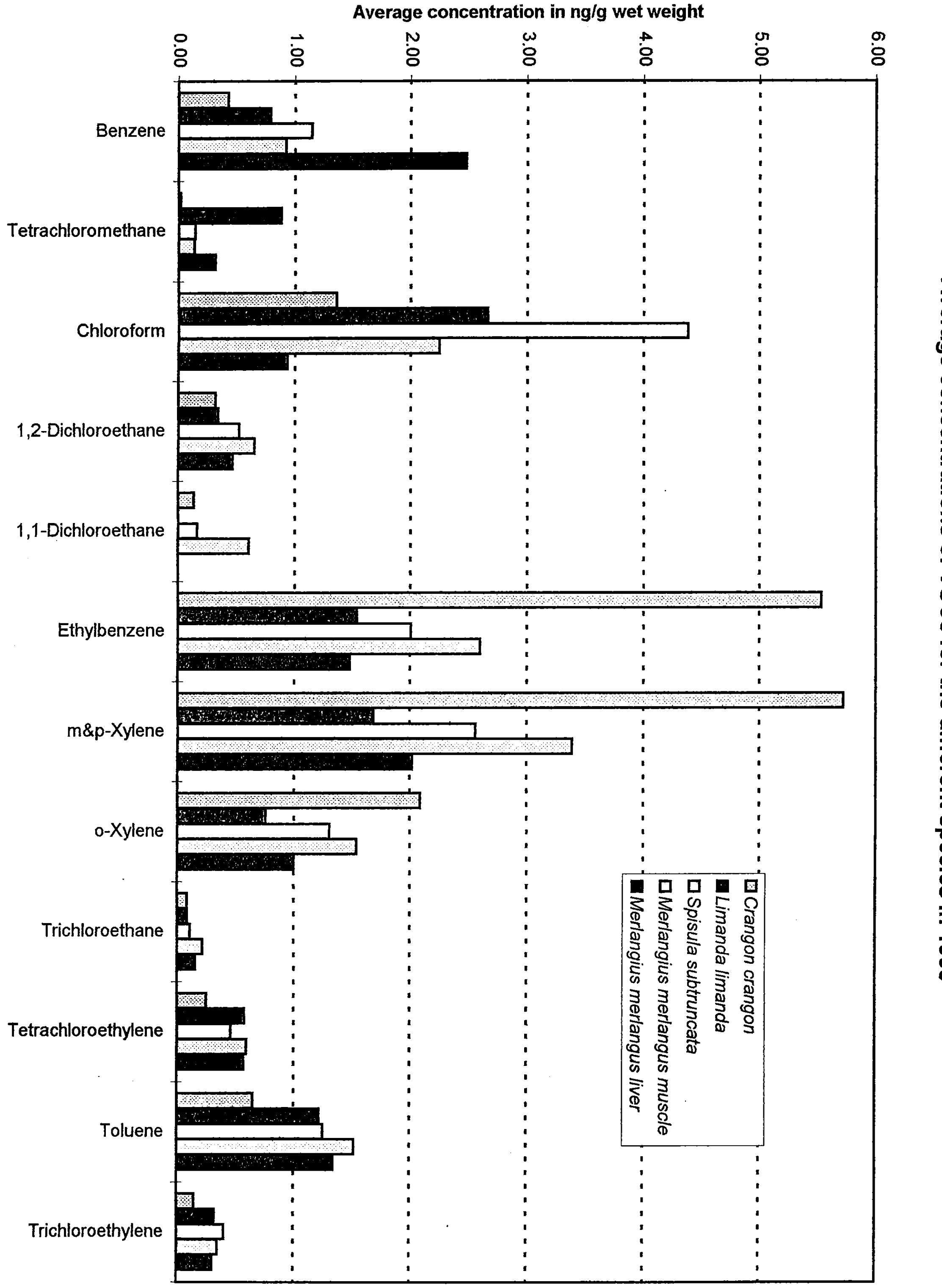


Figure III.4.48 Average concentrations of VOCs for the *species Crangon crangon, Limanda limanda, Spisula subtruncata* and *Merlangius merlangus* in 1995.

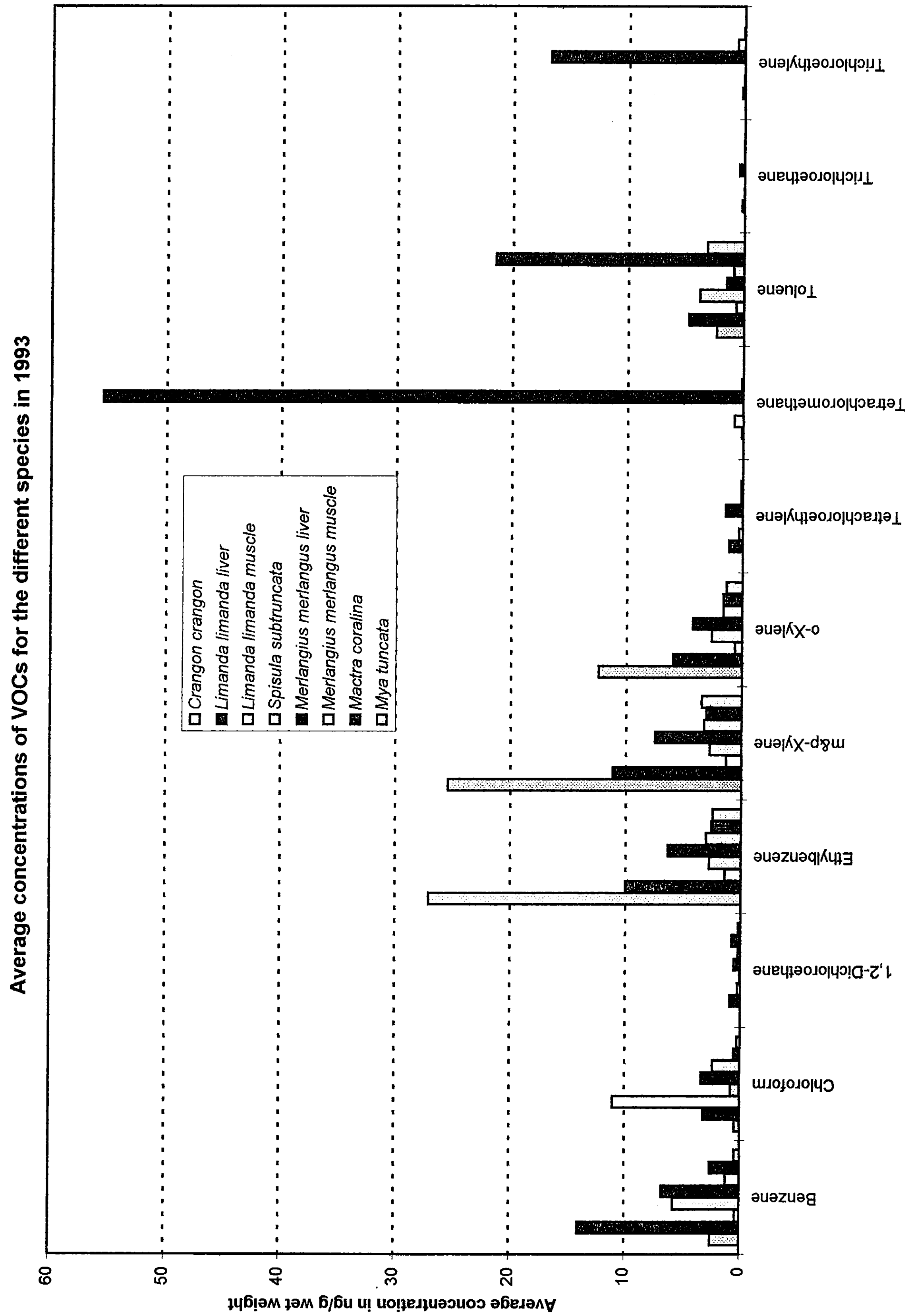


Figure III.4.49: Overview of the average concentrations of VOCs in the *species Crangon crangon, Limanda limanda, Spisula subtruncata, Mactrac corallina, Mya truncata* and *Merlangius merlangus* in 1993.

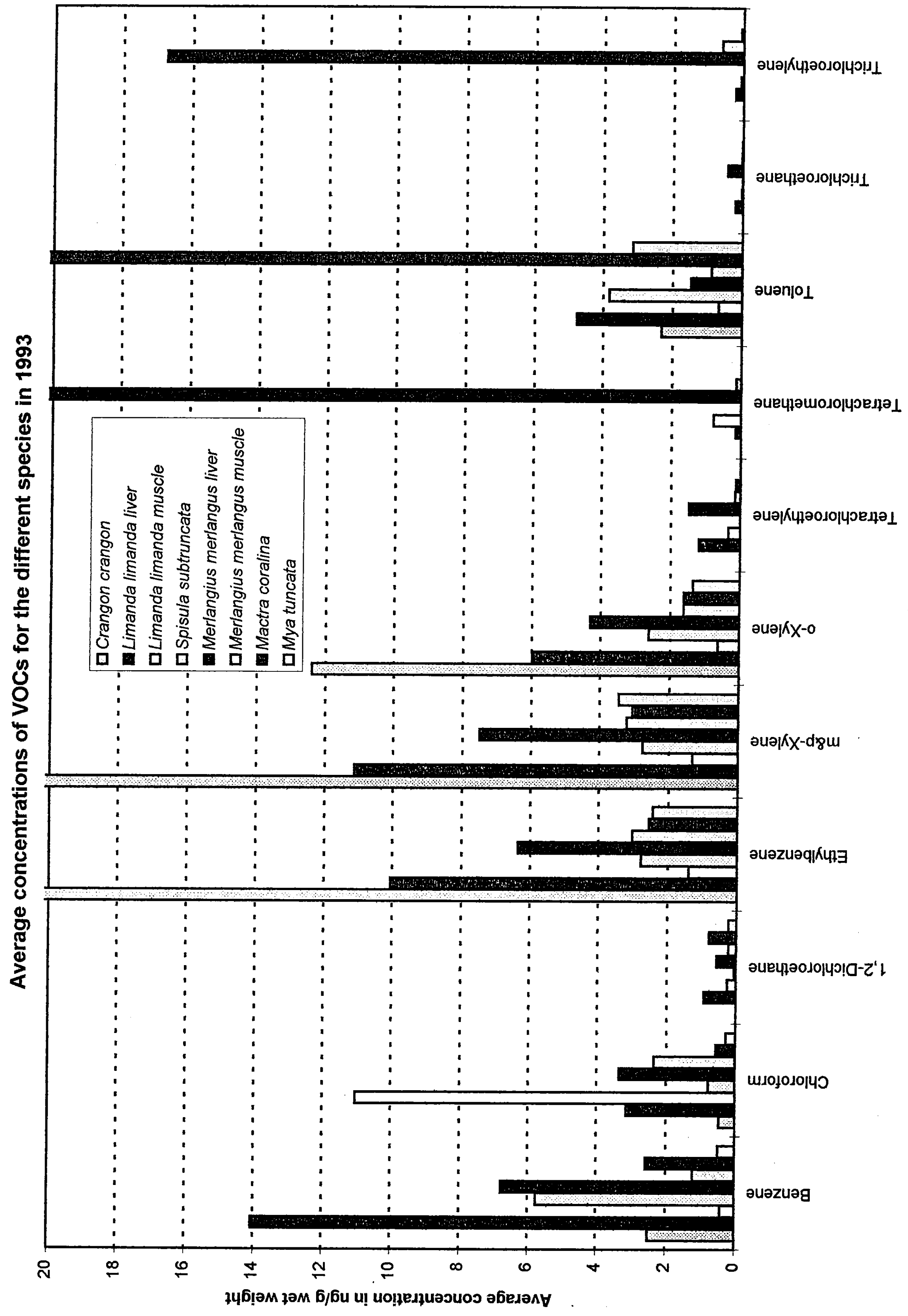


Figure III.4.50: Detail of the average concentrations of VOCs in the *species Crangon crangon, Limanda limanda, Spisula subtruncata, Mactrac corallina, Mya truncata* and *Merlangius merlangus* in 1993.

The concentrations found during this study are, on general, in the same order of magnitude as those previously reported in literature. Concentrations of VOCs in shrimp on the BCP are varying, when abstract is made of the sampling time and location, between 0.005 and 6 ng/g depending on the VOC. Pearson and McConnel (1975) reported CHC concentrations between 2 and 16 ng/g for the same species. For whiting concentrations averaging around 1 to 2 ng/g are observed for muscle tissue and around 1 to 6 ng/g for liver tissue. Similarly, concentrations of several CHCs averaging around 5 ng/g were reported for a related species like cod (*Gadus morhua*) (Pearson and McConnel, 1975; Dickson and Riley, 1976). Where concentrations of the different VOCs average between 1 and 10 ng/g during this study, they average around 5 for the same species in the work of Pearson and McConnel (1975). Concentrations reported in literature for various shellfish vary on average between 1 and 5 ng/g (Pearson and McConnel, 1975; Dickson and Riley, 1976; Ferrario *et al.*, 1985; Gotoh *et al.*, 1992). This is identical to the averages observed during this study.

The high concentrations found during this study are again not unusual. The highest concentrations observed during this study were more than 150 ng/g for trichloroethylene in liver of whiting and more than 550 ng/g of tetrachloromethane in the same tissue. Yasuhara and Morita (1987) reported a concentration of 4080 ng/g of 1,2-dichloroethane in mussel (*Mytilus edulis*). Reinert et al. (1983) reported a concentration of 590 ng/g of the same chemical in grass shrimp (*Paleomonetes pugio*). Pearson and McConnel (1975)observed concentrations up to 150 ng/g of chloroform in cockle (*Cerastoderma edule*) and 180 ng/g of the same compound in crab (*Cancer pagarus*). Finally, Ferrario et al. (1985) observed concentrations up to 1030 ng/g for benzene in killifish (*Fundulus sp.*).

In can be concluded from the results that the concentrations in the different species vary considerably but that no distinct differences can be observed between the species. Looking at different levels of the food chain shows that the levels are not increasing with higher levels in the food chain, so it can be assumed that the effect of biomagnification is not present. The highest concentrations are generally observed in invertebrates, with the exception of some high values in liver of whiting. This is not inconsistent with the findings in literature and it can be assumed that this is related to the effect of metabolisation. Fish frequently shows a better ability to metabolise exogenic compounds. The latter would also explain the fact that the highest values are found in the liver of fish as this is the centre of metabolisation. Future work could, as a result, concentrate on different species coming from different locations.

III.4.2.5 ESTIMATE OF THE BIOCONCENTRATION POTENTIAL

III.4.2.5.1 Introduction

The bioconcentration potential of a chemical compound is defined as the potential of that compound to concentrate from the surrounding water phase into biological tissue. Chemicals exhibiting a strong tendency to bioconcentrate can lead to concentrations in organisms that will eventually cause chronic effects even if the initial toxicity of the chemical is low and if the initial concentration in the water phase in low. The bioconcentration potential is generally represented by the bioconcentration factor, BCF, being the ratio between the chemical 's concentration in the organism and its concentration in the aquatic environment at equilibrium (Freitag *et al.*, 1985, Isnard and Lambert, 1988, Van der Kooij *et al.*, 1991). The BCF is supposedly constant, meaning independent of exposure time and concentration not highly dependent on the species and therefore an intrinsic property of the chemical (Isnard and Lambert, 1988).

In order to determine the BCF the average concentrations the different VOCs, obtained during the 1995 monitoring campaign, in a given species/tissue at a given sampling station were divided by the average concentration in the water column at that sampling station. The data for the water column were obtained form the results of the UG (see earlier). The resulting BCFs were then compared to those reported in literature.

III.4.2.5.2 Results and discussion

The results for the calculation of the BCF for the different VOCs is given for the fishes in table III.4.39 and for the invertebrates in table III.4.40.

As a result of the calculations bioconcentration factors up to 1269 were calculated. These high values should, however, be approached with the necessary caution, as they are often the result of some very high concentration on the average concentration in the organism. However, they do indicate that the concentrations are up to 1200 times higher in the organism than in the surrounding water. The potential to bioconcentrate is therefore considerable and much higher than what would be expected from looking at the BCFs reported previously in literature.

Table III.4.39: Calculated BCFs for fish.

Parameter	Station 120	Station 435	Station 780	Station 780	Station 800	Station B07	Mean	Literature
Merlangius merlangus								
Tissue	MU	MU	MU	LI	MU	MU		
Benzene	46	30	191	198	23	42	88	4-13[1,2,3,4,5]
Tetrachloromethane	70	na	119	193	na	34	104	<10-17[1,5,6]
Chloroform	115	54	408	82	22	10	115	2-10[1,7]
1,2-Dichloroethane	56	32	160	51	62	67	71	1-2[1,8]
1,1-Dichloroethane	992	37	287	na	na	158	369	1[9]
Ethylbenzene	56	103	250	82	66	44	100	5-16[2,10]
m&p-Xylene	48	66	125	45	45	22	58	6-23[1,2,3,10]
o-Xylene	48	51	137	48	39	30	59	6-21[1,2,10]
1,1,1-Trichloroethane	53	12	156	49	32	43	57	9-90[1,5]
Tetrachloroethylene	217	163	491	259	58	161	225	39-49[1,6]
Tolueen	39	30	195	68	31	30	65	4-90[2,3,5,10,11]
Trichloroethylene	34	8	92	36	21	15	35	17-39[9,8]
Limanda limanda (muscle tissue)								
Benzene	58	38	62			56	53	4-13[1,2,3,4,5]
Tetrachloromethane	995	139	109			28	318	<10-17[1,5,6]
Chloroform	147	228	234			20	157	2-10[1,7]
1,2-Dichloroethane	32	14	42			49	34	1-2[1,8]
1,1-Dichloroethane	1269	15	16			146	362	1[9]
Ethylbenzene	56	32	121			28	59	5-16[2,10]
m&p-Xylene	35	24	45			14	29	6-23[1,2,3,10]
o-Xylene	35	16	48			16	29	6-21[1,2,10]
1,1,1-Trichloroethane	23	8	27			41	25	9-90[1,5]
Tetrachloroethylene	267	78	134			338	204	39-49[1,6]
Tolueen	28	43	72			47	48	4-90[2,3,5,10,11]
Trichloroethylene	79	4	23			10	29	17-39[9,8]

[1] Isnard and Lambert, 1988. [2] Ogata *et al.*, 1984. [3] Lyman, 1981 in Howard 1991. [4] Korn et al., 1977 in Howard, 1991. [5] Freitag *et al.*, 1985. [6] Neely *et al.*, 1974. [7] Anderson and Lusty, 1980 in Howard, 1991. [8] Barrows, 1980 in Howard, 1991. [9] Lyman, 1981 in Howard 1991. [10] Nunes and Benville, 1979 in Howard, 1991. [11] Geyer et al., 1982 in Howard, 1991. MU= muscle tissue, LI = liver

For fish especially the BCF of first four compounds on the lists, namely benzene, tetrachloromethane, chloroform, and both dichloroethanes, and for tetrachloroethylene is underestimated in literature. The same is true for the bivalve

(*Spisula subtruncata*). For shrimp, especially the BCF of the BTEXs and chloroform, the dichloroethanes and again tetrachloroethylene is underestimated.

Table III.4.40: Calculated BCFs for invertebrates.

Parameter	Station 120	Station 780	Station 800	Station B07	Mean	Literature
Cragnon cragnon (tail muscle)						
Benzene	28	na	na	36	32	4-13[1,2,3,4,5]
Tetrachloromethane	na	na	12	6	9	<10-17[1,5,6]
Chloroform	148	73	68	20	77	2-10[1,7]
1,2-Dichloroethane	19	7	35	149	53	1-2[1,8]
1,1-Dichloroethane	na	na	115	61	88	1[9]
Ethylbenzene	208	157	307	270	235	5-16[2,10]
m&p-Xylene	125	87	121	147	120	6-23[1,2,3,10]
o-Xylene	105	61	104	86	89	6-21[1,2,10]
1,1,1-Trichloroethane	14	15	na	32	20	9-90[1,5]
Tetrachloroethylene	96	82	68	53	75	39-49[1,6]
Tolueen	22	31	26	32	28	4-90[2,3,5,10,11]
Trichloroethylene	10	5	na	28	15	17-39[9,8]
Spisula subtruncata (soft body)						
Benzene	85	74		88	82	4-13[1,2,3,4,5]
Tetrachloromethane	82	na		na	82	<10-17[1,5,6]
Chloroform	699	339		10	349	2-10[1,7]
1,2-Dichloroethane	29	69		66	55	1-2[1,8]
1,1-Dichloroethane	na	121		139	130	1[9]
Ethylbenzene	26	118		70	71	5-16[2,10]
m&p-Xylene	23	59		34	38	6-23[1,2,3,10]
o-Xylene	24	70		43	46	6-21[1,2,10]
1,1,1-Trichloroethane	na	35		na	35	9-90[1,5]
Tetrachloroethylene	314	170		101	195	39-49[1,6]
Tolueen	27	68		46	47	4-90[2,3,5,10,11]
Trichloroethylene	na	49		na	49	17-39[9,8]

[1] Isnard and Lambert, 1988. [2] Ogata *et al.*, 1984.. [3] Lyman, 1981 in Howard 1991. [4] Korn et al., 1977 in Howard, 1991. [5] Freitag *et al.*, 1985. [6] Neely *et al.*, 1974. [7] Anderson and Lusty, 1980 in Howard, 1991. [8] Barrows, 1980 in Howard, 1991. [9] Lyman, 1981 in Howard 1991. [10] Nunes and Benville, 1979 in Howard, 1991. [11] Geyer et al., 1982 in Howard, 1991. MU= muscle tissue, LI = liver

The BCF is supposedly independent of exposure time and concentration and not highly dependent on the species (Isnard and Lambert, 1988). The BCF obtained for the different sampling stations was therefore compared for the different species. This is illustrated in figures III.4.51 to III.4.55.

It can be observed that the BCFs calculated for the different stations for one species are, with some exceptions attributed to very high concentrations of the contaminant, generally quite comparable. This leads indeed to the conclusion that the BCF is

constant at equilibrium. The latter is quite important as it might explain the outlying values, which could be attributed to a non equilibrium situation.
The BCF calculated for concentrations in liver and muscle tissue are compared with each other in figure III.4.56.

The plot clearly illustrates that the calculated BCF is more or less identical for both tissue types. This proofs the fact that the BCF is independent of the tissue type and solely dependent on the chemical nature of the compounds.

Finally, the average BCFs obtained for the different species was compared in figure III.4.57. This plot suggests that the BCF is even independent of the species at equilibrium.

The general conclusions are that the calculated BCF is generally higher than those reported in literature. The latter leads to a considerable underestimation of the bioconcentration potential of the compounds and therefore the expected concentrations. It should in any case be investigated whether the observed concentrations will adversely affect populations of marine organisms. The calculated BCF seems further independent of sampling location, tissue type and species.

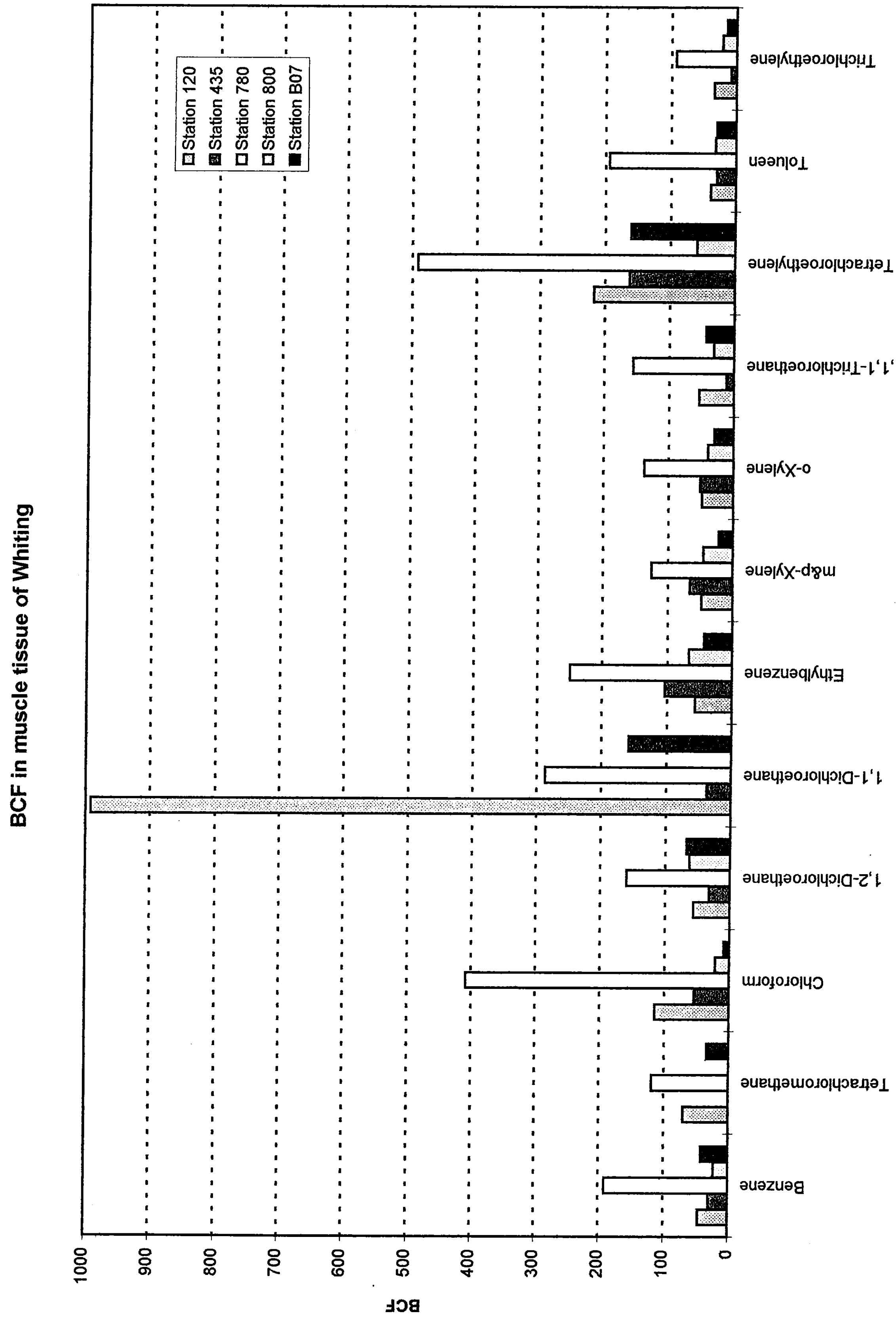


Figure III.4.51: Average BCFs, based of the average concentration in the water column and muscle tissue of whiting for different sampling locations.

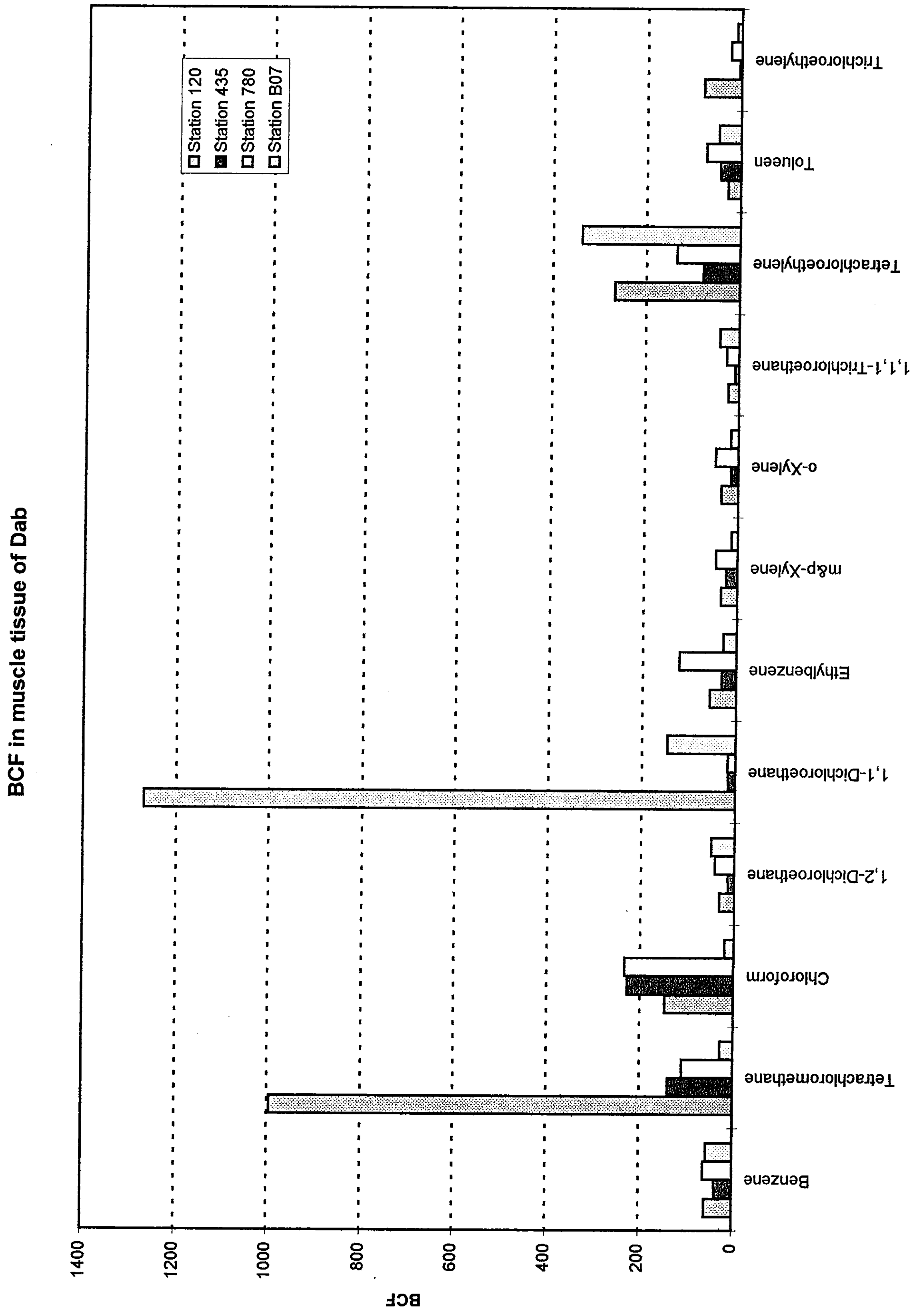


Figure III.4.52: Average BCFs, based of the average concentration in the water column and muscle tissue of dab for different sampling locations.

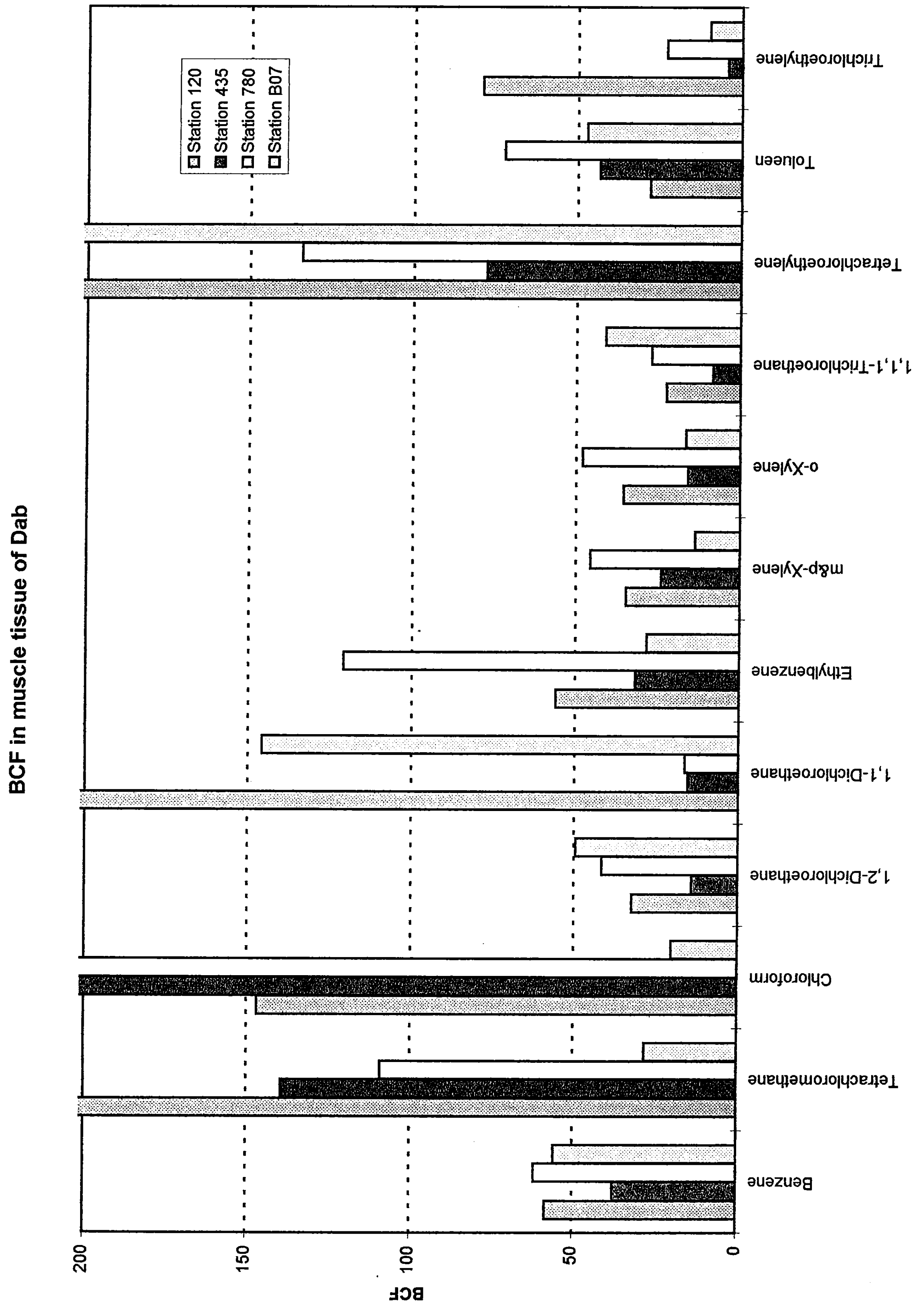


Figure III.4.53: Average BCFs, based of the average concentration in the water column and muscle tissue of dab for different sampling locations (detail).

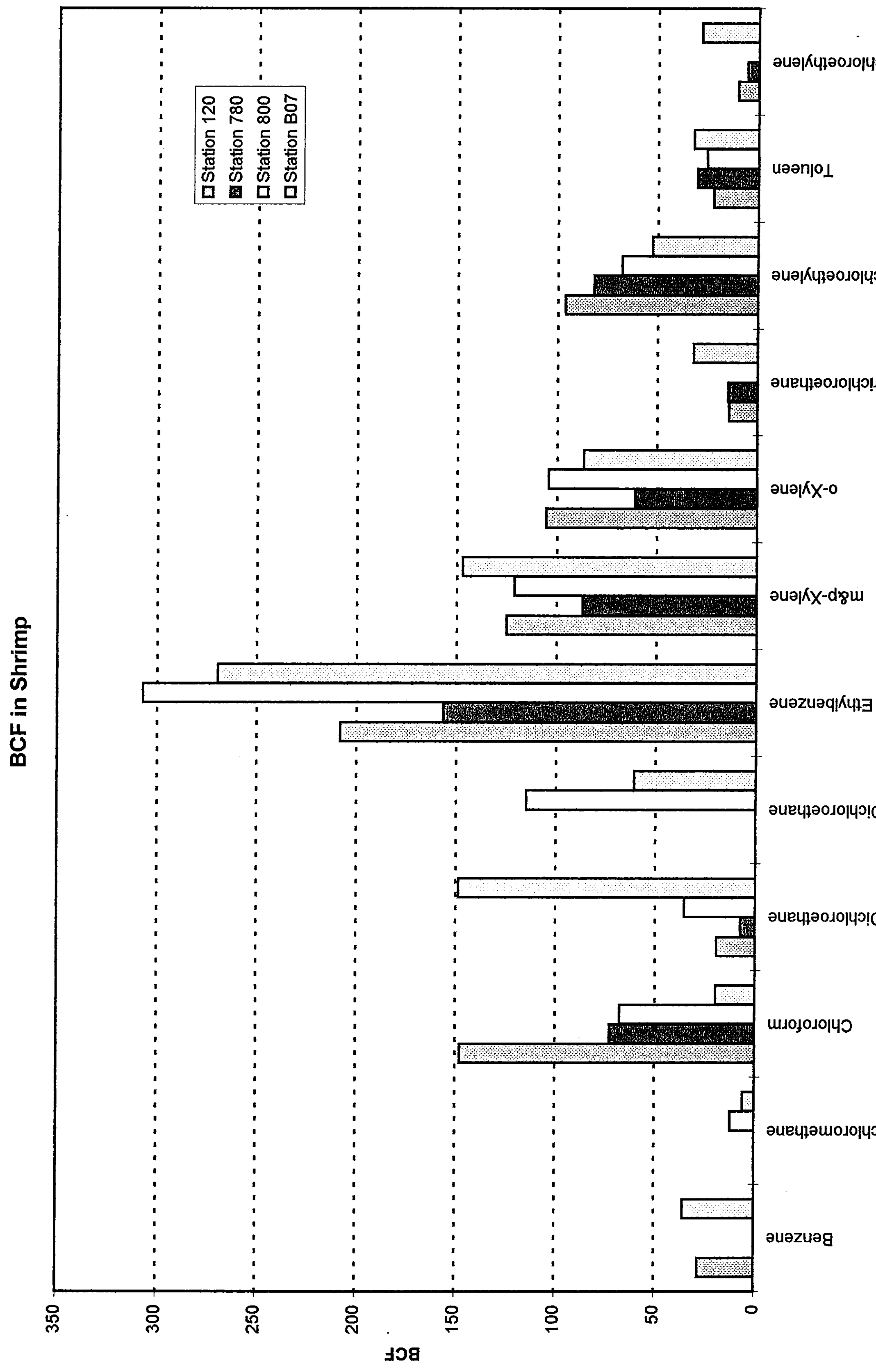


Figure III.4.54: Average BCFs, based of the average concentration in the water column and tail muscle of shrimp for different sampling locations.

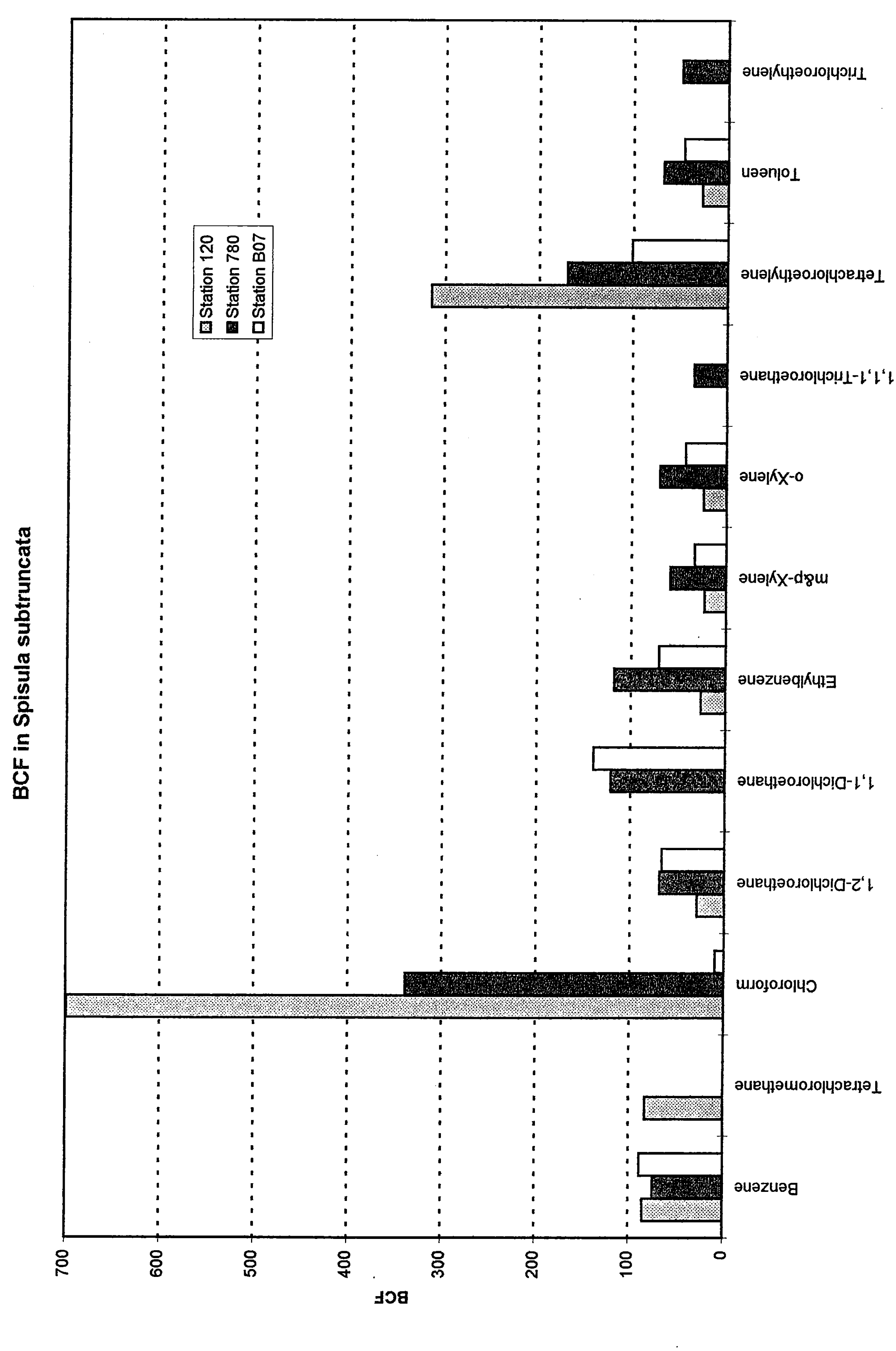


Figure III.4.55: Average BCFs, based of the average concentration in the water column and soft body tissue of *Spisula subtruncata* for different sampling locations.

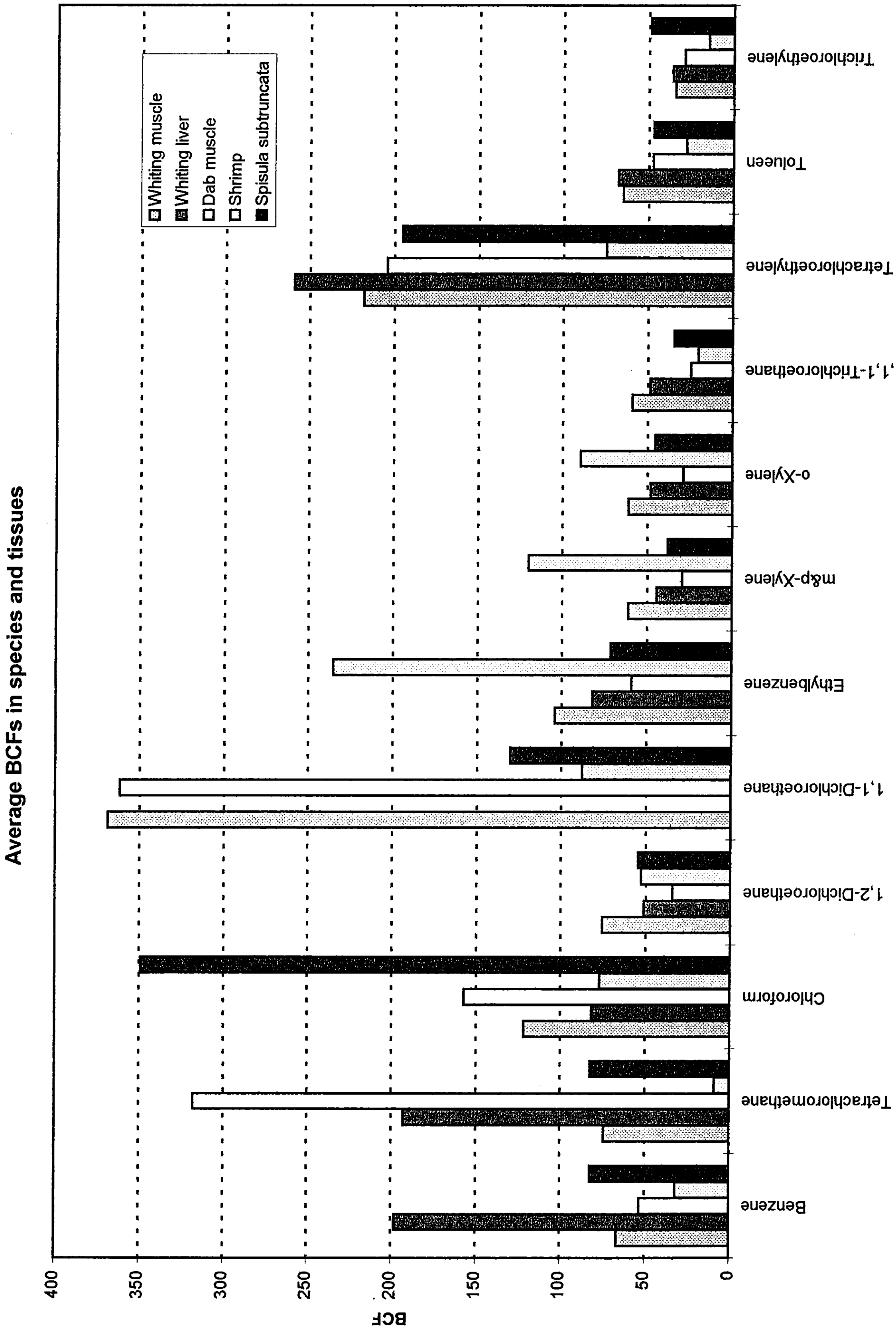


Figure III.4.56: Average BCFs, for the different species.

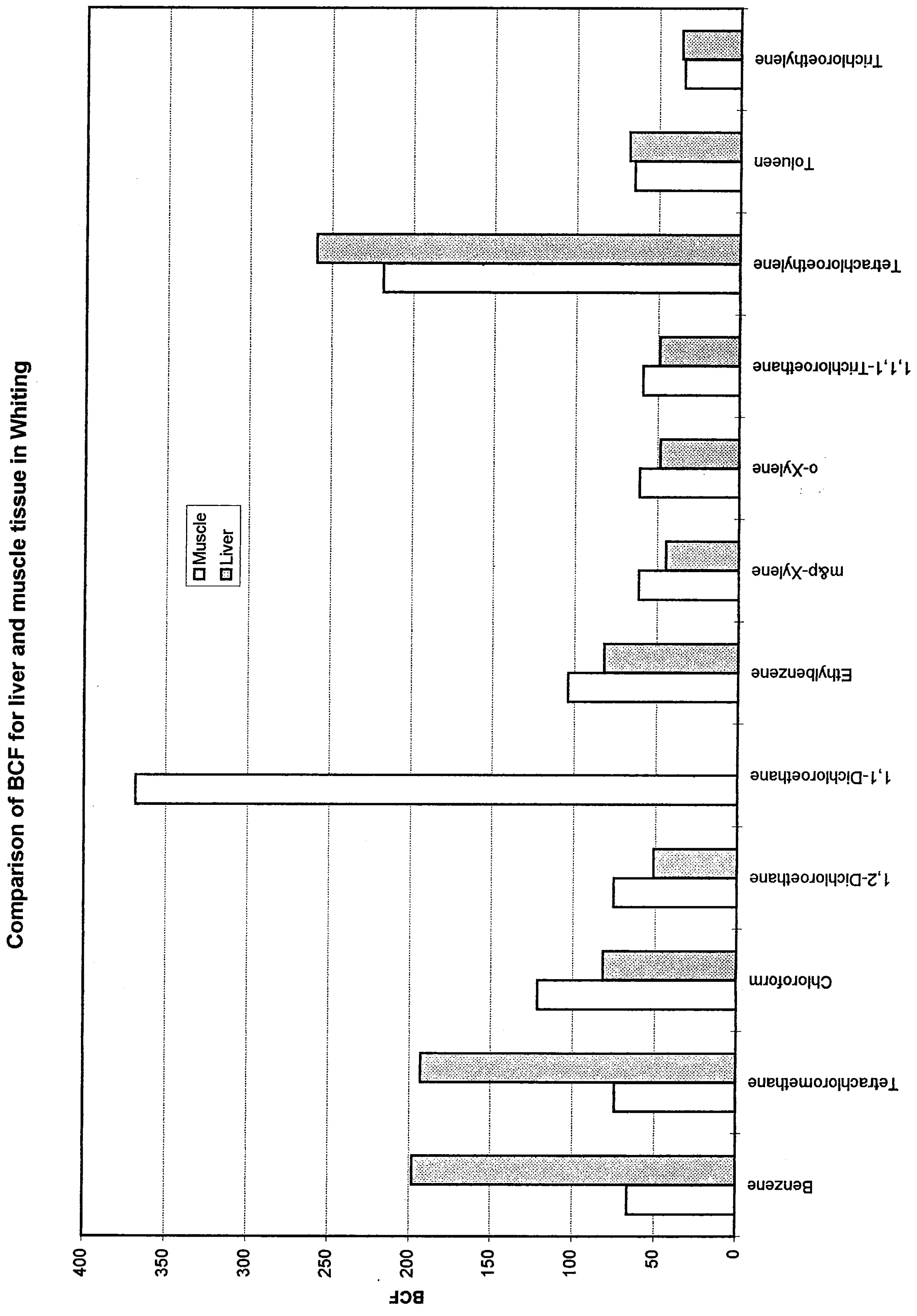


Figure III.4.57: Comparison of Average BCFs calculated for muscle and liver tissue of whiting.

III.4.3. CONCLUSIONS

The interspecies and interspecimen distribution and the seasonal and spatial distribution were investigated during the monitoring campaign. On one occasion the concentration of VOCs was compared with that of CBs and OCPs.

The concentrations of VOCs in organisms of the same population showed to be highly variable both between the organisms and within the organism. Although VOCs appear to be normally distributed in the tissues of organisms, this could not be unambiguously proved. Correlating the VOC concentration with the length of the organism and the fat content of the tissue only gave a few significant results. It was therefore concluded, on the basis of the current findings, that VOCs do not show a tendency to biomagnify in fish and that the distribution in the tissue in not solely related to the fat content of the tissues. VOCs therefore behave differently in the organism compared to other organic contaminants such as CBs and OCPs. VOCs were further correlated with the presence of CBs and OCPs and no distinct relationship could be demonstrated. This further suggests different pathways and a different behaviour. The concentrations levels are, however, generally in the same order of magnitude as those of CBs and OCPs but the maximum concentrations are a lot higher. Comparing the levels found in liver and muscle tissue suggest that at least for dab, concentrations in the liver are higher. This is not unexpected as the liver is the main site of metabolisation. No clear relationship could further be established between concentrations in liver and muscle tissue.

No distinct spatial and seasonal effects could be demonstrated for the presence of VOCs on the Belgian Continental Schelf. It was therefore concluded that the shelf could be regarded as one zone.

The concentrations vary significantly between organisms of different levels of the food chain, but again not in such a way that the higher concentrations are always related to the higher trophic levels. On the contrary, concentrations in brown tend to be higher compared to fish.

Finally, the bioconcentration factors of the different VOCs were estimated on the basis of the concentrations found in the surrounding water. The calculated BCFs are for most VOCs considerably higher than those previously reported. The latter could lead to a serious underestimation of the concentrations in organims. No marked differences could further be observed when the BCFs were compared for different organisms and different sampling locations. The latter indeed suggests that the BCF at equilibrium is inherent to the physico-chemical properties of the chemical and not related to biological factors.

III.4.4. REFERENCES

Bligh, E.G. and Dyer, W.J. Can. J. Biochem. and Physiol., 37:911-917. (1959).

De Boer, J. 1994. *Proc. North Sea Task Force-Quality Status Report Symposium*, Ebeltoft 1994 (In Press).

Delbeke, K., Teklemariam, T., de la Cruz, E. and Sorgeloos, P. Intern. J. Environ. Anal. Chem., (1995).

Dickson, A.G. and Riley, J.P. Mar. Poll. Bull. 7 (9):167-169 (1976).

Ferrario, J.B., Lawler, G.C., DeLeon, I.R. and Laseter, J.L. Bull. Environ. Contam. Toxicol. 34:246-255 (1985).

Freitag, D., Ballhorn, L., Geyer, H. and Korte, F., CHEMOSPHERE 14:1589-1616, (1985).

Gotoh, M., Sekitani, Y., Aramaki, T., Kobayashi, H., Ogino, K. and Hobara, T. Bull. Environ. Contam. Toxicol. 49:186-191 (1992).

Goerke, H., Eder, G., Weber, K. and Ernst, W. Mar. Poll. Bull., 10:127-133 (1979).

Howard, P.H. *Handbook of environmental fate and exposure data for organic chemicals. Volume 2 (solvents)* (1991).

Isnard, P. and Lambert, S. CHEMOSPHERE 17:21-34 (1988).

Kruse R. and Krüger K.E., Allgemeine Fishwirtschaftszeitung, 33: 168-169 (1981).

Neely, W.B., Branson, D.R. and Blan, G.E., Env. Sci. Technol. 8:1113-1115, (1974).

Ogata, M., Fujisawa, K., Ogino, Y. and Mano, E., Bull. Environ. Contam. Toxicol. 33:561-567, (1984).

Pearson, C.R. and McConnell, G. PROC.R.SOC.LOND.B. 189:305-332, (1975).

Roose, P., Cooreman, K. and Vyncke, W., ICES E:15, 14 pp (1993).

Roose, P., Cooreman, K. and Vyncke, W. *16th Symposium on Chlorinated dioxins and Related Compounds*, 29: 23-27 (1996).

Reinert K.H., Hunter, J.V. and Sabatino T., J. Agric. Food Chem., 31: 1057-1060.

Schaefer, R.G., Ernst, W., Goerke, H. and Eder, G. Berichte Deutsche Wissenschaftliche Kommission Meeresforschung, 24:225-233 (1976).

Schneider, R. Meeresfor., 29:69-79 (1982).

Van Der Kooi, L.A., Van De Meent, D., Van Leeuwen, C.J. and Bruggeman, W.A. Wat. Res., 25: 697-705 (1991).

Yasuhara, A. and Morita, M. CHEMOSPHERE 16:10-12, (1987).