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Committee Marine Environmental Quality

CONCENTRATION GRADIENTS OF THIRTEEN PRIORITY VOLATILE CHLORINATED AND MONOCYCLIC AROMATIC HYDROCARBONS IN THE SCHELDT ESTUARY

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1. Introduction

The chlorinated C_1- and C_2-hydrocarbons chloroform, tetrachloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene, and the monocyclic aromatic hydrocarbons benzene, toluene, ethylbenzene and the xylenes are priority volatile organic compounds. They are important compounds in environmental studies because of their stability, their toxicity and their possible contribution to tropospheric processes. Moreover, tetrachloromethane and 1,1,1-trichloroethane are known as ozone depleting compounds. Because of their properties the mentioned chlorinated compounds were classified in the list of 36 priority pollutants in the Ministrial Declaration of the Third International North Sea

Conference. The monocyclic aromatic compounds were simultaneously classified in the list of priority pollutants which will be further taken as a basis for the setup of national priority lists.

2. Objective

In the work presented here, the concentrations of 13 volatile chlorinated and monocyclic aromatic hydrocarbons were investigated in the Scheldt estuary between Antwerp (Belgium) and Vlissingen (The Netherlands). At eight to ten locations in the estuary samples were taken four times in 1995 by means of the Belgian Oceanographic research vessel the 'Belgica' (Figure 1). The samples were analysed by a purge and trap preconcentration method combined with gas chromatographic separation and mass spectrometric detection (1).

3. Results

3.1. Concentration levels

The concentration ranges of the thirteen target compounds in the Scheldt estuary are presented in Table 1 for each sampling campaign. The concentrations are in the 1 to 1000ng.L^{-1} range (0.001-1ppb). The lowest levels are observed for tetrachloromethane (<34ng.L^{-1}) and 1,1-dichloroethane (<45ng.L^{-1}). The compounds with the highest concentrations are chloroform (up to 1281ng.L^{-1}) and tetrachloroethylene (1082ng.L^{-1}).

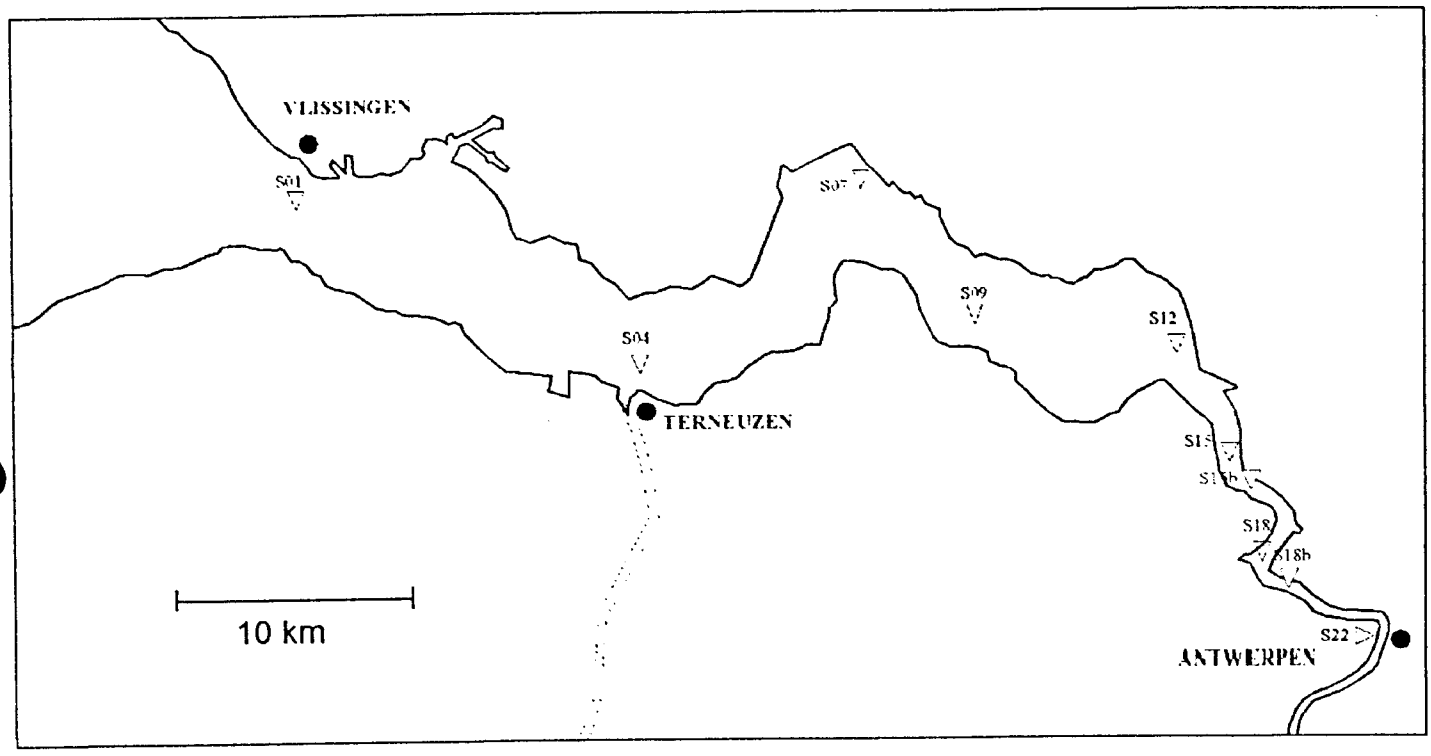

Figure 1. Map of the Scheldt estuary trajectory Antwerp-Vlissingen with the sampling locations indicated

Further on, it is noticed that the concentrations of the monocyclic aromatic hydrocarbons are very dependent on the sampling time. They show higher concentrations in May and October (e.g. m/p-xylene up to 558 and 126ng.L^{-1}) in comparison with the measurements in March and December (m/p-xylene up to 11 and 16ng.L^{-1}).

Table 1. Concentration ranges of the 13 target compounds in the Scheldt estuary on four sampling days in 1995. Concentrations are in $ng.L^{-1}$

Compound	27 March	18 May	18 October	4 December
Chloroform	27 - 1281	23 - 390	15 - 823	7 - 224
Tetrachloromethane	2 - 34	2 - 7	1 - 19	<1 - 4
1,1-Dichloroethane	2 - 43	<1 - 45	1 - 35	<1 - 26
1,2-Dichloroethane	9 - 84	20 - 224	11 - 366	13 - 160
1,1,1-Trichloroethane	5 - 461	6 - 719	3 - 298	2 - 173
Trichloroethylene	9 - 327	16 - 252	5 - 134	4 - 216
Tetrachloroethylene	2 - 486	3 - 901	3 - 699	2 - 1082
Benzene	14 - 30	7 - 111	14 - 347	13 - 21
Toluene	10 - 116	21 - 77	29 - 120	21 - 46
Ethylbenzene	10 - 22	30 - 164	8 - 51	5 - 16
m/p-Xylene	6 - 11	80 - 558	14 - 126	6 - 16
o-Xylene	5 - 10	22 - 144	9 - 84	6 - 18

3.2. Comparison with concentration measurements in the North Sea

The concentrations can be compared to measurements made in the North Sea on the Belgian Continental Plat (2). From 1993 until 1995, 46 samples were taken in this area. The median values for the concentrations of these samples for tetrachloroethylene and toluene were 2.3 and $31.4 ng.L^{-1}$ respectively. They are typical for the two groups of the compounds. The chlorinated compounds are present in higher concentration levels in the Scheldt estuary than

on the Belgian Continental Plat in the North Sea, whereas the concentrations of the monocyclic aromatic hydrocarbons in the North Sea and in the Scheldt estuary are in the same order of magnitude.

3.3. Concentration profile

The concentration profiles of tetrachloroethylene and toluene along the sampling trajectory are presented in Figure 2. The tetrachloroethylene plot shows a decreasing concentration gradient from Antwerp towards the North Sea in all sampling periods. This pattern was typical for all chlorinated compounds (tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane and trichloroethylene) except for chloroform. For chloroform a same trend could be noticed. However, at some sampling locations higher levels were observed than expected from the gradient line. From the profiles of the chlorinated compounds it is clear that the major sources of the compounds are to be found at Antwerp or stream up from Antwerp. The plot of the concentration profile of toluene (Figure 2) does not show an increasing gradient towards Antwerp as it was found for the chlorinated compounds. The same observation was made for the MAHs.

3.4. Factors affecting the observed concentration profile

From the profiles of the chlorinated compounds it can be assumed that the major sources of these compounds are to be found at Antwerp or before Antwerp. The compounds show a typical decrease from Antwerp towards Vlissingen, which can be explained by mixing of the

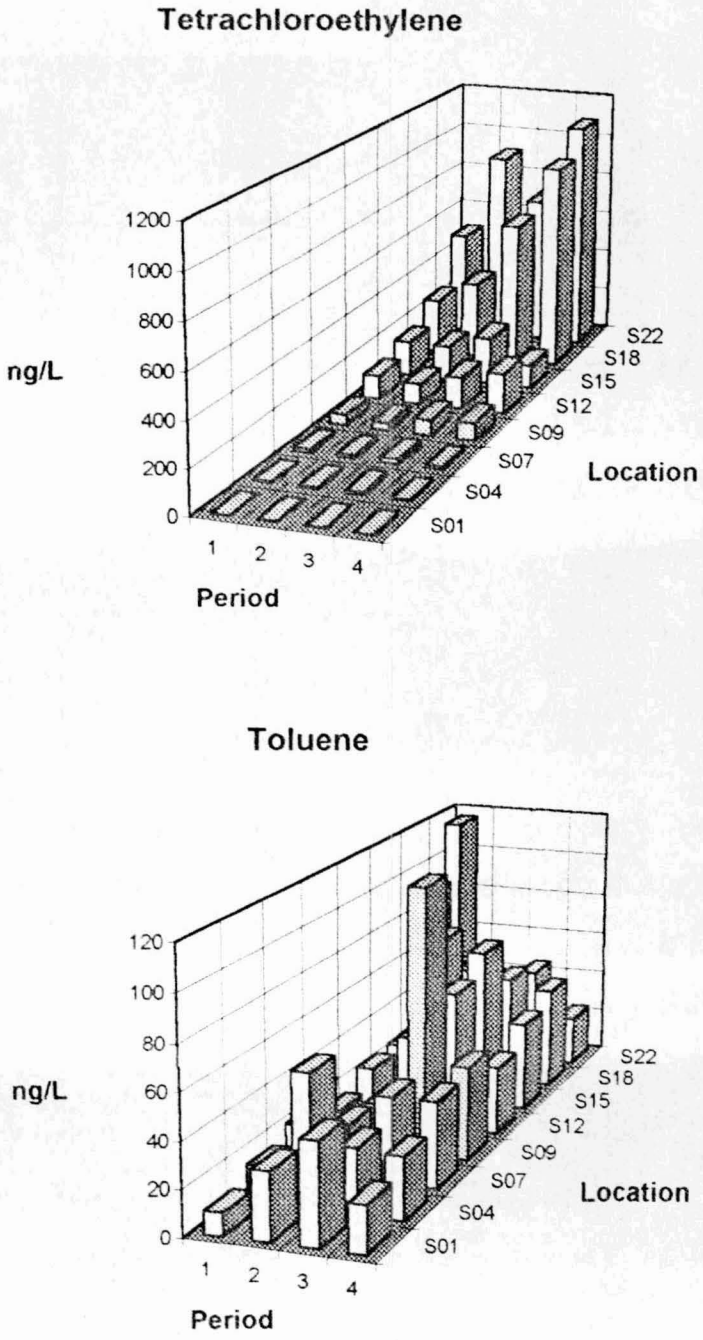

Figure 2. Plots of the concentration of tetrachloroethylene and toluene for the four sampling periods in the trajectory Antwerp-Vlissingen. Location labels refer to the sampling locations indicated in Figure 1. Period 1: March '95; period 2: May '95; Period 3: October '95 and Period 4: December '95

fresh water with less polluted salt sea water in the estuary. The concentration profile of tetrachloroethylene is plotted as a function of the salinity in Figure 3. The plot illustrates the dilution of the chlorinated compounds by less polluted sea water. Secondly, it indicates that other removal processes occur since the plot does not reveal a linear relationship between the concentration and the salinity. Because of the volatility of the compounds and the unequilibrium with the atmospheric concentrations it can be expected that a water/air exchange of these compounds can explain partionally the concentration gradient.

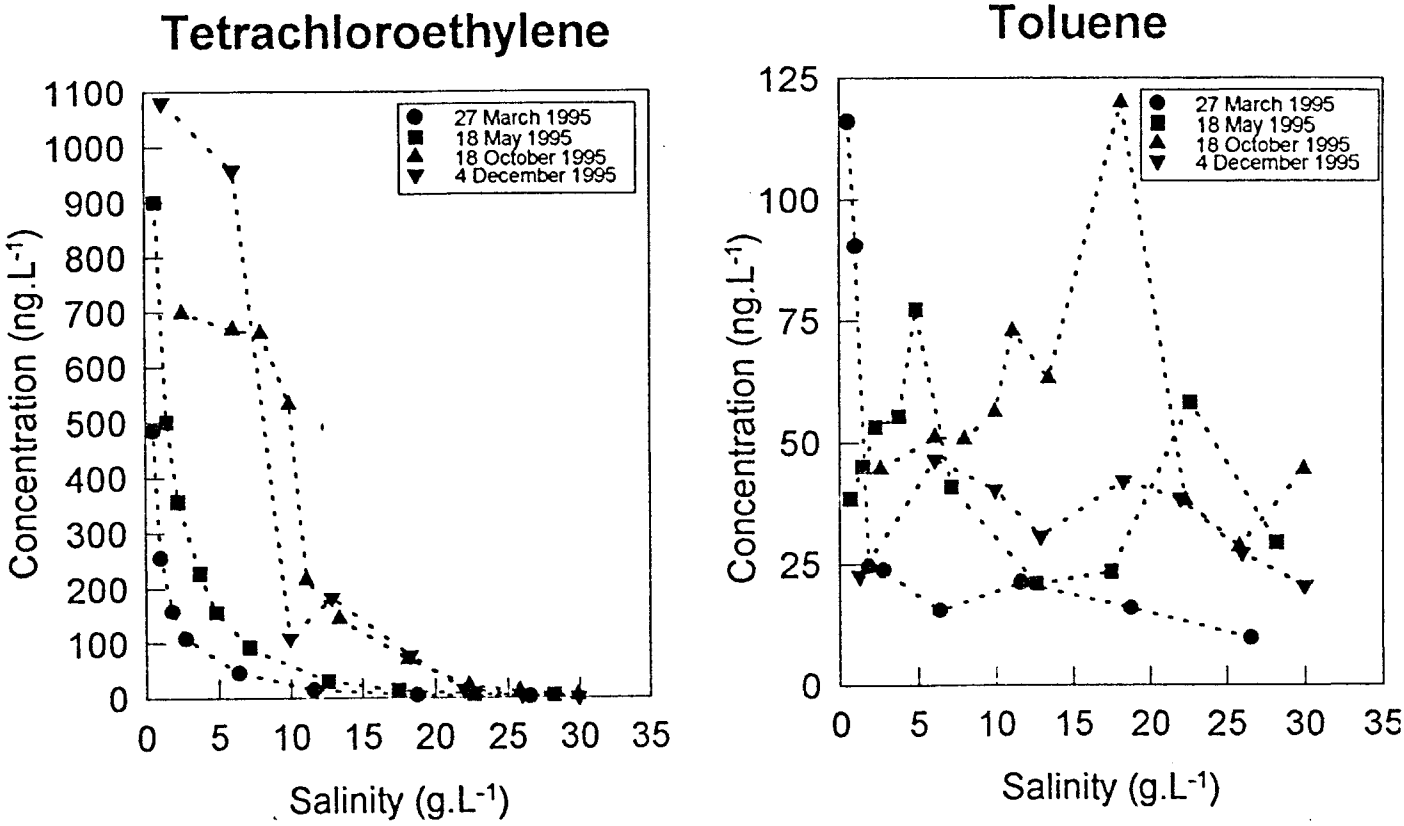

Figure 3. Plots of the concentrations of tetrachloroethylene and toluene as a function of the salinity for the four sampling campaigns

The plots of the concentrations as a function of the salinity of toluene (Figure 3) do not show this typical gradient. A similar pattern was found for the other monocyclic aromatic hydrocarbons. For these compounds other source locations and/or removal mechanisms have to be mentioned in order to explain the concentration profile. However, the information to date is insufficient to reveal these factors.

4. Conclusion

The volatile chlorinated hydrocarbons and the monocyclic aromatic hydrocarbons, with concentrations in the 1 to 1000ng.L^{-1} range, show a different concentration pattern in the Scheldt estuary trajectory Vlissingen-Antwerp. The gradient and the concentration levels of the chlorinated compounds can be explained by anthropogenic sources. This is clear from the concentration level when a comparison is made with measurements of these compounds in the North Sea. Secondly, the plots of the concentrations as a function of the salinity indicate sources at or before Antwerp. In addition the profiles suggest removal mechanisms additional to dilution with less polluted salt sea water.

The monocyclic aromatic hydrocarbons show higher concentrations during the second and third sampling period. The other two campaigns show concentrations similar to the North Sea concentrations. To date there is insufficient information to explain these differences and to interprete the concentration patterns.

The data presented are immission concentrations. They result from emission sources for the estuary and from physical and physicochemical processes, such as mixing, degradation and

exchange processes with the atmosphere, sediment and biota. Modeling of these processes can be considered if immission and emission data are available, next to data on the physicochemical properties of the compounds and knowledge of the estuarine system. However, at this moment more detailed information on the emissions of these priority compounds for the Scheldt estuary is necessary in order to model the fate of the compounds in the estuary.

Acknowledgements

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References

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(2) H. Van Langenhove and J. Dewulf, unpublished results (1996).