The River Rhine as a source of micropollutants in the canal sediments of the city of Delft (The Netherlands)

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Abstract This paper presents a statistical analysis of the pollution levels for heavy metals and organic micropollutants at 182 sediment stations in the city canals of Delft. High pollution levels were especially observed in the inner city canal sediments, probably related to the import of polluted river Rhine water. In contrast, the more-or-less isolated outer city sites were generally much less polluted.

Regression analysis on the database generally showed highly significant correlations between individual heavy metal contents. The heavy metal contents were usually significantly correlated with polycyclic aromatic hydrocarbons (PAHs) as well. This points to one or more common sources for these micropollutants.

Factor analysis and the K-means cluster analysis technique were applied on the above database; it showed a large cluster of stations, nearly all located in the outer city of Delft, characterized by relatively low heavy metal and organic micropollutants' contents. Another cluster of 18 stations, mostly located in the inner city of Delft, possessed intermediate pollution levels, directly related with the supply of river Rhine water. Finally, the stations of a third cluster, situated in the inner city as well, were highly polluted, especially by local pollution sources. The above hypotheses were further supported by a more detailed statistical analysis for a number of inner city stations, together with 10-year river Rhine pollution data.

Keywords Cluster analysis; heavy metals; PAHs; polluted sediments; river Rhine

Introduction

The city of Delft is situated in the south-west of The Netherlands (see Figure 1). The city has a population of *ca*. 100,000 of which 15,000 are permanent residents of the historical inner city. The Delft inner city canal system occupies a total length of 6.5 km and an open water area of 55,000 m^2; the average water depth of the canals is 1.1 m. The inner city canal system is surrounded by the Rijn-Schie canal, with which it has five open connections. Water from the latter is continuously imported into the inner city canals, via a pumping station that flushes the water system. The Rijn-Schie canal is a main shipping route between the river Rhine (at some 20 km distance), and the Delft area. At the same time, this Rhine water is imported into the Delft area, especially during dry summer periods.

The Delft outer city canals mostly comprise isolated waterways for navigation and recreation; on the other hand, there are certainly hydrological connections between the inner and outer city canals (see Figure 1), which may lead to an extended influence of the Rhine water imports.

A long-term study has been undertaken on the extent and sources of aquatic sediment pollution at *ca*. 200 sediment stations in Delft. For the inner city canals, the sediments were, in 95% of the cases, found to be in the quality classes 3+4 ("highly polluted"). For these sediments, remedial actions such as special storage and/or treatment are necessary (Donze, 1990; Calmano *et al*., 1997). The main contributors to the pollution were, in decreasing

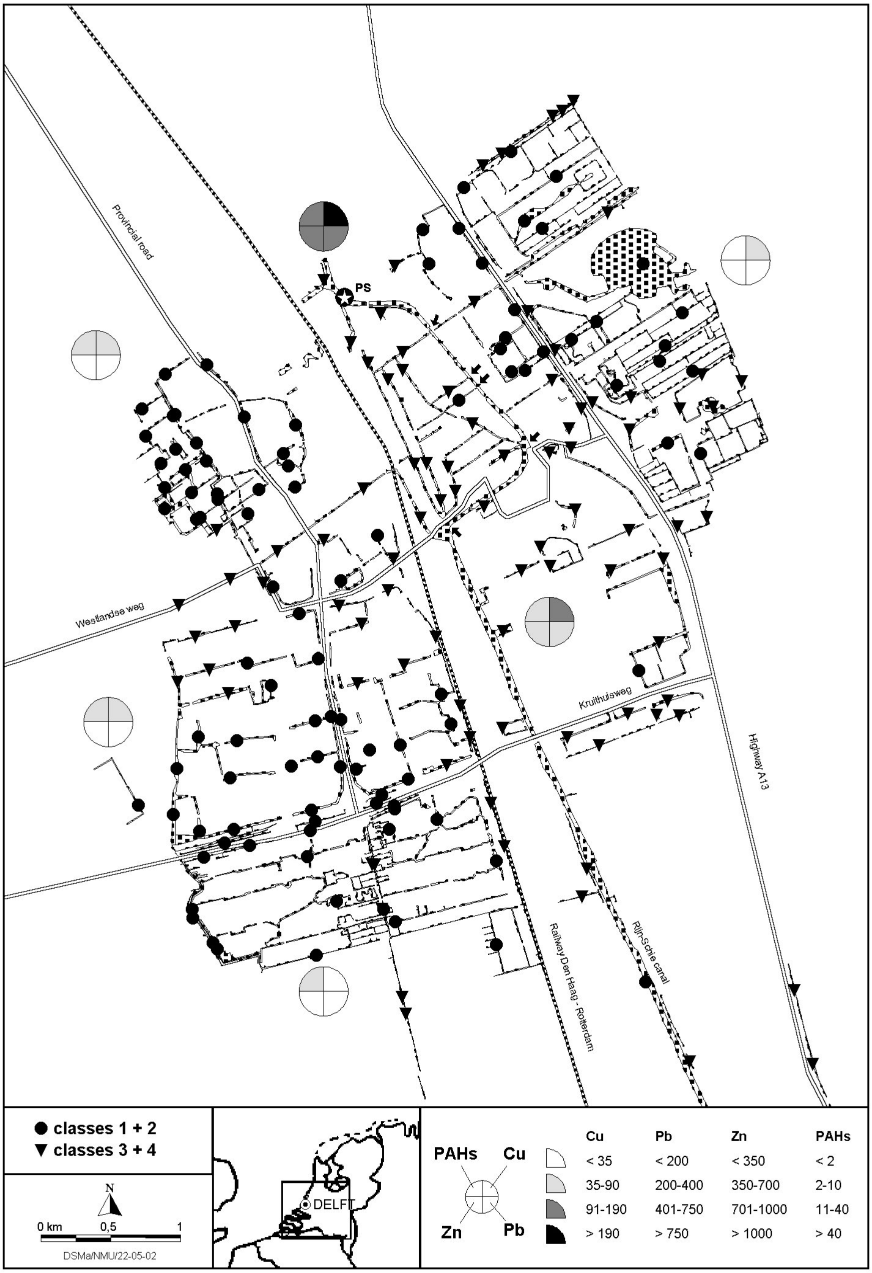

Figure 1 Quality classes of dredged sediments at around 200 stations in Delft over the years 1993–2000; the shaded area indicates the Delft inner city ([▶] = inlet points Rijn-Schie canal; PS = pumping station). Classes 1+2 represent acceptable sediment pollution levels, whereas sediments of classes 3+4 are highly polluted. Also indicated are pie diagrams for the relative, average sediment pollution levels, in mg/kg dry weight, for Cu, Pb, Zn and PAHs, in the different regions in Delft

order: Cu, PAHs, Zn and Pb. In contrast, the majority of the outer city canal sediments are of acceptable (class 1+2) quality, although “hotspots” of pollution may often be found here as well, especially at locations in (in)direct connection with the inner city and/or Rijn-Schie canal (Kelderman, 2002); see Figure 1.

Earlier mass budget calculations (Kelderman *et al.*, 2000) have shown that, for the inner city canal pollution, fractions of 65%, for Pb and Zn, and even 85%, for Cu, may be attributed to external loadings from the Rijn-Schie canal. The busy shipping traffic on the Rijn-Schie canal plays an important role here, through constantly high suspended solids levels (Kelderman *et al.*, 1998). It is thought that import via the river Rhine, through the Rijn-Schie canal, will be of major importance in the supply of polluted suspended solids to the inner city. In spite of a continuous improvement of the river Rhine water quality over the last 30 years, the pollution with respect to especially "diffuse" components such as Cu, Zn and PAHs, is still quite substantial (*Anonymous*, 1988–1997; Van der Weijden and Middelburg, 1989; Stigliani *et al.*, 1993).

This paper presents a statistical evaluation for the pollution levels of micropollutants in the sediments at 182 stations in Delft. Statistical techniques such as regression and cluster analysis were applied to derive possible relationships between the sources of the different micropollutants, and to trace geographical areas of common sediment and pollution characteristics. In view of the apparent influence of the river Rhine on, especially, the inner city of Delft, the above statistical techniques have also been used for the heavy metal contents at three selected inner city stations, on the one hand, and river Rhine heavy metal contents, on the other.

Materials and methods

Over 200 sediments stations for general sediment quality assessment were monitored during the period 1993 to 2000; of these the 182 stations that constituted a complete data set for all the sediment parameters, were selected. The data set comprised 18 stations located within the inner city; the remaining 164 were located in the outer city of Delft (see Figure 2). Sediment samples (20–50 cm length) were sampled with a Beeker core sampler (length 1.0 m; diameter 6 cm); they were analysed in a quality-accredited laboratory for the following components (Kelderman *et al.*, 2000):

- Particle size distribution, and organic matter, dry matter, heavy metal and arsenic contents;
- Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs);
- DDT and its derivates as well as mineral oil.

An SPSS statistical package was used for data analysis at the 182 stations (Yang Xuedong, 2001). Firstly a linear regression analysis was applied between the individual components' values (Boot and Cox, 1974). Subsequently, factor analysis (FA) and principal component analysis (PCA) were applied on the above data base (Malinowski and Howery, 1980), in order to establish independent sets of co-varying variables (factors) responsible for the variance in the Delft sediment quality. For the contributions of the different factors, Eigenvalues were calculated, using a varimax rotation method (Kundson *et al.*, 1977). Finally, the 182 sediment stations were subdivided into spatial groups (clusters) with maximum internal coherence; for this the K-means clustering technique was used (Anderberg, 1973).

To investigate in more detail the impact of the river Rhine quality on the Delft inner city canal sediments, additional sediment cores were collected, in triplicate, in June 1999, in three Delft inner city canals (see Figure 2), *viz.* at station 1, 9 and 10 (Qu Wenchuan, 1999). Stations 1 and 9 are two inlet canals in open connection with the Rijn-Schie canal. In contrast, station 10 is closed off at the inner city side; there is a high density of boathouses along this canal, which may give rise to local pollution. Directly after sampling, the sediment cores were cut into 7 equal sections, in order to investigate possible time trends in pollution (Qu Wenchuan, 1999; cf. Kelderman *et al.*, 2000); the samples were analysed according to standard procedures (Kelderman *et al.*, 2000). In contrast, the ("historical") heavy metal contents of the suspended solids in the river Rhine have not actually been measured here. They were, over the years 1988–1997, estimated from the differences between total and dissolved heavy metal contents, using the corresponding suspended solids contents. Monthly data for the river Rhine monitoring station “Lobith” (at the German-Dutch border) were used (Anonymous, 1988–1997). Statistical analysis, namely by Factor and Cluster analysis on the three canal sediments and the above river Rhine data, followed the same procedure as described before.

Results and discussion

Details of the physico-chemical characteristics at the 182 sediment stations are presented in Yang Xuedong (2001). Linear regression analysis between these parameters showed, in general, highly significant ($p < 0.01$) correlations between all heavy metals, indicating one or more common sources for these components. Especially high correlation coefficients ($r > 0.7$), were found between the pairs Cd-Zn, Hg-Cu, Cu-Zn, Zn-As and Ni-Cr (Table 1); it may be anticipated that e.g. corrosion of metal structures as well as metal plating manufacturing will play important roles here (Nriagu, 1978, 1979, 1980; Förstner and Wittman, 1983; Stigliani *et al.*, 1993). Surprisingly high regressions were also observed between the above metals and PAH contents. Further statistical analysis, also including the individual, rather than summed, PAH components may reveal the reasons behind this (Gschwend and Hites, 1981; Mastran *et al.*, 1994). The same may be stated for the DDT and PCB components.

A next step in the statistical evaluation of the database of 182 sediment stations, was the application of factor analysis. In this way, new sets of variables (“factors”) were formed that can explain the variations between the different sites. It could be thus shown (Yang Xuedong, 2001), that the factor contributing most (*viz.* for 43%) to the variations constitutes the variables: Cd, Zn, As and ΣPAHs. Apparently, there are common sources of pollution that may be attributed to the above chemical components. Less contributing factors comprised: Hg, Pb, and Cu. Subsequently, cluster analysis was used to gain more insight into the spatial distribution of the sediment pollution sources (Ausili *et al.*, 1998; Rachdawong *et al.*, 1998). Clusters of stations, based on the factor scores of the above factor analysis and using the K-means clustering technique, indicate that the 182 sediment stations can be subdivided into 7 different, although not sharply separated, spatial groups (see Figure 2; Yang Xuedong, 2001):

- Clusters 1 and 2 can mainly be found in the outer city of Delft. Both clusters are characterized by low micropollutants levels, but are different with respect to sediment grain size distribution.

Table 1 Values for the correlation coefficients *r* for linear regression between heavy metal and micropollutants levels at 182 sediment stations in Delft. Figures in bold indicate significant ($p<0.01$) correlations. ΣPAH is the sum of fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, naphthalene, chrysene, phenanthrene, anthracene and benzo(a)anthracene.; ΣDDT expresses the sum of all DDT, DDD and DDE congeners; ΣPCB is the sum of PCB-28, 52, 101, 118, 138, 153 and 180

	Cd	Hg	Cu	Ni	Pb	Zn	Cr	As	ΣPAH	ΣDDT
Cd	1.00									
Hg	**0.45**	1.00								
Cu	**0.68**	**0.79**	1.00							
Ni	**0.45**	**0.36**	**0.44**	1.00						
Pb	**0.44**	**0.59**	**0.60**	**0.34**	1.00					
Zn	**0.85**	**0.42**	**0.70**	**0.47**	**0.59**	1.00				
Cr	**0.47**	**0.52**	**0.56**	**0.83**	**0.32**	**0.45**	1.00			
As	**0.68**	0.20	**0.51**	**0.34**	0.23	**0.80**	**0.33**	1.00		
ΣPAH	**0.67**	**0.41**	**0.62**	**0.32**	**0.52**	**0.71**	**0.31**	**0.48**	1.00	
Σ-DDT	0.24	0.13	0.20	0.20	0.20	**0.30**	0.13	0.22	0.18	1.00
ΣPCB	**0.51**	0.28	**0.36**	**0.31**	**0.28**	**0.50**	**0.27**	**0.33**	**0.43**	0.14

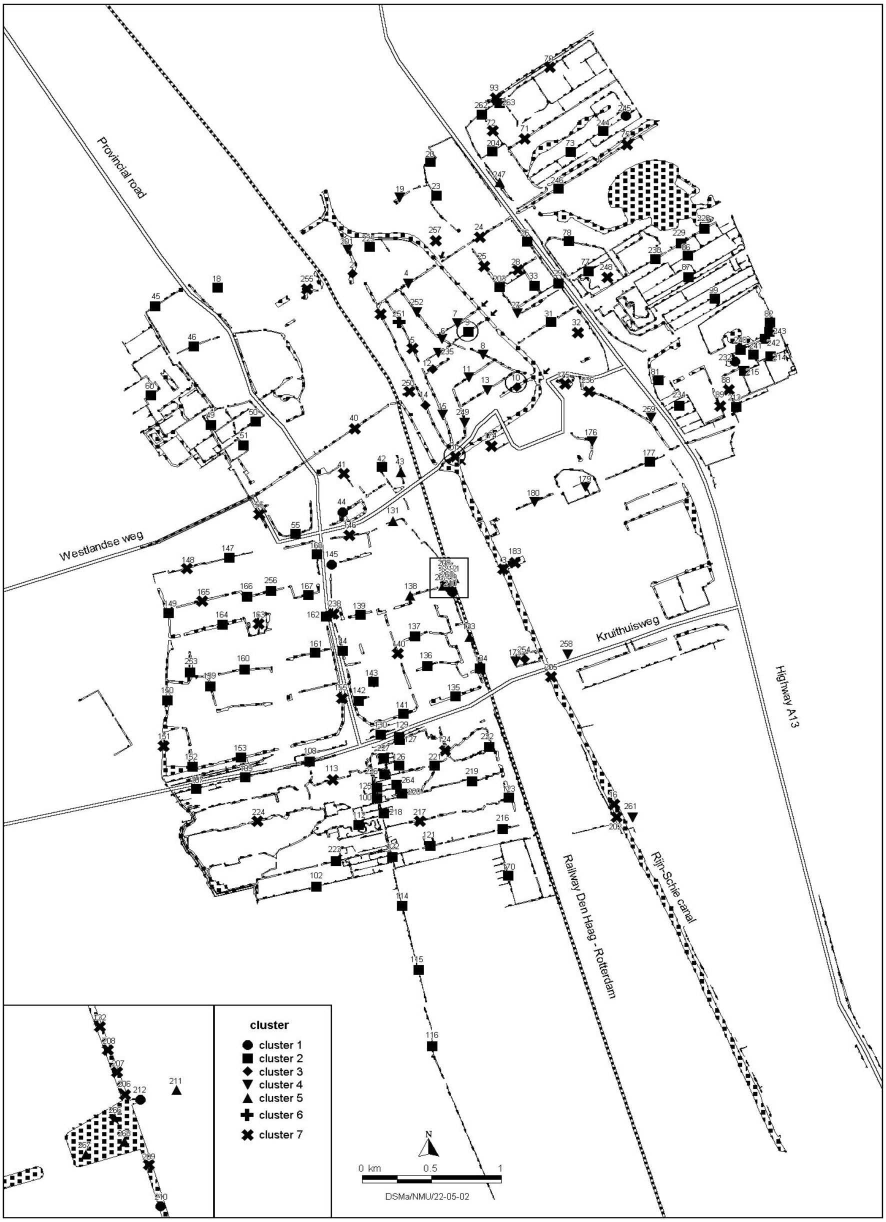

Figure 2 Subdivision, using cluster analysis, of 182 Delft sediment stations, into 7 spatial clusters; see text. Compared to Figure 1, sediment stations with incomplete data sets have been left out of the cluster analysis. At the same time, some extra stations (see e.g. the insert) have been included here. The three sediment stations 1,9 and 10 in the Delft inner city, for a more detailed statistical analysis (see text) have been encircled

- Virtually all of the stations of cluster 4 are either located in the inner city, or are in close connection to the "Rijn-Schie canal" (see Figure 2). The stations of this cluster, generally showing "intermediate" pollution, thus seem to be under direct influence of river Rhine import water.
- Stations of cluster 3 can also dominantly be found in the inner city; however, these stations show much higher pollution levels (especially for heavy metals) than cluster 4. It is probable, therefore, that these stations are much more under the influence of *local* pollution sources than cluster 4.

- Less consistent results were found for the remaining clusters 5 and 6 (each consisting of only one or a few stations, all with very high pollution levels) and for cluster 7.

From the above, it is apparent that a distinct spatial separation can be observed between 1) the inner and outer city of Delft and 2) between certain inner city stations as well. In a further statistical analysis, by excluding the stations of clusters, 3–7, no further differentiation *inside* clusters 1+2 was found (that could e.g. be expected, related with differences in land use and with local effects of the railway line or highways).

The above-found differences between the 18 inner city canal stations were further investigated by comparing the characteristics at three stations (#1, 9 and 10; see Figure 2), together with river Rhine data. The results for the heavy metals contents for 63 Delft sediment core samples (3 stations in triplicate; 7 sediment depths) and the 10 suspended solids data in the river Rhine, are shown in Table 2. The temporal trends for the heavy metal contents (as evident from the 1988–1997 river Rhine data and the vertical sediment profiles, the latter roughly representing the period 1987–1999 (Kelderman, 2002)) have been presented elsewhere (Qu Wenchuan, 1999).

The heavy metal contents in the suspended solids of the river Rhine were found to be comparable with those in the sediments of stations 1 and 9. A substantially higher sediment contamination was observed for station 10. This can probably be connected to the presence of boathouses along this canal, giving rise to e.g. local domestic wastewater discharges and use of rust-preventive coatings for ships. Additionally, this canal is closed off on the inner city side, in contrast to the other two canals.

Subsequently, factor and cluster analyses were applied to the above canal sediment and river Rhine data (for details, see Qu Wenchuan, 1999). It was found that for the total of 73 results (63 Delft sediment data; 10 river Rhine data), a subdivision could be made according to three different clusters (see Table 3). Thus it can be seen that 100% of station 1 and 81% of station 9 data belong to cluster 2 (characterized by "intermediate" pollution levels); for the river Rhine data, 100% belongs to this cluster as well. This is a strong indication for one common source of the sediment pollution parameters, namely the river Rhine, for these two Delft canals. In contrast, 81% of the station 10 data was found to be positioned in cluster 3, characterized by high heavy metal contents. This must mainly be due to the effect of internal pollution sources, as discussed before.

Table 2 Mean values for heavy metal contents (mg/kg) in three Delft canal sediments and in the suspended solids of the river Rhine (the latter as averages over the years 1988–1997)

	Zn	Pb	Cu	Cd
Station 1	541	246	120	5.0
Station 9	482	429	94	2.0
Station 10	920	611	210	7.2
River Rhine	515	109	83	2.3

Table 3 Grouping results for cluster analysis on three Delft canal sediments and river Rhine suspended solids

	Number of data	Cluster 1	Cluster 2	Cluster 3
Station 1	21	0 (0%)	21 (100%)	0 (0%)
Station 9	21	0 (0%)	17 (81%)	1 (5%)
Station 10	21	1 (5%)	3 (14%)	17 (81%)
River Rhine	10	0 (0%)	10 (100%)	0 (0%)

Conclusion

In this study, multivariate analysis was used to investigate the pollution sources for the sediments of the inner and outer city canals in Delft (The Netherlands). It is apparent that the river Rhine water quality has a large impact on the sediment quality in, especially, the inner city of Delft; the same holds probably for many other locations in The Netherlands. In the longer term, the continuing efforts to improve the water quality in this international river will undoubtedly have beneficial effects on the environmental quality here.

A further study on the detailed data base of 182 sediment stations in Delft, e.g. taking into account the individual PAHs, PCB and DDT components, could offer more insight into the various sources (such as: industries, households, agriculture, traffic, urban run-off, and others) of this urban sediment pollution.

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