Monitoring concentrations of microcontaminants in sediment and water in the Rhine delta: a comparison to reference values

Sediment and suspended solid concentrations of many microcontaminants in the Rhine delta are above the levels permitted by the Dutch quality standards. Levels of cadmium, copper, mercury, zinc, hexachlorobenzene, polycyclic aromatic hydrocarbons and chlorobiphenyls are of especial concern. Some chlorobiocides, such as dirins, have become less significant, but others, such as \( \gamma \)-endosulfan and hexachlorocyclohexanes are still important. The quality standards are believed to protect most species and may be considered a minimum for achievement of the goals set by the "Rhine Action Program."

The sharp decline in the concentration of some heavy metals in water seems to slow down close to the quality standards. A review of the major pollution incidents in the period 1988–1991 indicates that half of these probably did not reach lethal levels. The impact of other incidents remains unknown due to the lack of information.

INTRODUCTION

The Dutch Rhine delta comprises several interconnected rivers and lakes, as shown in Fig. 1. It serves as a source of industrial, drinking, fishing and irrigation water. Surface water in lower areas of the Netherlands, in particular, may contain 50% or more of Rhine water. The rivers and lakes are also used for shipping and recreation and as sinks for municipal and industrial effluents and agricultural runoff. The concern for the consequences of this exploitation led to the “Rhine Action Program.” One of the main objectives of this plan is to reduce pollution and to restore the habitats of indigenous species [1]. As a first step, the countries taking part in the Rhine Action Program have agreed to reduce regular emissions of priority micropollutants [2] by 50% during the period 1985–1995 [1]. Unfortunately, even if emissions are reduced by 50% or more, this does not guarantee that indigenous species will return.

Although the pollutants which have been given the most attention are probably the most hazardous, other compounds among the thousands estimated to be present in the Rhine may be important as well. In addition, contaminants that are no longer tolerated can be substituted by other toxic compounds; an example of this is the possible replacement of chlorobiphenyls (Aroclor) by chlorobenzyltoluenes (Ugliec). Reduction does not necessarily lead to an immediate proportional decline in concentrations. Concentrations of some compounds, such as metals, will decrease less than expected from reducing emissions due to natural input. It may take up many years to reach new steady states for persistent chemicals in sediments. The average degree of contamination achieved after this reduction may still be too high for indigenous species. Current estimations of “safe levels” are mainly derived from experiments in which a limited set of standard species and effects are studied; however, large temporal (accidental spillages) and spatial (mixing zones) variations may still prevent permanent and widespread residence of indigenous species.

These potential bottlenecks have been studied in a series of projects looking at concentrations in water, sediment (this paper) and in organisms [3], as well as at the effects observed in bioassays [4,5]. This paper focuses on the monitoring of micropollutants in both the sediments and water in the Dutch Rhine delta. The data presented cover the period 1985–1990. The

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Figure 1. Major rivers and lakes of the Rhine delta (bold lines) and sample locations (underlined). Numbers represent the

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North Sea

Markermeer

Usselmeer

Ketelmeer

Nedermijn 351

Ussel 368

Nedermijn 351

Waal 1540

Maasvluis

Haringvliet

Hollands Diep

Lobith
METHODS

Water concentrations

Monitoring programmes carried out by the Institute for Inland Water Management and Waste Water Treatment have provided most of the data on concentrations of toxic substances in water [6]. The samples were taken from the river branches at the monitoring stations of Lobith and Maassluis, as illustrated in Fig. 1. Concentrations of most compounds were registered monthly at each location from 1985 to 1989. The averages used in the analysis cover at least 6 individual measurements per location. The coefficient of variation (\(\sigma/\mu\)) exceeded 2 for some concentrations of dichloronitrobenzenes, dichlorobenzenes and some chlorobiocides; the average coefficient was 0.7.

Long-term differences are presented by comparing annual averages of metal concentrations in 1980, 1985 and 1990. Since 1988, lipophilic organic microcontaminants have no longer been monitored in total water but in suspended solids samples [7]; this means that no trends can be given. Short-term variations due to accidental spillages since 1988 are also reported [8].

Spatial variation in water concentrations along the river branches turned out to be small on a national scale. We therefore confine ourselves to data from Lobith and Maassluis. At Maassluis pollution levels may be diluted by the inflow of sea water but samples were taken at the time of minimal dilution.

The importance of local variation along the river branches may be roughly estimated by the ratio of input (in \(\mu g \cdot s^{-1}\)) from [9]) to river discharge (in \(1 \cdot s^{-1}\), shown in Fig. 1), assuming immediate and complete mixing. This is reported as a percentage of the concentration measured at the upstream location of Lobith. This simple estimation does not take into account the response of non-conservative compounds and extra dilution due to tidal movement.

Sediment concentrations

Concentrations in sediments were investigated by a number of local authorities during the period 1985-1989. Some of the variability reported may thus be due to differences in methods of sampling and chemical analysis. Therefore, levels are interpreted as indicative values. The sediment samples have been arranged into five regions. Scarse data for the upper branches IJssel, Waal and Nederrijn have been merged into one group. The northern region is represented by Ketelmeer and Markermeer and the western area by the series of lakes of the Hollands Diep and Haringvliet. On average, 80 measurements were available for each region and compound.

The coefficient of variation (\(\sigma/\mu\)) lies within a mean that the extra number of samples per sediment location that contribute to the average conceals a larger spatial variation. Coefficients of variation higher than 2 were calculated for chlorobiophenyl concentrations in Haringvliet.

As an indication of long-term variation, suspended solids concentrations measured at Lobith in 1990 have been added to the sediment graphs. Sediment concentrations are reported in dry weight, as \(\mu g \cdot kg^{-1}\) dry weight, after normalization to 5% organic carbon and 25% lutem contents, according to a common procedure [e.g. 7]. For suspended solids, these percentages were 10% and 40%, respectively.

Reference concentrations

The concentrations in water and sediment are compared to current Dutch quality standards [10,11]. These standards generally reflect the highest concentration of a chemical in water or in food which does no chronic damage to laboratory species, corrected for combined exposure by concentration addition. Concentrations in water, sediment and organisms were translated under the assumption of equilibrium partitioning [12]. Estimated natural background concentrations for heavy metals and polycyclic aromatic hydrocarbons [13] also may serve as a guideline.

No standard has been derived for most of the irregularly released compounds. To obtain at least some idea of their impact, we refer to acute median lethal concentrations from the literature [14,15].

RESULTS AND DISCUSSION

Heavy metals

Concentrations of heavy metals in water and sediment are scattered around the levels of the Dutch quality standards, while natural background levels are one order of magnitude lower. The average chromium and lead concentrations are about 5 times lower than these water quality standards but contamination by other metals is worse.

The decline in the concentrations of heavy metals in water that started in the 1970s continued in the 1980s, as illustrated in Fig. 2. Comparing annual averages of 1980, 1985 and 1990 shows that the trend tends to level off.

Concentrations at Maassluis are lower than at Lobith, with the exception of cadmium in 1985. A comparison of industrial emissions [9] and river discharges with the upstream concentration suggests that this high cadmium concentration may be attributed to input in the Rotterdam harbour area. Similar estimations indicate that relatively important inputs of zinc are found
Monocyclic aromatic hydrocarbons

Monocyclic aromatic hydrocarbons, such as (ethyl)benzene, styrene, toluene and xylene, are no longer regularly monitored in water. Current levels of ethylbenzene and benzene are about 50 times lower than quality standards. Large industrial emissions of benzene of 1,000–10,000 kg y\(^{-1}\) [9] may induce higher concentrations near point sources but concentrations will decrease rapidly due to volatilization.

Polycyclic aromatic hydrocarbons

Samples collected in both water and sediment have yielded averages and maxima of polycyclic aromatic hydrocarbon concentrations that are well above standard and natural background values. Non-reported data showed a decline in Bornoff polycyclic aromatic hydrocarbon concentrations in water. All known industrial point emissions into the Rhine are less than 5 kg y\(^{-1}\) [9] except one input in Rotterdam, which may add several percent to the concentration measured at Lobith. Diffuse input of these hydrocarbons into Dutch water exceeds major industrial point discharges by more than a factor of 10 [9].

Figure 4 shows that sediment quality standards are exceeded in all regions. Nieuwe Merwede and Upper Rhine are highly polluted with all kinds of compounds, but concentrations of some polycyclic aromatic hydrocarbons are especially high in comparison to other regions. This may indicate the importance of small local sources, because they are probably more than proportionally represented in samples from rivers compared with lakes.

Chloroaliphatic hydrocarbons

Contamination by traditional volatile chloroaliphatic hydrocarbons has dropped sharply since 1980.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>Haringvliet</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>Hollands Diep</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>upper Rijn</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>Ketelmeer</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>Markermeer</td>
</tr>
<tr>
<td>Indeno(1,2,3-c,d)pyrene</td>
<td>standard</td>
</tr>
<tr>
<td>PAHs (Bornoff)</td>
<td>natural</td>
</tr>
<tr>
<td>PAHs (Bornoff)</td>
<td>Lobith</td>
</tr>
</tbody>
</table>

Figure 4. Normalized Bornoff polycyclic aromatic hydrocarbon concentrations in suspended (Lobith) and sediment (other locations) dry mass of the Rhine delta during 1985–1990, compared to standard and natural conditions.
Figure 5. Chloroaliphatic hydrocarbon concentrations in the waters of the Rhine delta during 1985–1990 compared to standard concentrations.

Figure 6. Maximum concentrations in water during accidental spillages reported from 1989 to 1991, compared to the estimated lethal concentrations for Cypinnidae fish after 1 day of exposure [8,14].

Figure 7. Monocyclic substituted aromatic hydrocarbons in the water volume of the Rhine delta during 1985–1990 compared to standard concentrations.

Figure 8. Normalized chlorobenzene and hexachlorobenzene concentrations in suspended (Lobith) and sediment (other locations) dry mass of the Rhine delta during 1985–1990 compared to standard concentrations.

Figure 9. Normalized chlorobiphenyl concentrations in suspended (Lobith) and sediment (other locations) dry mass of the Rhine delta compared to standard concentrations.

Figure 5 shows current levels. In 1989, concentrations for most compounds were below detection limits. Figure 6 shows that reported calamities were also well below the median lethal concentrations extracted from the literature [14,15]. Around Maassluis some local problems might exist due to large industrial emissions of 1,2-dichloroethane and tetrachloroethylene.

**Monocyclic chloroaromatic hydrocarbons**

The regularly monitored monocyclic substituted aromatic hydrocarbons consists of chlorobenzenes, with or without hydroxy- or nitro-groups. Figures 7 and 8 demonstrate that (in general) the problematic compounds in this category are pentachlorophenol and, especially, hexachlorobenzene. The comparison of sediment concentrations and recent suspended solid concentrations in Lobith in Fig. 8 shows that contamination is decreasing.

Substituted benzenes are often reported as calamities but Fig. 9 shows that median lethal concentrations are usually higher than 500 µg l⁻¹ for these compounds. Two main industrial point emissions of hexachlorobenzene in Lobith caused a significant increase in concentration in 1990.

their loads were less than 10 kg y⁻¹ [9] in 1985 this input may increase the river concentration by 25%.

**Chlorobiphenyls and chlorodibenzodioxines**

Routiney monitored chlorobiphenyls include the compoments 28, 62, 101, 118, 138, 163 and 180. Spatial trends show no significant differences between locations.
emissions of 0.1 kg y\(^{-1}\) [9] located along the upper branches are insignificant compared to communal and diffuse input.

In sediments, concentrations are also well above quality standards, even in relatively unspoilt lakes such as Markermear and IJsselmeer (Fig. 9). Related compounds, such as chlorodibenzodioxins and chlorodibenzo furans have also been measured. Concentrations of total chlorodibenzodioxins and chlorodibenzofurans in normalized suspended solids ranged between 0.01 and 0.1 \(\mu g\) kg\(^{-1}\) TCDD (2,3,7,8-tetrachlorodibenzodioxine) equivalents [18]. Up to 0.2 \(\mu g\) kg\(^{-1}\) and 5 \(\mu g\) kg\(^{-1}\) TCDD equivalents were detected in river [19] and harbour [18] sediments, respectively.

**Chlorobiocides**

Pollution by some traditional accumulative chlorobiocides in suspended solids has dropped substantially. The average suspended solid concentrations of \(\alpha\)-endosulphan, several drins, heptachlor(epoxide) and hexachlorobutadiene are now close to detection limits, and about one order of magnitude below quality standards. This coincides with low residues of these compounds in sediment-dwelling organisms [3]. From Fig. 10 one can conclude that \(\gamma\)-hexachlorocyclohexane (lindane) and \(\alpha\)-endosulfan are the most troublesome in sediments. Concentrations of dichlorodiphenyltrichloroethane (DDT) and its derivatives (DDD and DDE) are often below detection limits in sediments. Nevertheless, the average suspended solid concentration was 24 \(\mu g\) kg\(^{-1}\) at Lobith in 1990, which is above the quality standard.

In general, chlorobiocide load comes from communal and diffuse emissions and from abroad [19]. In the Netherlands industrial point input is confined to input of drins near Rotterdam.

**Other compounds**

Some compounds, not mentioned so far, are monitored less intensively. Maximum concentrations of the nitrogrenbiocides simazine and atrazine varied around quality standards and detection limits of about 0.1 \(\mu g\) l\(^{-1}\) on average in 1989. Phosphorbiocides, monitored as the sum of choline-esterase inhibition, have stayed just above the quality standard of 0.5 \(\mu g\) l\(^{-1}\) for many years.

Figure 6 shows the maximum concentrations reported for about half the accidental spillages during 1988–1991. These are generally below median acute lethal concentrations. However, this is no guarantee that species were not harmed because no or insufficient toxicity data could be found for the other half of the accidental spillages. Additional information from recently installed continuous biological monitors will

**CONCLUSIONS**

Sediment and suspended solid concentrations for many compounds are still well above Dutch quality standards. In particular, cadmium, copper, mercury, zinc, hexachlorobenzene, poly cyclic aromatic hydrocarbons and chlorobiphenyls are problematical. Some chlorobiocides, such as drins, have become less significant but others, such as \(\alpha\)-endosulphan and hexachlorocyclohexanes are still important. Careful interpretation is required because concentrations below detection limits are no guarantee that compounds are of no concern, as illustrated by DDT and its derivatives. The quality standards are believed to protect most species and may be considered as a minimum for achievement of the goals set by the “Rhine Action Program."

The sharp decline in water contamination by some heavy metals seems to stagnate just above or below quality standards. Reviewing accidental spillages during the period 1988–1991 indicates that half of the short-term increased concentrations probably do not reach lethal levels. The impact of other calamities remains unknown due to a lack of information. In particular, rough estimations showed that large emissions may increase the concentrations measured at Lobith by 10–100%. In addition, contamination of flood plains may be comparable to that of wet sediments.

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