MONITORING CONCENTRATIONS OF MICROCONTAMINANTS IN AQUATIC ORGANISMS IN THE RHINE DELTA: A COMPARISON WITH REFERENCE VALUES

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Abstract

In this study, we measured residues of accumulating microcontaminants in seven aquatic species at seven locations in the Dutch Rhine delta and collected additional data from other papers. Comparison with preliminary quality standards suggests that a certain impact of micropollutants on biota of the aquatic community cannot be excluded. Concentrations of some traditional micropollutants, like chlorobiphenyls, mercury, and DDT tend to increase slightly in a downstream direction with exception of the last section. Residues of heavy metals are higher in invertebrates than in fish. On average, accumulation of organic compounds in invertebrate fat is half the level in fish fat. Residues that are somewhat higher than reflected by these ratios have been observed for chlorobiphenyls in fish and for mercury in pike-perch, Stizostedion lucioperca. Residues in livers of cormorants, Phalacrocorax carbo, from Ketelmeer are one order of magnitude higher.

Comparison with previous studies shows that residues of many traditional compounds have decreased substantially during the last decade. But recently the decline is suspected to level off. Residues of some other compounds have not declined. This trend is most striking for PCB153 and PCB180 in eel, Anguilla anguilla.

1. Introduction

The Dutch Rhine delta consists of several interconnected rivers and lakes, shown in Figure 1. It serves as a source for industrial, drinking, fishing and irrigation water. In particular, surface water in lower areas of the Netherlands may contain up to 50% or more Rhine water. The rivers and lakes are also used as
media for shipping and recreation and as sinks for municipal and industrial effluents and agricultural runoff. The concern for the consequences of this exploitation has brought about the "Rhine Action Program". One of its main objectives is to reduce pollution and to restore destroyed habitats of indigenous species (I.R.C. 1987).

As a first step, the countries concerned have agreed to reduce regular immissions of priority micropollutants by 50% during the period of 1985 to 1995 (I.R.C. 1987). Unfortunately, even the realization of higher percentages is no guarantee for achievement of the goal set.

Though priority pollutants are probably the most hazardous, other compounds among the thousands estimated to be present may be important too. Also, contaminants that are no longer tolerated might be substituted by other toxic compounds, such as the possible replacement of chlorobiphenyls (Aroclor) with chlorobenzyltoluenes (Ugilec). Reduction does not necessarily lead to an immediate proportional decline in concentrations. Concentrations of compounds that occur naturally will decrease less than proportionally, and it may take up many years to reach new steady states for persistent chemicals in sediments. The average degree of contamination achieved after reduction may still be too high for indigenous species. Current estimations of "safe levels" are mainly derived from experiments in which one observes a limited set of standard species and effects. Besides, large temporal (calamities) and spatial (mixing zones) variations may still prevent permanent and widespread residence of indigenous species.

These potential bottle-necks are studied in several projects. Concentrations in water, sediment (Hendriks 1992) and organisms (this study) as well as damage observed in assays (Hendriks et al. 1992, Hendriks and Stouten 1992) have been studied. This paper focuses on monitoring micropollutants in aquatic organisms. We will primarily confine ourselves to a comparison between residues in organisms, reference values and concentrations in sediment and suspended solids.

The compounds chosen stand for traditional micropollutants suspected to accumulate in organisms (e.g. Biddinger and Gloss 1984).
Table 1. Niches of several taxa that thrive in the Rhine delta. Groups in bold type are sampled in this study, others have been studied in other projects mentioned in this paper.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Water</th>
<th>Wet sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plants</td>
<td>Schizophyta, Tracheophyta</td>
<td>Detritus</td>
</tr>
<tr>
<td>Arthropods, molluscs</td>
<td>Cladocera Oligochaeta</td>
<td></td>
</tr>
<tr>
<td>Fish, amphibians, birds, mammals</td>
<td>Bivalvia Chironomidae</td>
<td>Riparia</td>
</tr>
<tr>
<td></td>
<td>O. eperlanus Aythya Chiroptera</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R. rutilus A. anguilla</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S. lucioperca</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P. carbo L. lutra</td>
<td></td>
</tr>
</tbody>
</table>

The taxa selected represent the major trophic levels of the (semi-)aquatic community in the Rhine delta, as characterized in Table 1. As representatives of zoobenthos that feed on phytoplankton and suspended or sedimented detritus we sampled midge larvae, Chironomidae, and mussels, Bivalvia. If no zebra mussels, Dreissena polymorpha, were found, another clam, Anodonta cygnea, was sampled instead. Sediment-dwelling Oligochaeta could not be collected in quantities large enough for chemical analyses. The zooplankton collected consisted mainly of waterfleas, Cladocera. In Markermeer we could not collect enough of this genus and took scuds, Gammarus, known to thrive near stony shores.

As an example of a fish predator for both zooplankton and zoobenthos we collected roach Rutilus rutilus, a dominant species of the Cyprinidae. Smelt, Osmerus eperlanus, was collected as a species exclusively feeding on zooplankton. The polyphagous eel Anguilla anguilla preys on Chironomidae, Bivalvia, and small planktivorous Pisces (De Nie 1982). Finally, pike-perch, Stizostedion lucioperca almost exclusively feeds on fish (Bergers 1991). Adults are considered to be top-predators, too large to be eaten by piscivorous birds and mammals.

Several mollusci-, insecti- and piscivorous birds and mammals feed on the taxa sampled. Sand martin, Riparia riparia and several bats, Chiroptera, feed on pupated Chironomidae. D. polymorpha is an important food source for pochards, Aythya. Cormorant, Phalacrocorax carbo, largely feeds on Cyprinidae and Percidae species. The absence of otter, Lutra lutra, which feeds for 25% on eel, A. anguilla (Broekhuizen and de Ruiter-Dijkman 1988) is especially associated with chlorobiphenyl pollution.

2. Methods

2.1. Water and sediment concentrations

The Institute of Inland Water Management and Waste Water Treatment nowadays monitors contamination of water by lipophilic compounds as the concentration adsorbed to suspended particles
(Venema 1991, Hendriks 1992). In this paper, we will compare residues in biota with suspended solids concentrations monitored at the nearest upstream location. Markermeer residues are related to suspended solid concentrations measured at the IJsselmeer monitoring spot, residues of Haringvliet to the suspended solid concentrations at Haringvliet and the other samples to data from the monitoring station at Lobith. This is illustrated by Figure 1. The average of sediment concentrations measured during 1985-1989 in each region is also taken into account. Concentrations are normalized to standard sediment and suspension consisting of 10% and 20% organic matter respectively. Concentrations at suspended solids and sediments will be expressed per $\mu g \cdot kg^{-1}$ dry organic matter in case of organic microcontaminants per $\mu g \cdot kg^{-1}$ dry dry matter matter in case of metals. More extensive discussions on variation of contamination in time, space and among compounds can be found in another paper (Hendriks 1992).

2.2. Organism concentrations

In accordance with the goal of the Rhine Action Program, this study aims to provide a general impression of current accumulation levels of some 20 compounds in 7 groups of organisms at 7 locations.

Throughout the summer of 1990, each taxon was sampled once at the location and in the period expected to yield the largest amounts. Even then it turned out to be difficult to sample enough material at some locations. In particular, invertebrates were hard to collect in quantities large enough for complete chemical analyses above detection limits. We aimed to capture different taxa close to each other, but if the amount collected was insufficient, a wider range was sampled. A complete analysis in duplicate required approximately 140 g wet weight. Fish were usually caught into sufficient amounts, ranging from 10 to 20 individuals. Adults with a length of 30 - 40 cm for A. anguilla and 40 - 50 cm for S. lucioperus were selected to be analyzed. R. rutulus was divided in three length classes. In this paper we will use the average of juveniles and adults. Since concentrations in both sediment and biota may show substantial variability within short periods and distances and within the same taxon, small differences will be neglected. Fluctuations in concentrations during summer are largely unknown and might hamper analysis but Kraak et al. (1991) reported seasonal differences of heavy metal concentrations in D. polymorpha in uncontaminated lakes to be a factor 3 or less.

2.3. Analytical methods

The analysis of chlorobiphenyls and other organochlorine compounds consisted of drying 5 to 50 g (depending on expected concentration and lipid content) with $Na_2SO_4$ followed by soxhlet extraction with dichloromethane / n-pentane for 15 hours. The extract was cleaned up over an alumina column and fractionated on a silica column. Determination was carried out by gas chromatography using an ECD.
Mercury and arsenic analysis were performed by cold vapor atomic absorption spectrometry (CVAAS). Lead and cadmium were determined by differential pulse anodic stripping voltammetry (DPASV), copper and zinc by graphite furnace atomic absorption spectrometry (GFAAS), respectively flame atomic absorption spectrometry (FAAS). Polyaromatic hydrocarbon analysis was performed using HPLC with fluorescence detection.

With the exception of polycyclic aromatic hydrocarbons measurements, chemical analysis was carried out in duplicates. In more than 90% of the cases, deviation between duplicates turned out to be less than 20%. Larger differences especially occurred in species of lower trophic levels and in β-hexachlorocyclohexane. Pieters (1991) describes further details.

Lipophilic microcontaminants tend to accumulate in the fat of organisms, so that the concentrations per wet weight are considered linearly proportional to the fat fractions (e.g. Mackay 1982). To stress differences in locations and species rather than those in lipid fractions, we will express concentrations of organic micropollutants in μg·kg⁻¹fw, that is per fat weight. Heavy metals may accumulate throughout several components of organisms and will be given in μg·kg⁻¹dw or dry weight. Concentrations below detection limits will be reported as half the detection limit.

2.4. Reference concentrations

Consumption standards offer a first impression of more or less safe concentrations. Some of the standards applied or proposed in the Netherlands are summarized in Table 2.

Table 2. (Proposed) consumption standards for animals (Stortelder et al. 1991), man (Van der Valk 1989) and birds and mammals (Romijn et al. 1991, Van de Plassche et al. 1991).

<table>
<thead>
<tr>
<th>microcontaminant</th>
<th>(proposed) standards</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>animals</td>
<td>man</td>
<td>birds mammals</td>
</tr>
<tr>
<td></td>
<td>μg·kg⁻¹ww</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>5.0×10¹</td>
<td>5.0×10¹</td>
<td>1.6×10²</td>
</tr>
<tr>
<td>Hg</td>
<td>1.0×10³</td>
<td>1.0×10³</td>
<td>4.0×10²</td>
</tr>
<tr>
<td>HCB</td>
<td>2.0×10²</td>
<td>5.0×10¹</td>
<td>5.0×10²</td>
</tr>
<tr>
<td>PCBs</td>
<td>1.0×10²</td>
<td>2.0×10³</td>
<td></td>
</tr>
<tr>
<td>PCB153</td>
<td>1.0×10¹</td>
<td>1.0×10²</td>
<td>1.0×10³</td>
</tr>
<tr>
<td>DDD+DDE</td>
<td>1.5×10²</td>
<td>5.0×10²</td>
<td>1.3×10²</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>3.0×10²</td>
<td>5.0×10¹</td>
<td>1.0×10²</td>
</tr>
<tr>
<td>HCH</td>
<td>2.0×10²</td>
<td>1.5×10²</td>
<td>1.6×10²</td>
</tr>
</tbody>
</table>

The first set consists of product standards, collected by Stortelder et al. (1991) and Van der Kooij et al. (1991), which were used for setting water quality standards. Stortelder et al. (1991) derived lower standards for both cadmium and for hexachlorobenzene. This was because exposure to water was considered more important for cadmium, while the hexachlorobenzene standard was corrected for
combined exposure of all chlorobenzenes. As we focus on accumulation we took the original product
standard collected for these compounds. Van der Valk (1989) reviewed standards for fishery products
from several countries. Omitting differences in water contents and within chemical groups, we inserted
the lower values in Table 2. Concentrations in food, thought to be safe for most but not all bird and
mammal species, have been estimated from various diet studies with a few laboratory species (Romijn et
al. 1991, Van der Plassche et al. 1991). As this branch of ecotoxicology has only just begun to develop
quantitative relationships, no "safe levels" for all or specific (semi-)aquatic birds and mammals can be
derived. From Table 2, one may learn that application of various methods and data sets on different
species yields quite different values. The subject of this article is to compare field concentrations with
levels thought to be safe for most species, rather than to argue the validity of these procedures of
extrapolation. Surprisingly, for each compound, the lowest of all (proposed) standards is close to 1*10^2
μg·kg⁻¹·ww in food. One may use this value as an impression of a low degree of damage rather than focus
on relatively small variations for combinations of compounds and species that may partly be generated by
differences in availability of knowledge. Using typical values of Table 3., the reference value of 1*10^2
μg·kg⁻¹·ww (wet weight) may be converted to 5*10^2 μg·kg⁻¹·dw (dry weight) and 2*10^3 μg·kg⁻¹·fw (fat
weight) for an average animal consisting of 20% dry matter and 5% fat.

3. Results and discussion

3.1. General

<table>
<thead>
<tr>
<th>taxon</th>
<th>proportion of dry to wet weight</th>
<th>proportion of fat to dry weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dry weight of wet weight %</td>
<td>fat weight of dry weight</td>
</tr>
<tr>
<td>Crustacea</td>
<td>9 (3-15)</td>
<td>15 (10-27)</td>
</tr>
<tr>
<td>Bivalvia</td>
<td>12 (8-13)</td>
<td>14 (6-28)</td>
</tr>
<tr>
<td>Chironomidae</td>
<td>5 (2-7)</td>
<td>13 (9-42)</td>
</tr>
<tr>
<td>O. eperlanus</td>
<td>18 (16-19)</td>
<td>14 (9-21)</td>
</tr>
<tr>
<td>R. rutilus</td>
<td>24 (19-29)</td>
<td>12 (6-23)</td>
</tr>
<tr>
<td>A. anguilla</td>
<td>38 (31-45)</td>
<td>53 (48-68)</td>
</tr>
<tr>
<td>S. lucioperca</td>
<td>23 (19-23)</td>
<td>4 (3-9)</td>
</tr>
</tbody>
</table>

Table 3. Proportion of dry to wet weight and proportion of fat to dry weight. Averages with minimum and maximum between brackets.
weight approximates 15% for most taxa. Half of the dry biomass of A. anguilla consists of fat reserves. Only 4% of the other top-predator, S. lucioperca, consists of fat. Thus, the proportion of fat to wet weight ranges from 1% for S. lucioperca, 3% for R. rutilus and O. eperianus to 20% for A. anguilla.

Residues of most organic micropollutants increase slightly in a downstream direction from Lobith to Ketelmeer in the north and Haringvliet-East in the west. The most downstream locations, Markermeeer and Haringvliet-West are clearly less polluted. This series is in agreement with concentrations in sediment and suspended solids measured between 1985 and 1990 (Hendriks 1992).

On the average, concentrations of organic compounds in fish fat are on the same level as those in/at organic sediment. The same applies to inorganic compounds in total fish and total sediment if expressed per dry weight. Contamination in fish is generally twice as high as in invertebrates. We will now elaborate this general picture.

3.2. Cadmium

Figure 2. shows the cadmium residues in invertebrates and fish. The levels in invertebrates tend to decrease in a downstream direction from Lobith to Ketelmeer in the north and to Hollands Diep and Haringvliet in the west. Salomons (1989) attributed this to the increase of pH, which reduces the dissolved -and therefore available- proportion of cadmium. In the German part of the river cadmium concentrations in D. polymorpha increased steadily, with a maximum in the Dutch river branches (Van der Valk et al. 1989).

The concentrations in Bivalvia are higher than the 1 µg kg⁻¹dw measured by Kraak et al. (1991) in D. polymorpha of uncontaminated lakes, among which lake Markermeeer. Cadmium accumulation in the same species at Lobith decreased from 7.4*10⁴ to 1.5*10³ µg kg⁻¹dw between 1976-1988 (Kraak et al.

![Diagram of Cadmium concentrations in biota dry weight and suspension/sediment dry weight](image-url)
1991), which coincided with a similar sharp trend in total water concentrations (Hendriks 1992). Figure 2. shows that all residues measured in this study at other locations are below this level. Cadmium accumulation in invertebrates is 3 to 5 times more severe in Hollands Diep than in Ketelmeer (Anonymous 1991). This is reflected in sediment and less clearly in fish concentrations. Figure 2. shows that cadmium concentrations in sediment/suspension, invertebrates and fish are about $5 \times 10^3$, $5 \times 10^2$ and $1 \times 10^1$ $\mu$g·kg$^{-1}$·dw. All fish samples do meet the reference value of $5 \times 10^2$ $\mu$g·kg$^{-1}$·dw but most invertebrate residues exceed this level.

3.3. Mercury

Variation of mercury concentrations in the Rhine delta in both organisms and sediment fits in the general pattern already described. Van der Valk et al. (1989) showed that D. polymorpha suffers the same degree of mercury contamination throughout Germany. In contaminated areas, total mercury concentrations in fish on dry weight basis are generally 3 times higher than those in invertebrates. The concentration of total mercury along the food chain is in proportion of 0.5 : 1 : 4 for invertebrates, young and old fish respectively. The general reference value of $1 \times 10^2$ $\mu$g·kg$^{-1}$·ww or $5 \times 10^2$ $\mu$g·kg$^{-1}$·dw is often exceeded in fish samples but these levels meet the less severe human consumption standard of $1 \times 10^3$ $\mu$g·kg$^{-1}$·ww.

3.4. Lead and copper

The level of lead contamination in invertebrates and fish of Figure 4. is somewhat above consumption standards and ranges from $5 \times 10^2$ to $2 \times 10^3$ $\mu$g·kg$^{-1}$·ww. Copper concentrations in D. polymorpha at Lobith
were stable on a level of 20 to 25 μg·kg⁻¹·dw during the period 1976-1988 (Kraak et al. 1991). In the same period total water concentrations declined by a factor 3 (Hendriks 1992).

3.5. Polycyclic aromatic hydrocarbons

Concentrations of most polycyclic aromatic hydrocarbons do not increase along food chains (Biddinger and Gloss 1984). Thus, polycyclic aromatic hydrocarbons were only measured in invertebrate samples large enough to assess concentrations of magnifying compounds as well. At some locations, Bivalvia turned out to be present in amounts large enough for analysis of these compounds. The
data shown in Figure 5. do not coincide with sediment contamination, but this may be due to the scarcity of data. Nevertheless, Figure 5. shows that accumulation in the Rhine delta Bivalvia is higher than the level in a small control lake (Anonymous 1991).

Some polycyclic aromatic hydrocarbons and their metabolites have a mutagenic and/or carcinogenic potential but knowledge on safe concentrations is scarce. If one converts the quality standard for benzo(a)pyrene of $1 \times 10^5 \; \mu g \cdot kg^{-1} \cdot ww$ (Stortelder et al. 1991, Canadian Council 1987) to Bivalvia that contain 2% fat one obtains a reference concentration of $5 \times 10^4 \; \mu g \cdot kg^{-1} \cdot fw$. In Haringvliet-Oost benzo(a)pyrene residues in Bivalvia are approximately 50 times lower, so that poisoning via the food chain seems unlikely for this compound alone. The importance of accumulation of other Borneff polycyclic aromatic hydrocarbons, that is benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, fluoranthene and indeno(1,2,3-c,d)pyrene cannot be assessed.

The degree to which concentrations in Figure 5. are harmful to the organism itself is also difficult to estimate. Internal concentrations are seldom recorded and cannot be derived from external concentrations since elimination seems specific for combinations of compounds and species.

3.6. Monocyclic chloroaromatic hydrocarbons

Some monocyclic chloroaromatic hydrocarbons are known to accumulate and penta- and hexachlorobenzene are best known in this respect. Accumulation of chlorobenzenes increases with the degree of chlorination. Since pentachlorobenzene concentrations were generally 2 to 10 times lower than those of hexachlorobenzene we will confine ourselves to the latter compound only.

Figure 6. shows that hexachlorobenzene contamination in organic suspended solids, organic sediment, invertebrate fat and fish fat is in the proportion of 0.3 : 1.2 : 0.6 : 1 respectively. The reference value of
2\times10^3 \, \mu g\cdot kg^{-1}\text{fw} is not exceeded in any sample. Only A. anguilla from highly contaminated areas contains more hexachlorobenzene than allowed by consumption standards, if applied to wet samples.

3.7. Chlorobiphenyls

On average, chlorobiphenyl concentrations in organic suspension, organic sediment, invertebrate and fish fat are in the proportion of $0.1 : 0.9 : 0.5 : 1$. Residues of higher chlorinated chlorobiphenyls in fish and invertebrates differ by approximately a factor 3. This is in line with a less than 3-fold difference between PCB 153 concentrations in A. anguilla and phytoplankton measured in a Dutch freshwater lake by Van der Oost et al. (1988). More specifically, concentrations in Chironomidae from the highly contaminated lakes Hollands Diep and Ketelmeer were higher than those in Crustacea and Bivalvia. The reverse occurred in less contaminated Haringvliet-West and Markermee. In our study, PCB028, PCB052, PCB101, PCB118, PCB(138+163), PCB153, PCB180 generally contributed 2%, 9%, 13%, 10%, 20%, 36%, and 11% to the internal total PCB concentration of Figure 7., but lower chlorobiphenyls were present at much lower concentrations in A. anquilla (Pieters 1991).

After a sharp decrease in the early eighties the decline of chlorobiphenyls concentrations in abiotic and biotic compartments now seem to level off. This tendency is most apparent for higher chlorinated congeners in organisms as illustrated by Figure 8.

Recently, non-ortho (PCB77, PCB126 and PCB169) and mono-ortho (PCB105, PCB118, PCB156) chlorobiphenyls have turned out to be more important than the regularly measured standard set, because these have properties similar to those of chlorodibenzodioxins. Figure 9. contains preliminary data of non-ortho chlorobiphenyls by De Boer and Hagel (1992) and residues of mono-ortho chlorobiphenyls,
chlorodibenzodioxines and -furanes by Hagel (1990) in eel, A. anguilla.

In Figure 9, Lauwersmeer is added as a control location. Non-ortho chlorobiphenyls were only measured at Lobith, values for other locations were calculated in proportion to the mono-ortho chlorobiphenyls (dashed lines). All concentrations are expressed in 2,3,7,8-tetrachlorodibenzodioxine (TCDD) equivalents (Ministry of Public Housing and Environmental Protection 1990). Total TCDD-equivalent values in A. anguilla from the Rhine delta varied by a factor of 5, but were at a level 20 to 100 times higher than those for the less contaminated lake Lauwersmeer. Dioxine-like toxicity of the "toxic" chlorobiphenyls, expressed as TCDD-equivalents, accounted for more than 80% of the total TCDD-equivalents in yellow eel from the Rhine delta. Ongoing debates have not yielded widely accepted standards for these compounds. Some indicative values (Turkstra and Pols 1989, Canadian Council 1987) are in the range of tens of ng·kg⁻¹ ww TCDD.
equivalents. Concentrations of mono-ortho- and non-ortho chlorobiphenyls and dioxines of Figure 9 exceed this level. The same holds for concentrations of chlorodibenzo(dioxines and -furoles in some fish samples from the Rhine delta (Turkstra and Pols 1989).

3.8. Chlorobiocides

Hendriks (1992) reported that measured average suspended solid and sediment concentrations of most traditional chlorobiocides are now below or just above quality standards. Unfortunately, these levels are close to detection limits, which also explains the missing sediment data in Figure 10 and Figure 12.

Figure 10 shows that dieldrin concentrations in organisms are on average 20 times lower than the reference value of $2 \times 10^3 \, \mu\text{g} \cdot \text{kg}^{-1} \text{fw}$. These low levels endorse the conclusion by Biddinger and Gloss (1984) that residue levels of dieldrin will drop after reduction of immission. As dieldrin is a metabolite of aldrin degradation, aldrin contamination will probably be even less severe.

Apart from the A. anguilla samples, most of the residues met the reference value for hexachlorocyclohexane. On the average, concentrations in organic suspended solids, organic sediment, invertebrates and fish were in the proportions of $0.1 : 2 : 0.6 : 1$. The contribution of $\alpha$-, $\beta$-, $\gamma$-isomers to the total hexachlorocyclohexane concentration was 20%, 55%, 25% respectively in sediment (Hendriks 1992), and 10%, 20% and 70% respectively in invertebrates and fish.

The total (DDX) concentration of dichlorodiphenyltrichloroethane (DDT) and its derivatives (DDD and DDE), in organisms are close to reference levels. The relative accumulation concentrations in organic suspension, invertebrate and fish fat were $0.1 : 0.4 : 1$. Reference values for DDX compounds in Table 2. refer to DDE and DDD, because DDE, DDD and DDT contributed respectively about two-third, one-third and less than 2% to the total DDX in our samples.
3.9. Birds and mammals

Interpretation of concentrations in birds and mammals at the end of the aquatic and terrestrial food chain in the Rhine delta is hampered because of migration. In contrast to lower taxa, residues in birds and mammals are often measured in specific organs. Large variations in the liver:muscle ratios exist. For mercury, this ratio ranged between 0.9 and 2 in fish (R.I.V.O. 1991) and 0.2 to 3 in floodplain cattle (Van der Ven et al. 1977). Ratios for chlorobiphenyls in fish vary between 1 and 2.5. This may hold for several chlorinated compounds, but in birds a large accumulation in (affected) specimen have been found (Koeman et al. 1973, Walker 1990). Van Eerden (personal communication) investigated residues in birds that thrive near lake Ketelmeer during 1990 and 1991. The average contamination level of 18 livers of pochards, Aythya, and for organic compounds- 20 livers of cormorants, P. carbo are compared to average food residues in Figure 13. The internal concentrations of cadmium, copper, lead and zinc have been analysed in two cormorants livers only.
These birds are known to migrate over small and large distances. Ketelmeer is one of the most contaminated large lakes in the Netherlands, so that differences between concentrations in bird livers and food in Figure 13. reflect a minimum if uptake abroad is excluded.

Despite these complications, the pattern shown in Figure 13. agrees with other papers on accumulation. Heavy metals concentrations in Aythya tend to be somewhat higher or lower than in Mollusca. The conclusion by Biddinger and Gloss (1984) that cadmium accumulation in invertebrates is important, is confirmed by the increased levels in Mollusca and their predators Aythya. However, the cadmium, lead and mercury residues in these birds do not exceed the background level of about 5*10^3 μg·kg^-1·dw mentioned by Scheuhammer (1987). The accumulation of copper is clearly increased compared to the levels in Mollusca. Mercury accumulation is higher in the livers of piscivorous cormorants, compared to those of the molluscivorous pochards.

Organic contaminants accumulate in the highest order consumer P. carbo, particularly those that are more persistent. Geometric averaged concentration ratios of mercury, higher chlorobiphenyls, DDE, dieldrin, hexachlorobenzene in cormorant liver and fish were in the proportion of 60, 10-20, 30, 15 and 3. In 1970, Koeman et al. (1973) collected several cormorants, P. carbo. In livers of 3 animals shot at Naardermeer they measured accumulation of these compounds that was 4 (DDE) to 14 (PCBS) times higher than those of Ketelmeer in 1990. Residues in a set of six birds found dead throughout the Netherlands in 1970, were at most 6 times higher, with the exception of hexachlorobenzene. Koeman et al. (1973) concluded that the chlorobiphenyls residues measured in their study are likely to cause death of cormorants. Ignoring details on life history of individual cormorants in each study, one may conclude that a decline in residues -if present- is less than one order of magnitude. A similar low decline is found for higher chlorobiphenyls in fish, as illustrated by Figure 8.

In his review, Walker (1990) concludes that liver residues of more than 2*10^5 μg·kg^-1·ww are likely to be lethal to birds. This level is close to the residues shown in Figure 13. after conversion to fat weight.
During the period 1982 to 1987, 4 specimens of the (almost) extinct population of otters, Lutra lutra, the northern part of the Netherlands were collected and analysed. Broekhuizen and de Ruiter-Dijkman (1988) report liver and kidney residues of chlorobiphenyls that vary between $3.4 \times 10^3$ and $-10^3$ for a diseased male- $2.4 \times 10^3$ mg kg$^{-1}$ fw. Their habitat is partially supplied with Rhine water and fish contained about $1 \times 10^3$ to $1 \times 10^4$ mg kg$^{-1}$ fw chlorobiphenyls. The minimum level in fish and the maximum level in otter are close to the averages of Figure 13. The lower levels in otter are close to chlorobiphenyls concentrations $5 \times 10^3$ to $5 \times 10^4$ mg kg$^{-1}$ fw found in fat tissue of otter, Lutra canadensis, trapped throughout New York State (Foley et al. 1988). Liver concentrations of chlorobiphenyls above $1 \times 10^3$ mg kg$^{-1}$ ww (Wren 1991) tend to affect Mustelidae. Occasionally, lower values are reported, such as about $5 \times 10^2$ mg kg$^{-1}$ ww after consumption of food containing $2.5 \times 10^2$ mg kg$^{-1}$ ww (Den Boer 1983).

Terrestrial food chains in the Rhine delta floodplains have hardly been investigated. Ma and Broekhuizen (1989) found cadmium residues in badger, Meles meles, along floodplains of the river Meuse that exceeded critical levels. On the other hand, Van de Ven et al. (1977) concluded that accumulation of heavy metals in Rhine delta cattle is probably of minor importance. As in aquatic communities, concentrations of heavy metals do not seem to increase very much along terrestrial foodchains (e.g. Laskowski 1991, Hunter and Johnson 1982).

Fuchs and Thissen (1981) studied contamination in eggs of the carnivorous little owl, Athene noctua, and the omnivorous magpie, Pica pica, in Rhine delta floodplains. Concentrations of dieldrin, hexachlorobenzene, DDE and chlorobiphenyls in both species varied around 20, 50, 200 and over 1000 mg kg$^{-1}$ ww respectively. Assuming 5% fat in eggs, these values are roughly in the same order of magnitude as those in liver fat of Keitmeier cormorants. Chlorobiphenyl residues decreased if the distance of nest sites to the river was increased.

4. Conclusions and recommendations

This study provided accumulation trends of some 20 microcontaminants in space, time and foodchains throughout the Rhine delta. To overcome the lack of costly multiple sampling - inherent to applied research- observed trends were compared to other information. Together, these yield the following picture.

Over the past decades residues of some traditional compounds have decreased substantially, but during the last decade the decline is suspected to level off. This coincides with similar trends of contamination in abiotic compartments and may reflect the decreasing yields of additional emission reduction measures. Residues of other compounds did not decline at all. This trend is most striking for PCB153 and PCB180 in the eel, A. anguilla. The importance of chlorobiphenyls is also stressed by preliminary data on "dioxin-like" PCBs. Moreover, concentrations of DDT and its derivatives are usually below detection limits in sediments, but these compounds still accumulate substantially in organisms. The general reference value
of $1 \times 10^2 \, \mu g \, kg^{-1} \, ww$ is exceeded in samples for cadmium, mercury and chlorobiphenyls. Residues of other compounds are below this reference value. The difference between actual and reference concentration increases from dichlorodiphenyltrichloroethane (DDT) and its derivatives (DDD and DDE), to hexachlorobenzene, hexachlorocyclohexanes and dieldrin. This suggests that an impact of micropollutants on species of the aquatic community cannot be excluded.

Concentrations of most traditional micropollutants in aquatic taxa tend to increase slightly in a downstream direction but the most downstream location of both branches is clearly less polluted.

On the average, concentrations of organic compounds in organic suspended solids, organic sediment, invertebrate and fish fat are in the proportion of 0.1 : 1 : 0.5 : 1. Residues that are somewhat higher than reflected by these ratios have been observed for chlorobiphenyls in fish and mercury in pike-perch, S. lucioperca. The taxa sampled represent three trophic levels so that the predator-prey accumulation ratio is 2 or less. This ratio was also noticed by Thomann (1989) in his review on ratios of fat-corrected residues of organic compounds in predator and prey fish. Though complicated by impact of migration and variability among organs, residues in birds are probably at least one order of magnitude higher than in fish.

Combining the foregoing we arrive at the following recommendations. As stagnation of downward trends cannot be excluded, monitoring should continue. Our results show that accumulation in aquatic species generally differs less than a factor 3. For a rather cheap and general impression of accumulation in aquatic species, we suggest analysis of heavy metals and polycyclic hydrocarbons in lower taxa, preferably Bivalvia, and mercury and persistent chloroaromatic hydrocarbons in one of the fish species. Substantial accumulation by other compounds not covered in this paper cannot be excluded and deserves attention in experimental studies. The same holds for species, especially those that occupy niches not represented in this paper. Scarce data on accumulation in birds and mammals demonstrate that residues in more terrestrial species deserve more attention in future. Some combinations of compounds and species, such as "dioxin-like" chlorobiphenyls and fish, are ready for more regular monitoring programs.

If current levels of pollution in the Rhine delta are compared to critical values, one has to conclude that a return of indigenous species cannot be guaranteed. If pollution decline is indeed levelling off, more subtle knowledge of "safe" levels becomes crucial. Therefore attention should shift to toxicological studies on relevant taxa. Especially reviews like those by Scheuhammer (1987), Wren (1991), Walker (1990) and others are important for assessing taxon specific requirements.

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