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ACCUMULATION OF METALS, POLYCYCLIC (HALOGENATED) AROMATIC HYDROCARBONS, AND BIOCIDES IN ZEBRA MUSSEL AND EEL FROM THE RHINE AND MEUSE RIVERS

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Abstract—Concentrations of heavy metals and various groups of organic microcontaminants were measured in zebra mussel and eel from the Rhine–Meuse basin. Residues in mussel from the Rhine and Meuse were on average 2.3 and 2.9 times higher than in those from the reference location of IJsselmeer. Total body burdens of organic microcontaminants in mussel and eel varied between 0.05 to 0.07 mmol/kg fat weight in six out of seven samples. The largest contribution in mussels and eel came from polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), respectively. Concentrations of bromodiphenylethers, chlorobenzenes, chloronitrobenzenes, chloroterphenyls, and chlorobenzyltoluenes were lower. Total polybrominated biphenyl residues appear lower than total PCB levels. The largest chlorobiocide residues were noted for 4,4′-DDE, toxaphene, trichlorophenylmethane, and γ-hexachlorocyclohexane. An extraordinary high body burden of 1.2 mmol/kg fat weight, largely consisting of acenaphthene, was observed in one sample. Ratios of concentrations in organism fat and dry organic suspended solids varied between 1 and 10 for traditionally monitored organochlorines, independent of the octanol–water partition coefficient (K_{ow}; for $K_{ow} < 10^6$). The values did not deviate significantly from a value of about 3.3, expected for equilibrium partitioning of persistent chemicals. Lower values were observed for PAHs and some chloro(nitro)benzenes. Most ratios of concentrations in eel and mussel fat were within the range of 1 to 10, also largely independent of K_{ow}. Yet, values tended to be higher at $K_{ow} > 10^6$. Ratios below 1 were noted for pentabromodiphenylether, pentachloro(thio)anisol, chlorobenzyltoluenes, and some chloronitrobenzenes, chlorobiphenyls, and chlorobiocides. These field data confirm recent modeling efforts on bioconcentration and biomagnification. For heavy metals, atomic mass explained 67% of the variation in zebra mussel residues.

Keywords—Body burden Bioaccumulation Organohalogens Biocides Metals

INTRODUCTION

During the last few decades, several groups of microcontaminants have been identified as hazardous substances because of their accumulation in food chains. Many of them, in particular chlorinated biphenyls, benzenes, and organic anthropogenous biocides, have been selected as priority or benchmark chemicals by regulatory agencies [1,2]. The bioaccumulation potential of these chemicals has been investigated in laboratory, field, and modeling studies (see minireview by Hendriks [3]). In addition, several studies have indicated that other groups of chemicals, such as bromobiphenyls, bromodiphenylethers, and chloroterphenyls, may be important as well [4–7].

In the Rhine and Meuse rivers, accumulation of priority pollutants is regularly monitored in zebra mussel (*Dreissena polymorpha*) and fish (*Anguilla anguilla*) at about 30 locations. The number of substances measured is limited to a few heavy metals, seven polychlorinated biphenyls (PCBs), and several chlorobiocides [8,9]. Yet, other substances may be important as well. For instance, moderately hydrophobic compounds that could not be identified individually in river water were likely to be responsible for the toxicity observed in waterfleas [10]. In addition, the total amount of substances accumulated in a biomimetic system was much higher than the sum of the priority compounds measured in fish during routine monitoring [11]. Following these results, it was considered appropriate to extend the number of substances analyzed in some zebra mussel and eel samples.

The purpose of the present study was to demonstrate the presence of priority and nonpriority compounds in zebra mussel and eel of the Rhine–Meuse basin (monitoring objective) and derive indicative values for organism–organic solids and organism–food concentration ratios of these compounds (modeling objective).

The first objective is met by extensive chemical analysis of zebra mussel and eel sampled at the regular monitoring locations Lobith (Rhine) and Eijsden (Meuse). The second objective is accomplished by relating fish and invertebrate residues to each other and to concentrations measured in water or suspended solids samples, taken at the same location and in the same period if possible. The values derived will be compared to values expected from equilibrium partitioning.

The monitoring objective will help to set future priorities for water quality management in effluent and surface water control. In particular, these data are useful for the International Rhine Commission, currently in the process of selecting additional priority chemicals. Obviously, this requires the concentrations found in our study to be compared to critical values, which is beyond the purpose of the present paper. The modeling objective will facilitate validation of bioaccumulation models for less well-tested substances.

The substances selected for the present study are widely recognized as hazardous or have received increasing attention

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in the last few years. Heavy metals and polycyclic aromatic hydrocarbons (PAHs) are natural substances with various anthropogenous sources, the latter usually associated with fossil fuel. Polybrominated diphenylethers and biphenyls (PBBs) are used as flame retardants in, e.g., electronic devices and furniture. Chlorobenzenes are released as by-products of tri- and tetrachloroethylene production. In addition, hexachlorobenzene has been used as a fungicide. Chlorophenols have been applied as fungicides too, in particular for wood preservation. Chloronitrobenzenes on the other hand were mostly used as insecticides. Polychlorinated bi- and terphenyls (PCTs) can be found in waxes, printing inks, paints, and hydraulic fluids. In mines, chlorobiphenyls have been substituted by chlorobenzyltoluenes in hydraulic fluids. Phthalates are used as plasticizer in plastics. Finally, about 60 chloro-, phosphor-, and nitrogenbiocides were selected. Obviously, analysis is also limited by practical and financial restrictions.

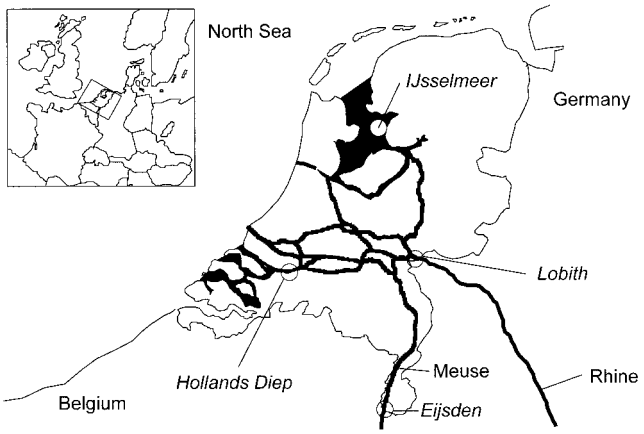

Fig. 1. Major rivers and lakes of the Rhine–Meuse delta with sample locations (F) in italics.

METHODS

Concentrations in suspended solids

Concentrations in suspended solids were obtained from regular monitoring programs. Samples of suspended solids were taken at monitoring containers or stations according to a standard procedure protocol [12]. Surface water was taken upstream, at least 1.5 m away from the monitoring vessel, and led to a flow-through centrifuge (Cepa type 61 or Sharpless AS 16) at 1,000 L/h and 15,000 rpm. The material collected was transferred to jars and conserved at −20°C. Chemical analysis in suspended solids and water was performed according to standard procedures [13]. These will not be repeated here, because we focus on the residues measured in zebra mussel and eel.

Samples of suspended solids were taken at the same location (Lobith, Eijsden) or in the same area (IJsselmeer, Hollands Diep) where the organisms were caught. To cover long-term exposure of zebra mussel and eel, suspended solids concentrations were collected for the period 1993–1994. The number of samples analyzed over this period varied between 6 and 52, depending on the substance concerned. We took the average of all values, including detection limits, per substance and per location. Averages were marked if more than 33% of the values were below detection limits. A few less hydrophobic substances are measured in water only. For these substances, suspended solids concentrations were estimated according to a common procedure [14].

Concentrations in zebra mussel and eel

Sampling. The pollution levels were determined with passive and active biomonitoring. In the case of passive biomonitoring, indigenous organisms are captured directly from the location of interest. For active biomonitoring, organisms are taken from a clean reference area and exposed to the location of interest for a certain period of time.

Active monitoring was carried out with zebra mussels (*D. polymorpha*), collected from a clean reference area in Lake IJssel, near the harbor of Medemblik (Fig. 1). After transportation to the laboratory the mussels remained in an aquarium with running freshwater at 15°C until deployment started. About 10–25 zebra mussels were exposed to the water column at roughly the same locations at which eel were caught. For deployment the mussels were placed unsorted and uncut in nets of synthetic material to avoid stress due to handling activities or byssus destruction. These nets had a length of 60 cm, a diameter of 15 cm, and a mesh size of 9 mm. Deployments started at the beginning of April and lasted for 6 weeks. The nets with zebra mussels were attached to twigs hanging over the water surface or to wooden sheet piling along the border of the river. The distance from the mussels to the bottom of the river was about 30–50 cm. Zebra mussels are very useful for active biomonitoring because they have a long lifespan and are easy to collect and handle. In addition, this sedentary species can withstand high pollutant levels without suffering mortality. They are widely distributed in the inland waters of the Netherlands.

For passive monitoring, eel (*A. anguilla*) were caught in the Rhine at Lobith, the Meuse at Eijsden, and the Hollands Diep near Moerdijk in the period April to June 1994, using electric fishing techniques. Pooled samples of fillets of 25 to 70 fishes were stored at −20°C until analysis. The pooled eel samples were directly used to determine tissue levels of micropollutants. For Lobith, two pooled samples were available for analysis. Thus, four pooled samples of 25 to 70 eel and three pooled samples of 10 to 25 mussels were analyzed.

Analyses of heavy metals

Total mercury was determined by means of flow injection analysis and flameless atomic absorption spectrometry (AAS). Destruction of the samples was performed with the help of a microwave destruction apparatus with 65% HNO_3 as destruction acid. Cadmium and lead were determined by differential pulse anodic stripping voltammetry, copper by carbon-furnace AAS, and zinc by flame-AAS. Chromium, manganese, and antimony have been determined according to an inductively coupled plasma mass spectrometry (ICP-MS) technique.

Analyses of organic microcontaminants

The samples were homogenized in a Waring blender. Subsamples were ground with Na_2SO_4 until a free-flowing powder was obtained. This powder was left overnight and then extracted in a Soxhlet apparatus for 6 (eels) to 10 (mussels) h with 100 ml of dichloromethane–pentane (1:1, v/v). Dichloromethane was evaporated on a rotary evaporator after adding 5 ml of iso-octane as a keeper. The extract was transferred to a 100-ml volumetric flask with *n*-pentane and adjusted. A 10-ml portion was pipetted and the pentane was evaporated. The residue was weighed, resulting in the extractable lipid content.

A portion of the extract containing not more than 250 mg of fat was transferred to the top of an alumina column (internal diameter [i.d.] 2 cm), containing 15 g Al_2O_3·6% H_2O prepared the day before and a layer of 1 cm Na_2SO_4 on top. Elution took place with 150 ml *n*-pentane. After concentration of the quantity of pentane to 2 ml, a silica column, 1.8 g SiO_2·3% H_2O, i.d. 0.6 cm, was used to partition the extract over two fractions: I, 11 ml iso-octane containing the chlorobiphenyls, chlorobenzenes, chlorostyrenes, and *p,p′*-DDE; II, 10 μl 15% diethylether in iso-octane containing the remaining chlorinated pesticides. After a dilution or concentration if necessary, 1 to 2 ml were injected for the quantitative determination of the chlorobiphenyls and chlorinated pesticides with capillary gas chromatography (GC) [15].

To analyze mono-*ortho* PCBs (IUPAC congener numbers 74, 114, 157, 167) [16] in tissue samples, a multidimensional GC procedure with heart-cutting techniques was used [17]. The clean-up procedure was the same as for normal PCB analysis.

For analyzing non-*ortho* PCBs (PCB077, PCB126, PCB169), a modified clean-up procedure is used in which the Soxhlet extraction has been replaced by saponification followed by *a*-pentane extraction in order to analyze more material in less time. After clean-up over alumina and silica, a high-performance liquid chromatography (HPLC) fractionation over porous graphite carbon was introduced. Diode array detection was used for the control of the gradient. For the final analysis, GC/MS with negative chemical ionization was used. For quantification, ^{13}C-labeled PCB congeners were used [18].

Most chlorobiocides were determined after the same clean-up as used for PCBs. However, for the analysis of endosulfan, some minor modifications in the clean-up procedure were introduced. The analyses of pentachloroanisol (PCA) and pentachlorothioanisol (PCTA) were performed by GC/MS detection.

PCTs and PBBs were determined using the same clean-up procedure as for PCBs with some modifications, followed by GC/MS detection [7,19], using electron-capture negative ionization (ECNI) on a Hewlett-Packard 5988A GC/MS (Hewlett-Packard, Avondale, PA, USA). The PCTs were quantified by comparing the total area of all relevant peaks in the total ion chromatogram of the samples with those of the technical mixed standards used.

Tetrachlorobenzyltoluenes (Ugilec) were also determined by GC/MS using electron-impact (EI) ionization and selected ion monitoring. Details of the detection and calculation methods are given elsewhere [20].

Determination of tris(4-chlorophenyl)methanol and tris(4-chlorophenyl)methane (TCPM and TCPMe, respectively) was carried out as described by De Boer et al. [21]. Samples were dried with Na_2SO_4 that had been heated for 24 h at 400°C. After drying for 6 h they were Soxhlet extracted for 6 h with *n*-pentane/dichloromethane (1:1, v/v). The sample intake was 1–5 g for eel and around 40 g for mussels. Therefore, the mussels were transferred to larger Soxhlet thimbles and extracted for 12 h. Gel permeation chromatography (GPC) was carried out on S-X3 Biobeads (column length 33 cm, i.d. 2 cm). Dichloromethane/hexane (1:1, v/v) was used as a solvent. By application of a low nitrogen pressure (0.5 bar) during elution of the TCPM/TCPMe fraction, the elution rate was accelerated to 10 ml/min. TCPM and TCPMe eluted between 70 and 150 ml, whereas 99% of the lipids eluted before 70 ml. The GPC step was repeated to remove the lipids that remained in the extract after the first elution. The GPC eluate was concentrated on a rotary evaporator after adding 2 ml iso-octane as a keeper. Final concentration to 2 ml took place under a gentle nitrogen stream. A fractionation was subsequently carried out on 1.8 g SiO_2·2% H_2O columns to separate TCPM and TCPMe, together with the chlorinated pesticides, from the PCBs. TCPM and TCPMe eluted in the second fraction of 10 ml diethylether/iso-octane (15:85, v/v), after a first 11-ml iso-octane fraction that contained all PCBs. TCPM was determined by GC/ECNI-MS and TCPMe by GC/EI-MS. 1,2,3,4-Tetrachloronaphthalene was used as an internal standard.

PAHs were determined by HPLC and fluorometric detection after sample destruction with alcoholic KOH solution, hexane extraction, and a clean-up. After homogenization of the sample, 30 g is thoroughly shaken with 160 ml ethanolic KOH solution during 3 h at a temperature of 37°C. The destruction solution is subsequently extracted with 100 ml hexane during 1 min, which is repeated twice. After drying and evaporation of the hexane extract to 10 or 20 ml, a clean-up procedure was carried out over a combined SiO_2–Al_2O_3 column. To analyze the PAH compounds, 6-μl injections were made on two coupled reverse-phase ChromSpher PAH columns during a gradient elution procedure. Three HPLC runs were needed at different wavelengths for the determination of all 15 PAH compounds.

Similar analytical procedures were followed for nitrogen PAHs (NPAHs). Details have been reported by Van Velzen et al. [22] and will not be repeated here because no concentrations were detected above detection limits. The same holds for nitrogen- and phosphorbiocides. They were determined by GC as described by Specht and Tillkes [23].

RESULTS

Concentrations in zebra mussel and eel

The concentrations of heavy metals, PAHs, and organohalogens measured in zebra mussel and eel are given in Appendix 1. Residues of bromobiphenyls, chlordenes, and organotins were largely below detection limits. Concentrations of nitrogen- and phosphorbiocides as well as those of NPAHs were all below detection limits (Appendix 2).

The analysis of chlorophenols was characterized by poor calibration, low recovery, and high blank values. Concentrations of 4-monochlorophenol, 2,4- and 2,6-dichlorophenol, 2,4,5- and 2,4,6-trichlorophenol, and pentachlorophenol in mussel appeared between 10 and 30 μg/kg wet weight per compound. High control values were also noted for phthalates, despite many precautions, like distillation of solvents and rinsing of glassware. The same kind of problems apply to the analysis of phthalates in suspended solids. Dimethylphthalate concentrations appeared to be 0.24 to 0.46 and 0.05 for mussel and eel, respectively. Diethylphthalate residues might be in the range of 3.3 to 3.6 and 0.14, respectively, whereas dioctyl and di-2-ethyl-hexylphthalate levels were uncertain. The analysis of individual bromobiphenyls turned out to be difficult, and the procedure has been optimized since then. New results suggest that concentrations of PBB congeners may be up to about one-tenth of the residues for the analogous PCB congeners (de Boer, personal communication). Thus, concentrations of chlorophenols, phthalates, and individual bromobiphenyls were disregarded in the interpretation.

Concentrations of organic microcontaminants in zebra mussel from the Rhine and Meuse were on average 2.3 and 2.9

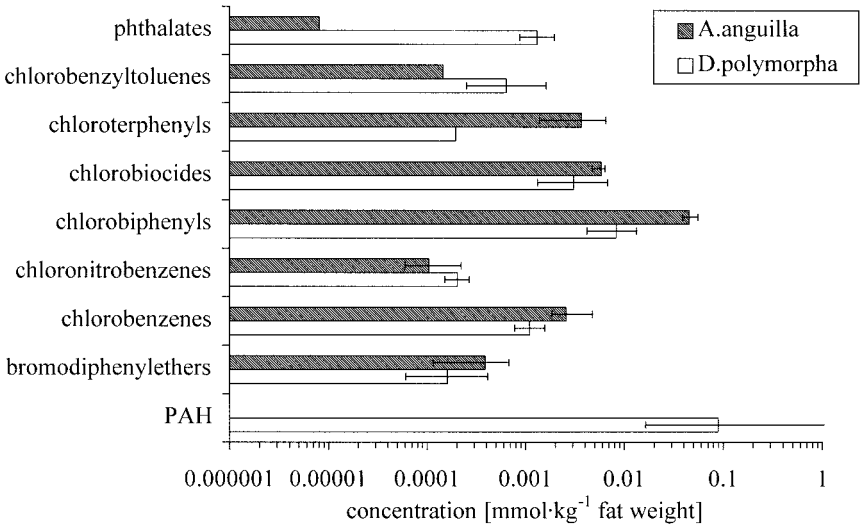

Fig. 2. Concentrations of organic microcontaminants in zebra mussel (*Dreissena polymorpha*) and eel (*Anguilla anguilla*); geometric average and minimum–maximum range from various locations in the Rhine–Meuse delta in 1994.

times higher than those from IJsselmeer. This trend is in agreement with earlier data [9]. It also confirms the general idea that IJsselmeer may serve as a relatively unpolluted reference location. In contrast with this trend, concentrations of some chloronitrobenzenes in IJsselmeer mussel were more than two times those in *D. polymorpha* from either Rhine or Meuse.

Concentrations in eel from the Rhine sampled at different moments were within a factor two for four of the five compounds on a lipid-weight basis. Larger differences were noted for some chloro(nitro)benzenes and chlorobiphenyls. On average, residues in eel from Lobith were similar to those from Hollands Diep. Concentrations in Meuse eel were, on average, 10% higher than those in Rhine eel. Concentrations of trichlorophenylmethane, bromodiphenylethers, β-hexachlorocyclohexane, 1-chloro-4-nitrobenzene, and benzo(*g*,*h*,*i*)perylene, however, were more than five times higher in some eel or mussel samples from the Rhine compared with those from the Meuse. The reverse was noted for α-endosulfan and several other PAHs.

Appendix 1 shows that the total concentration of organic microcontaminants ranged from 0.05 to 0.07 mmol/kg fat weight in six of the seven samples taken. An extraordinarily high body burden of 1.2 mmol/kg fat weight was observed in zebra mussels from Eijsden. About 70% of this burden was accounted for by acenaphthene.

As illustrated by Figure 2, the largest contribution to the overall organic microcontaminant burden in mussels comes from the classical chemicals, viz. PAHs, PCBs, and chlorobiocides. Chlorophenols may also be important, but their levels remain uncertain because of analytical problems. In the eel samples, chlorobiphenyls and chlorobiocides were dominant. PAHs were not analyzed in eel because studies have shown that their levels in fish are generally below or just above the detection limits [9].

Concentrations of most PCBs were several orders of magnitude higher than the detection limits reported for the analogous PBB congeners. An exception was noted for the non-*ortho* congener 169. On average, the largest contribution to the total chlorobiocide load came from 4,4′-DDE, toxaphene, trichlorophenylmethane, and γ-hexachlorocyclohexane.

Ratios of concentrations in suspended solids, zebra mussel, and eel

The average ratios of concentrations in suspended solids, zebra mussel, and eel are given in Appendix 1. Values are based on total lipid weight for animals and on dry weight for organic suspended solids because organic microcontaminants mainly accumulate in lipids and adsorb to organic matter.

Figure 3 gives the ratios of concentrations (above detection limits) in mussel fat and organic suspended solids dry weight as a function of the octanol–water partition ratio (K_{ow}) of the compound. One may conclude that the ratio varies between 1 and 10 for traditionally monitored organochlorines as chlorobiphenyls, chlorobiocides, and hexachlorobenzene (Appendix 1). This does not deviate significantly from the value of 3.3 (Fig. 3). Lower values were observed for some chloro(nitro)benzenes (0.2–0.5) and PAHs (0.03–0.7), sometimes significantly lower than 3.3 (expected from equilibrium partitioning as explained in the Discussion). These patterns are confirmed for substances with concentrations in suspended solids below detection limits (Appendix 1). The ratios for nitrogen- and phosphorbiocides, calculated from detection levels in organisms, were in the range of <30 to $<26{,}000$.

As illustrated by Figure 4, concentration ratios for eel and traditionally monitored organochlorines were somewhat higher than for mussels. Values for traditionally monitored chlorobiphenyls and chlorobiocides are between 1 and 30, with exception of α-endosulfan (0.26). In eel, ratios for chloronitrobenzenes are also lower (0.1–0.4). The results for the nitrogen- and phosphorbiocides are analogous to those of mussel.

Figure 5 demonstrates that concentrations of most compounds in eel fat were higher than those in mussel fat. Average ratios of 0.1 to 1 were noted for pentabromodiphenylether, pentachloro(thio)anisol, tetrachlorobenzyltoluenes, and in some chloronitrobenzenes, chlorobiphenyls, and chlorobiocides (including endosulfan and toxaphene). Ratios did not exceed the value of 11, with the exception of Σ6PBB and polychloroterphenyls.

DISCUSSION

Concentrations in zebra mussel and eel

The priority substances cadmium, mercury, pentachlorobenzene, hexachlorobenzene, chlorobiphenyls (PCB028,

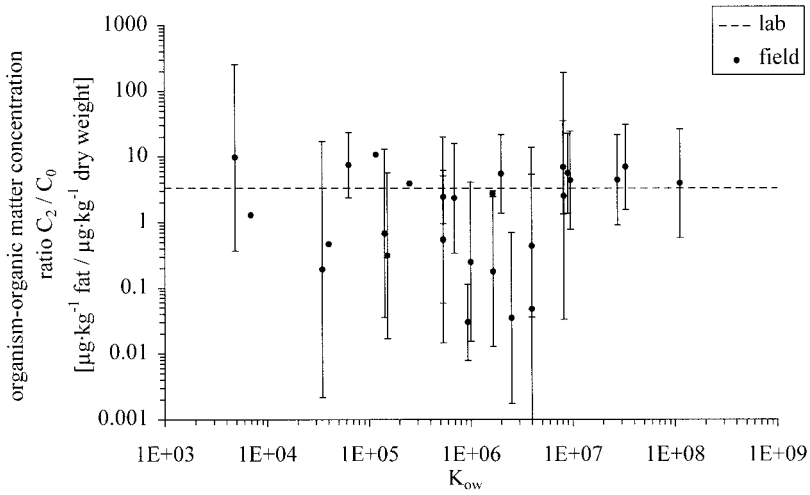

Fig. 3. Ratios of concentrations of organic microcontaminants in zebra mussel (*Dreissena polymorpha*) fat weight C_2 versus organic suspended solids dry weight $C_{0,osol}$ in Rhine–Meuse delta field surveys (geometric $\mu \pm 95\%$ confidence interval [CI]).

PCB052, PCB101, PCB138, PCB153, PCB180), α-, β-, γ-hexachlorocyclohexane, DDD, DDE, dichlorodiphenyltrichloroethane (DDT), α-endosulfan, dieldrin, endrin, α-, β-hexachlorepoxide, hexachlorobutadiene, and several PAHs are regularly monitored in zebra mussel from Lobith, Eijsden, and IJsselmeer. Concentrations measured in the present study were within a factor of three of the levels recently measured in the regular monitoring programs [24,25]. Exceptions were noted for lead, β-heptachlorepoxide, and several PAHs at more than one location. The exceptionally high residue levels of acenaphtene in zebra mussel from Eijsden were not found previously.

Some of the nonpriority substances have been measured in eel from Lobith and Hollands Diep in 1988 [26]. Concentrations of chlorobiphenyls (IUPAC numbers 031, 044, 047, 049, 052, 066, 087, 097, 105, 110, 128, 141, 149, 151, 170, 187, 194, 206) measured in that period are also within a factor of three of those from the present study. Mono-and dichloronitrobenzenes, oxychlordane, and *trans*-nonachlor concentrations in our study were below the detection limits reported for the 1989 data. TCBT concentrations were at the same level as in 1988 [20].

Residues of tetrabromodiphenylether, hexachlorobenzene, standard PCB congeners (IUPAC number 101, PCB118, PCB138, 153, 180), and γ-hexachlorocyclohexane in eel were more than 10 times higher than in whitefish (*Coregonus* sp.) in a pristine area in north Sweden [5]. Provided that accumulation in different fish species is similar (see, e.g., Hendriks [3] for evidence), these compounds may be suspected to be released at a larger scale in the Rhine–Meuse area. Swedish levels of non-*ortho* PCBs (77, 126, 169), pentabromodiphenylether, DDTs, α-hexachlorocyclohexane, dieldrin, *cis*-chlordane, and *trans*-nonachlor were within a factor of four from the concentrations observed in the Rhine–Meuse area. This may suggest that the levels of these compounds are determined by emission and distribution on a continental scale.

Metal concentrations in zebra mussel are plotted as a function of their atomic mass (Fig. 6). Heavier metals tend to be less abundant in mussel. About 67% of the variation can be explained by the atomic weight. Similar patterns are observed for metals in the earth's crust [27,28]. Heavier metals affected bacteria and waterfleas at lower concentrations [29–31], indicating that organisms are generally adapted to environmental concentrations of natural substances. However, variability in

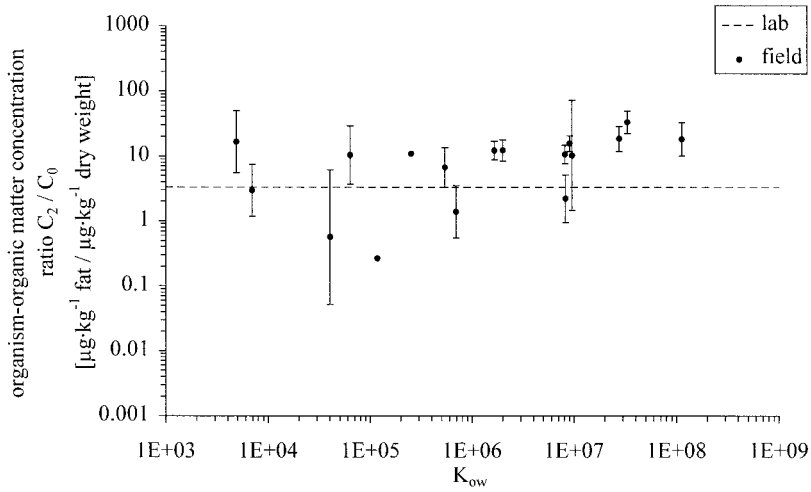

Fig. 4. Ratios of concentrations of organic microcontaminants in eel (*Anguilla anguilla*) fat weight C_2 versus organic suspended solids dry weight $C_{0,osol}$ in Rhine–Meuse delta field surveys (geometric $\mu \pm 95\%$ CI).

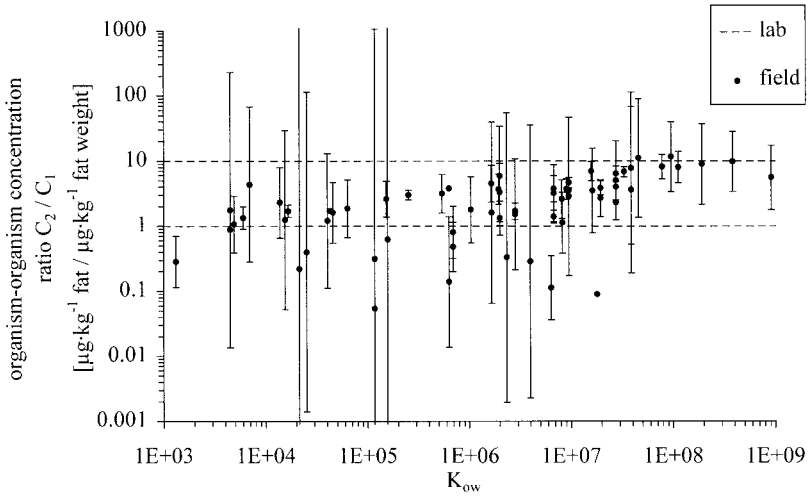

Fig. 5. Ratios of concentrations of organic microcontaminants in eel (*Anguilla anguilla*) C_2 and zebra mussel (*Dreissena polymorpha*) C_1 fat weight in Rhine–Meuse delta field surveys (geometric $\mu \pm 95\%$ CI).

metal accumulation and tolerance among species is large, suggesting that different strategies are possible.

Although an extensive risk evaluation is beyond our purpose, we may briefly compare the measured residues to (sub)lethal levels. The total body burdens of organic microcontaminants ranging from 0.05 to 0.07 mmol/kg fat weight in six of the seven samples are clearly below the level of about 2 to 20 mmol/kg fat weight at which nonpolar narcosis affects all species [31–33]. Yet, the exceptional body burden of 1.2 mmol/kg fat weight in the zebra mussel sample from the Meuse is close to the range of lethal and sublethal effects.

Below the range of 2 to 20 mmol/kg wet weight, some groups of chemicals are toxic to some groups of species via specific modes of action. Such chemicals are considered to have an excess toxicity in comparison with the minimum toxicity of narcotic compounds. The importance of most priority substances with a specific mode of action has already been evaluated by comparing Rhine–Meuse field residues to critical levels [31]. A similar risk analysis will be necessary for the other compounds measured in the present study. Yet, the largest contribution to the total body burden of organic microcontaminants came from traditionally monitored compounds such as PCBs, PAHs, and DDE. Thus, concentrations for compounds that recently have received increased attention are only relevant if their excess toxicity is substantially higher than that of related traditionally monitored chemicals.

For an organism with 5% fat, the total burdens in our study ranged from 0.003 to 0.004 mmol/kg wet weight. For the same area and period, Van Loon et al. [11] reported 0.05 to 0.15 mmol/kg wet weight of organic microcontaminants adsorbed to surrogate biological matter (C18 resins) after exposure to Rhine and Meuse water. Thus, there may be other chemicals with substantial accumulation potential that were not analyzed in our study. In order to be relevant for real organisms however, these compounds should be able to pass biological membranes and they should not be subjected to (substantial) biotransformation. A full comparison between compounds adsorbed to C18 and accumulated in organisms is beyond the purpose of the present study. Possible candidates that may explain the difference observed are substances such as PAHs (some biotransformation in invertebrates) and musks (not analyzed in the present study).

Ratios of concentrations in organism fat and organic solids

Figures 3 and 4 summarize the concentrations in organism fat relative to those in organic suspended solids measured in the present study. The higher values, related to persistent compounds, are fairly independent of the K_{ow}. This is confirmed by other field studies [3,34]. For a recent review including exceptions see Belfroid et al. [35]. The variation of more than one order of magnitude is likely to be due to small sample size. In the earlier study on seven instead of three locations, confidence intervals were about a factor of five [3].

The organism–solids concentration ratio of persistent compounds can also be calculated from laboratory studies on accumulation and sorption from water. The concentration accumulated in organisms (C_2) as well as the concentration adsorbed to organic solids ($C_{0,osol}$) (i = 0,osol) can be approximated by a linear function of the fat fraction p_{fat}, the K_{ow}, and the concentration in water $C_{0,wat}$. The ratio between the concentration in organisms and suspended solids can now be calculated as

$$\frac{C_2}{C_i} = \frac{p_{fat,2} \cdot K_{ow} \cdot C_{0,wat}}{p_{fat,i} \cdot K_{ow} \cdot C_{0,wat}} = \frac{p_{fat,2}}{p_{fat,i}} \qquad (10^2 < K_{ow} < 10^7) \quad (1)$$

where $p_{fat,i}$ is the octanol-equivalent fat fraction of organic matter (see Hendriks [3] for details). In the case where organism concentrations are expressed in lipid weight, $p_{fat,2}$ is set on 1. Based on empirical data collected by Karickhoff et al. [36] and Sabljic et al. [37], the octanol-equivalent fat fraction for organic solids can be estimated to be about 0.3 on a dry-weight basis. Thus, laboratory studies suggest that the ratio of the concentrations in organism lipid weight and that in organic suspended solids dry weight equals about 1/0.3 = 3.3. Because organic matter consists of about 50% organic carbon [14], ratios to organic carbon are about half this value ($\approx$1.7).

The results from the present study show that ratios of concentrations in organism fat and in organic suspended solids dry weight are indeed independent of the K_{ow}. The ratios are around the expected value of 3.3 for many priority compounds in zebra mussel (Fig. 3). Similar values were obtained for zebra mussel and other invertebrates in an earlier investigation [3]. For eel, ratios were on average 1.8 times higher than those for

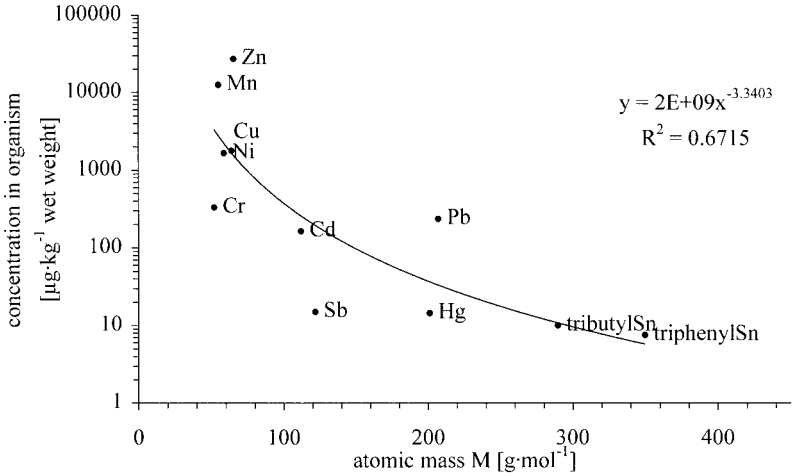

Fig. 6. Concentrations of heavy metals in zebra mussel (*Dreissena polymorpha*) wet weight as a function of atomic mass (Sn reflects half the detection limit).

mussel (Fig. 4). In the previous study, residues in three fish species, including eel, were also about twice as high as in the invertebrates [3]. Though eel, a mobile species in contrast to the sessile zebra mussel, may have picked up contaminants in other more polluted areas, additional exposure via food seems to be a more probable explanation for the increased levels of organochlorines.

As given in Appendix 1 and described in the Results, concentration ratios below 1 in Figures 3 and 4 were found for 1,2,4,5-tetrachlorobenzene, chloronitrobenzenes, and PAHs. The last group is known to have higher elimination rates than those for more persistent compounds of the same hydrophobicity, apparently due to biotransformation [38]. Concentration ratios for nitrogen- and phosphorbiocides varied from <30 to <26,000. Unfortunately, detection limits for these compounds turned out to be too high to decide whether their actual value is at or substantially below the 3.3 level found for persistent chemicals. This holds for nitrogen- and phosphorbiocides with K_{ow} of less than 100 too. For these compounds the contribution in the aqueous phase to the total body burden should be taken into account as well [3].

The concentration ratios for cadmium, copper, mercury, and zinc were within a factor of two of the averages measured for invertebrates, mainly zebra mussel and chironomids, in the previous field study [3]. No other metals were measured in that study. In addition, laboratory organism–water partition ratios from the literature divided by solids–water partitioning ratios for the Rhine–Meuse basin yielded organism-suspended solids ratios within the same range [3].

Thus, ratios of heavy metal concentrations in organism and standardized suspended solids, on a dry-weight basis, are fairly similar for different metals in zebra mussel. They can be applied for risk assessment in the Rhine–Meuse basin within the concentration range measured in the present study. However, extrapolation to other species and other conditions (pH, cation exchange capacity [CEC], metal concentrations, clay contents, etc.) is likely to fail, because of the large variability.

Ratios of concentrations in eel and mussel fat

Because zebra mussel (*D. polymorpha*) is part of the diet of the omnivorous eel (*A. anguilla*), the ratio of the concentrations in their fat may serve as a first indication of the biomagnification potential of the compounds. In the model of Equation 1, C_2 and C_1 ($i = 1$) now represent the concentrations in eel and mussel fat, respectively. In the case of an equilibrium between the fish and its food, $p_{fat,i}$ equals the fat fraction of the feces at the end of the digestive tract of the fish. The fraction of food assimilated by organisms varies between about 0.3 (detriti- and herbivores) to 0.95 (carnivores). See, e.g., Jobling [39] for assimilation efficiencies of fish. The food quantity in the gut and with it the capacity to store contaminants is expected to decrease by a factor of about $(1/[1 - 0.3]) = 3$ to $(1/[1 - 0.95]) = 20$ when it becomes feces. Thus, lipid-corrected organism–food ratios are expected to be in the range of about 3 to 20. In case of preferential assimilation of fat, such as noted by Sijm et al. [40] and Gobas et al. [41], these values may be somewhat higher. A more elaborate discussion, beyond the purpose of the present paper, is given by, e.g., Hendriks [3] and Gobas et al. [41].

The lipid-corrected organism–food ratios measured in laboratory experiments and field surveys are indeed often within the range of 3 to 10 [3,41,42]). In field surveys, values up to about 30 are observed for birds and mammals at the top of the food chain [3,43]. These high levels may perhaps be attributed to higher food assimilation efficiencies in (top) carnivores compared with herbivores [39,44]. The values of Figure 5 largely fit into the range of about 1 to 10, indicating that equilibrium analysis can roughly explain the ratios found. Here too, values far below 1 suggest that the compounds concerned may have been subjected to substantial biotransformation. The reduced ratio for chlorobenzyltoluenes, for instance, was confirmed by similar results in laboratory experiments with mussel and guppy [45]. Other substances with low organism–food ratios are given in the Results. Note that all confidence intervals of more than two orders of magnitude apply to compounds with averages below 1 (Fig. 5).

A more detailed look at the upper values of Figure 5 reveals that eel–mussel ratios tend to increase slightly at K_{ow}s of more than 10^6. This may be understood from the combined exposure to water (suspended solids) and food. Figure 5 suggests that exchange with water is dominant for K_{ow} below about 10^6. At $K_{ow} > 10^6$ food can contribute significantly to the total body burden. Combining empirical and theoretical evidence, Gobas et al. [41] and Belfroid et al. [42] reported similar results for fish and earthworms, respectively. A refinement of our model

for the concentration kinetics as a function of K_{ow}s and the adult size of species led to the same conclusion [38].

CONCLUSIONS

In the present study, concentrations of heavy metals and various groups of organic microcontaminants were measured in zebra mussel and eel from the Rhine–Meuse basin. The following conclusions can be drawn. Concentrations of chlordenes, organotins, nitrogen- and phosphorbiocides, and NPAHs were below detection limits. Concentrations for chlorophenols, phthalates, and bromobiphenyls are not reliable and were regarded as indicative values. Residues in mussel from the Rhine and Meuse were on average 2.3 and 2.9 times higher than in those from the reference location of IJsselmeer. Concentrations in Meuse eel were, on average, 10% higher than those in Rhine eel. Concentrations of most substances were within a factor of three of the levels measured in previous monitoring studies if available. The total body burden of organic microcontaminants varied between 0.05 to 0.07 mmol/kg fat weight for six out of seven samples. The largest contribution to the overall organic microcontaminant burden in mussels comes from traditionally monitored chemicals, viz. PAHs, PCBs, and chlorobiocides. This is far below the critical level of about 2 to 20 mmol/kg fat weight at which nonpolar narcosis will affect all species. Obviously, effects from compounds with other more specific modes of action cannot be excluded. The total body burden is also about 10 times lower than the total organic microcontaminants burden adsorbed to biomimetic material from the same locations. This suggests that other substances not covered in our study may be important for accumulation in organisms too. An extraordinarily high body burden of 1.2 mmol/kg fat weight, close to narcotic effect levels, was observed in zebra mussels from Eijsden. About 70% of this burden was accounted for by acenaphthene. Atomic mass explained 67% of the variation of metal concentrations in zebra mussel. Concentrations of PBB congeners appear to be lower than the analogous PBBs. The largest chlorobiocide concentrations were noted for 4,4′-DDE, toxaphene, trichlorophenylmethane, and γ-hexachlorocyclohexane. Ratios of concentrations in organism fat and dry organic suspended solids varied between 1 and 10 for traditionally monitored organochlorines, independent of K_{ow}. The values did not deviate significantly from the value of 3.3, expected for equilibrium partitioning of persistent chemicals. Lower values were observed for some chloro(nitro)benzenes and for PAHs. Most ratios of concentrations in eel and mussel fat were within the range of 1 to 10, also largely independent of K_{ow}. Yet, values tended to be higher at $K_{ow} > 10^6$. These field data confirm recent laboratory and modeling efforts on biomagnification. Ratios below 1 were noted for pentabromodiphenylether, pentachloro(thio)anisol, chlorobenzyltoluenes, and in some chloronitrobenzenes, chlorobiphenyls, chlorobiocides.

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APPENDIX 1

Concentrations of metals and organic microcontaminants in suspended solids, zebra mussel (*Dreissena polymorpha*), and eel (*Anguilla anguilla*) from various locations in the Rhine–Meuse delta in 1993–1994[a]

		Suspended solids, 1993–1994, μg/kg dry weight standardized (metals), organic matter (org. microcontaminants)				*Dreissena polymorpha*, 1994, μg/kg wet weight	
	K_{ow}	Rhine	Meuse	Ysselmeer	H. Diep	Rhine	Meuse
Dry matter fraction						0.12	0.11
Fat fraction						0.02	0.02
n		6–52	6–52	6–52	6–52	10–25	10–20
Metals							
Antimony		—	—	—	—	15	<10
Cadmium		2,400	14,000	2,000	5.2	160	420
Chromium		—	—	—	—	600	300
Copper		72,000	110,000	24,000	86,000	2,700	1,900
Lead		99,000	180,000	42,000	130,000	470	320
Manganese		—	—	—	—	19,000	9,000
Mercury		1,000	2,300	100	0.98	17	14
Nickel		48,000	55,000	22,000	48,000	2,500	1,100
Tributyltin		—	—	—	—	<20	<20
Triphenyltin		—	—	—	—	<15	<15
Zinc		480,000	1,600,000	220,000	10,000,000	29,000	46,000
PAHs							
Acenaphthene	7.6×10^3	—	—	—	—	15	2,500
Anthracene	3.5×10^4	1,600	870	260	1,200	1.0	21
Benzo(*a*)anthracene	5.4×10^5	4,600	4,500	320	3,400	20	250
Benzo(*a*)pyrene	1.7×10^6	5,200	4,700	400	4,100	6.0	15
Benzo(*b*)fluoranthene	4.0×10^6	6,800	7,700	530	6,100	20	63
Benzo(*e*)pyrene	1.7×10^6	—	—	—	—	13	55
Benzo(*g*,*h*,*i*)perylene	4.0×10^6	4,200	4,900	420	4,000	3.1	0.49
Benzo(*k*)fluoranthene	1.0×10^6	2,900	2,900	290	2,600	4.0	16
Chrysene	5.4×10^5	4,600	4,900	370	3,500	17	65
Dibenzo(*a*,*h*)anthracene	9.3×10^5	1,000	770	<250	850	0.51	0.49
Fluoranthene	1.4×10^5	10,000	9,300	710	7,500	33	270
Fluorene	9.8×10^3	—	—	—	—	1.0	250
Indeno(1,2,3-*c*,*d*)pyrene	2.5×10^6	4,000	5,000	390	36,000	1.0	2.1
Phenantrene	3.6×10^4	7,000	4,200	590	4,800	5.1	120
Pyrene	1.5×10^5	8,200	9,200	600	6,400	12	120
Σ6 Bromobiphenyls		—	—	—	—	<0.010	<0.47
Bromodiphenylethers							
Tetra	1.0×10^6	—	—	—	—	2.2	0.97
Penta	6.4×10^6	—	—	—	—	1.7	0.68
Chlorobenzenes							
1,2,3-Tri	1.4×10^4	—	—	—	—	0.080	0.14
1,2,4-Tri	1.7×10^4	—	<1,400,000	—	—	1.6	1.8
1,3,5-Tri	1.5×10^4	—	<480,000	—	—	0.14	0.12
1,2,3,4-Tetra	4.3×10^4	—	—	—	—	0.15	0.21
1,2,3,5-Tetra	4.5×10^4	—	—	—	—	0.080	0.082
1,2,4,5-Tetra	4.0×10^4	23	<3.8	—	—	0.20	0.21
Penta	1.5×10^5	—	<10,000,000	—	—	0.49	0.27
Hexa	5.4×10^5	140	24	4.8	62	4.2	1.6
Octachlorostyrene	1.9×10^6	—	—	—	—	1.2	0.49
Chloronitrobenzenes							
1-Chloro-2-nitrobenzene	1.7×10^2	15	<3.8	—	—	0.11	0.030
1-Chloro-3-nitrobenzene	2.6×10^2	13	<3.8	—	—	ND	ND
1-Chloro-4-nitrobenzene	2.5×10^2	31	<3.8	—	—	0.12	0.021
1,2-Dichloro-3-nitrobenzene	7.1×10^2	<10	<3.8	—	—	ND	0.010
1,2-Dichloro-4-nitrobenzene	1.3×10^3	—	—	—	—	0.29	0.36
1,3-Dichloro-4-nitrobenzene	—	—	—	—	—	0.11	0.10
1,4-Dichloro-2-nitrobenzene	—	—	—	—	—	0.030	0.021
Chlorobiphenyls							
2,4,4′-Tri	6.9×10^5	50	17	9.1	65	0.98	1.6
2,4′,5-Tri	6.9×10^5	—	—	—	—	0.91	1.3
2,2′,3,5-Tetra	1.7×10^6	—	—	—	—	1.6	1.8
2,2′,4,4′-Tetra	2.0×10^6	—	—	—	—	0.55	4.9
2,2′,4,5′-Tetra	2.0×10^6	—	—	—	—	1.7	3.2
2,2′,5,5′-Tetra	2.0×10^6	55	31	6.5	61	2.9	4.8

APPENDIX 1

Extended

Dreissena polymorpha, 1994, μg/kg wet weight		*Anguilla anguilla*, 1994, μg/kg wet weight			Bioaccumulation ratios		
Ysselmeer	Rhine	Rhine	Meuse	H. Diep	*D.p./s.s.* (fat/dry weight)	*A.a./s.s.*, 1994 (fat/dry weight)	*A.a./D.p.* (fat/fat weight)
0.07							
0.01	0.09	0.18	0.11	0.10			
10–25	25	70	41	25			
<10	—	—	—	—			
63	—	—	—	—	0.40		
200	—	—	—	—			
1,100	—	—	—	—	0.31		
86	—	—	—	—	0.027		
12,000	—	—	—	—			
13	—	—	—	—	0.24		
—	—	—	—	—	0.28		
<20	—	<60	<60	—			
<15	—	<45	<45	—			
15,000	—	—	—	—	0.50		
2.0	—	—	—	—			
0.40	—	—	—	—	0.19		
0.70	—	—	—	—	0.54		
2.0	—	—	—	—	0.18		
6.0	—	—	—	—	0.44		
3.0	—	—	—	—			
2.0	—	—	—	—	0.048		
2.0	—	—	—	—	0.25		
4.0	—	—	—	—	0.55		
0.50	—	—	—	—	0.030		
8.0	—	—	—	—	0.68		
0.40	—	—	—	—			
0.50	—	—	—	—	0.035		
2.0	—	—	—	—	0.28		
3.0	—	—	—	—	0.31		
<0.15	1.2	—	31	3.3			>11
0.13	30	44	5.9	27			1.8
0.17	1.2	2.5	0.26	1.0			0.11
0.050	0.70	3.3	1.4	0.60			2.3
1.1	ND	27	17	ND	>0.000067	>0.00011	1.7
0.040	0.20	2.9	2.2	0.41	>0.000013	>0.000041	1.2
<0.010	ND	2.5	<1.0	ND			
<0.010	0.60	1.4	<0.80	0.50			1.6
<0.020	1.0	2.9	<2.0	90	0.47	0.56	1.2
0.050	7.4	15	2.9	7.7	>0.0000014	>0.0000026	2.6
0.11	50	170	31	43	2.4	6.7	3.2
0.15	ND	46	10	ND			3.7
0.14	0.40	1.8	<0.080	0.60	0.41	44	1.1
ND	<0.10	0.35	<0.050	0.20		0.14	
0.16	0.50	1.5	<0.080	0.50	0.21	0.22	1.0
0.040	<0.10	0.47	<0.030	<0.10	>0.14	>0.25	<0.52
0.030	0.30	1.2	0.57	0.30			0.28
0.050	<0.10	0.80	0.69	0.20			0.93
<0.070	<0.10	0.82	<0.080	0.20			2.7
0.20	6.1	6.9	5.6	7.8	2.3	1.5	0.80
0.19	3.3	3.5	3.1	4.1			0.48
0.27	ND	33	13	ND			1.6
0.11	27	44	74	47			5.9
0.28	13	25	19	16			1.3
0.42	63	120	56	59	5.5	14	3.3

APPENDIX 1
Continued

		Suspended solids, 1993–1994, μg/kg dry weight standardized (metals), organic matter (org. microcontaminants)				*Dreissena polymorpha*, 1994, μg/kg wet weight	
	K_{ow}	Rhine	Meuse	Ysselmeer	H. Diep	Rhine	Meuse
2,3,3′,4-Tetra	2.3×10^6	—	—	—	—	2.7	2.5
2,3′,4,4′-Tetra	2.8×10^6	—	—	—	—	3.1	4.6
2,4,4′,5-Tetra	2.8×10^6	—	—	—	—	1.5	0.50
3,3′,4,4′-Tetra	4.0×10^6	—	—	—	—	0.12	0.10
2,2′,3,4,5′-Penta	6.8×10^6	—	—	—	—	1.4	2.1
2,2′,3′,4,5-Penta	6.8×10^6	—	—	—	—	0.95	1.4
2,2′,4,5,5′-Penta	8.1×10^6	83	55	8.9	85	5.5	7.2
2,3,3′,4,4′-Penta	9.5×10^6	—	—	—	—	0.64	0.98
2,3,3′,4′,6-Penta	6.8×10^6	—	—	—	—	4.0	5.7
2,3,4,4′,5-Penta	9.5×10^6	—	—	—	—	0.10	<0.10
2,3′,4,4′,5-Penta	9.5×10^6	56	32	7.6	58	2.1	3.1
3,3′,4,4′,5-Penta	1.6×10^7	—	—	—	—	0.012	0.012
2,2′,3,3′,4,4′-Hexa	1.6×10^7	—	—	—	—	0.69	0.80
2,2′,3,4,4′,5′-Hexa	2.8×10^7	—	—	—	—	0.14	0.17
2,2′,3,4,4′,5-Hexa	2.8×10^7	120	78	14	110	5.1	6.3
2,2′,3,4,5,5′-Hexa	2.8×10^7	—	—	—	—	1.4	1.5
2,2′,3,4′,5′,6-Hexa	1.9×10^7	—	—	—	—	6.0	8.4
2,2′,3,5,5′,6-Hexa	1.9×10^7	—	—	—	—	2.0	2.9
2,2′,4,4′,5,5′-Hexa	3.3×10^7	110	79	16	110	8.4	9.1
2,3,3′,4,4′,5-Hexa	3.9×10^7	—	—	—	—	0.32	0.40
2,3,3′,4,4′,5′-Hexa	3.9×10^7	—	—	—	—	0.10	0.10
2,3′,4,4′,5,5′-Hexa	2.8×10^7	—	—	—	—	0.40	<0.10
3,3′,4,4′,5,5′-Hexa	4.6×10^7	—	—	—	—	0.0020	0.0020
2,2′,3,3′,4,4′,5-Hepta	7.8×10^7	—	—	—	—	1.4	1.9
2,2′,3,4,4′,5,5′-Hepta	1.1×10^8	73	62	8.3	76	2.7	3.8
2,2′,3,4′,5,5′,6-Hepta	9.5×10^7	—	—	—	—	2.0	2.9
2,2′,3,3′,4,4′,5,5′-Octa	3.8×10^8	—	—	—	—	0.20	0.30
2,2′,3,3′,5,5′,6,6′-Octa	1.9×10^8	—	—	—	—	0.099	0.15
2,2′,3,3′,4,4′,5,5′,6-Nona	9.1×10^8	—	—	—	—	0.099	0.14
Chlorobiocides							
4,4′-DDD	1.6×10^6	20	8.1	<3.7	18	0.98	0.42
4,4′-DDE	9.0×10^6	48	24	5.3	44	3.5	1.9
4,4′-dichlorodiphenyltrichloroethane	8.2×10^6	29	13	<3.7	16	0.95	0.89
Trichlorophenylmethane	—	—	—	—	—	1.0	ND
Trichlorophenylmethanol	—	—	—	—	—	<0.0090	<0.012
α-Endosulfan	1.2×10^5	<9.9	8.0	<3.6	<7.3	0.42	1.6
β-Endosulfan	1.2×10^5	—	—	—	—	0.088	ND
α-Hexachlorocyclohexane	6.0×10^3	<9.4	<4.2	<3.5	<7.3	0.25	0.19
β-Hexachlorocyclohexane	7.0×10^3	12	<4.3	<3.4	<7.8	0.27	0.021
γ-Hexachlorocyclohexane	4.9×10^3	9.9	10	4.3	8.8	2.5	5.5
Dieldrin	2.5×10^5	<9.4	5.6	<3.5	<7.3	0.33	0.42
Endrin	1.6×10^5	<9.4	<5.3	<3.5	<7.3	0.060	0.18
α-Heptachlorepoxid	4.5×10^3	<9.4	<4.6	<3.5	<7.3	ND	0.030
β-Heptachlorepoxid	4.5×10^3	—	—	—	—	0.17	0.27
Heptachlor (α + β)	2.5×10^4	—	—	—	—	0.47	0.21
Hexachlorobutadiene	6.3×10^4	19	6.1	<3.4	10	2.4	0.95
Toxaphene	2.1×10^4	—	—	—	—	4.7	36
Cis-chlordane	6.3×10^5	—	—	—	—	ND	0.10
Trans-chlordane	6.3×10^5	—	—	—	—	0.82	0.67
Cis-chlordene	—	—	—	—	—	<0.10	<0.10
Trans-chlordene	—	—	—	—	—	<0.10	<0.10
Oxychlordane	—	—	—	—	—	0.11	0.13
Trans-nonachlor	—	—	—	—	—	0.17	0.19
Misc. chlorinated aromatic compounds							
Pentachloroanisol		—	—	—	—	0.27	0.25
Pentachlorothioanisol	—	—	—	—	—	0.78	0.97
Chloroterphenyls	—	—	—	—	—	1.8	<2.2
Tetrachlorodifon	—	—	—	—	—	P	NP
Tetrachlorobenzyltoluenes	1.8×10^7	—	—	—	—	8.9	<1.7
Σ Organic microcontaminants (mmol/kg fat weight)						0.057	1.2

[a] Concentrations in suspended solids reflect average of samples above detection limit; underlined data were estimated from water concentrations calculated according to Van der Kooij et al. [14]; K_{ow} = octanol–water partition ratios taken from the literature [46–48] and several individual studies; n = number of samples (for suspended solids), number of individuals per mixing sample (for organisms); < = more than 33% below detection limit (for suspended solids), lower than detection limit (for organisms); ND = not determined (searched for but not found because of interference, matrix effects, etc.); P = qualitatively present; NP = qualitatively not present; — = not analyzed (not searched for).

APPENDIX 1
Extended, Continued

Dreissena polymorpha, 1994, μg/kg wet weight		*Anguilla anguilla*, 1994, μg/kg wet weight			Bioaccumulation ratios		
Ysselmeer	Rhine	Rhine	Meuse	H. Diep	*D.p./s.s.* (fat/dry weight)	*A.a./s.s.*, 1994 (fat/dry weight)	*A.a./D.p.* (fat/fat weight)
0.83	ND	6.0	7.0	ND			0.33
0.48	31	49	41	34			1.7
0.11	10	—	5.1	—			1.5
0.024	0.12	—	0.24	—			0.29
0.21	9.3	18	19	5.7			1.4
0.25	21	35	16	24			3.2
1.1	92	150	80	74	6.9	12	2.6
0.15	16	31	24	19			4.7
0.88	84	170	98	97			3.7
<0.10	1.8	—	1.1	—			
0.58	8.7	150	71	140	4.4	7.9	2.8
0.0040	0.19	—	0.27	—			
0.15	29	44	31	33			7.0
0.040	ND	7.8	4.5	ND			
1.1	190	290	230	220	4.4	18	6.4
0.21	29	46	41	20			4.0
1.4	110	220	210	110			3.9
0.42	25	44	59	20			2.7
2.0	300	530	380	430	7.0	32	6.8
0.070	1.5	22	17	16			3.6
<0.10	4.9	—	3.6	—			7.8
<0.10	4.7	—	2.2	—			2.3
0.0010	0.096	—	0.15	—			11
0.39	66	93	95	59			8.2
0.71	120	170	210	120	3.9	19	8.0
0.55	93	170	340	110			12
0.070	12	12	23	10			9.8
0.050	8.6	5.5	6.6	9.9			8.9
0.050	3.9	3.3	5.6	3.2			5.6
0.16	25	33	13	23	2.7	12	4.5
0.54	68	110	46	83	5.6	15	3.7
0.050	3.6	17	5.5	2.4	2.5	2.5	1.1
1.2	29	53	0.74	40			5.5
<0.010	P	P	NP	P			
0.010	—	0.49	0.23	—	11	0.26	0.054
0.0080	—	0.27	0.21	—			0.31
0.020	1.6	3.1	1.7	2.0	>0.61	>1.8E-0	1.3
0.010	3.4	5.8	1.9	4.5	1.3	2.9	4.3
0.090	8.9	29	48	10	9.7	19	1.1
0.21	5.3	10	6.6	8.1	3.9	11	3.0
0.050	ND	0.75	0.33	ND	>0.35	>0.44	0.62
ND	ND	<0.091	0.15	ND	>0.35	>0.31	0.88
0.071	ND	2.0	3.9	ND			1.8
0.040	<1.0	1.2	0.74	<1.0			0.40
0.12	14	55	13	5.0	7.5	13	1.9
0.74	12	—	20	—			0.22
0.060	0.50	1.1	2.2	0.60			3.8
0.080	0.30	0.76	1.5	0.30			0.14
<0.030	ND	<1.0	<1.0	ND			
<0.030	ND	<2.0	<2.0	ND			
0.028	0.60	0.96	2.4	1.0			1.5
0.028	1.1	3.3	6.8	1.6			2.5
0.030	0.70	0.86	0.24	0.30			0.30
0.15	1.0	0.91	0.50	0.80			0.14
<2.2	310	—	76	290			34
NP	—	—	NP	—			
0.71	4.1	—	<3.3	—			0.090
0.074	0.058	0.051	0.065	0.061			

APPENDIX 2

Concentrations and detection levels of nitrogen- and phosphorbiocides as well as of nitrogen polycyclic aromatic hydrocarbons (NPAHs) in suspended solids, zebra mussel (*Dreissena polymorpha*), and eel (*Anguilla anguilla*) from various locations in the Rhine–Meuse delta in 1993–1994[a]

		Suspended solids, 1993–1994, μg/kg dry weight organic matter		*D. polymorpha*, 1994, μg/kg wet weight	*A. anguilla*, 1994, μg/kg wet weight	Bioconcentration ratios (fat/dry)	
	K_{ow}	Rhine	Meuse			*D.p*/*s.s*	*A.a.*/*s.s.*
Carbamates							
Chlorpropham	1.3×10^3			<10	<10		
Pirimicarb	3.0×10^1	<0.079	<0.079	<5.0	<5.0		
Propham	2.4×10^2			<10	<10		
Propoxur	3.5×10^1	<0.27	<0.27	<10	<10		
Nitrogenbiocides							
Ametryn	3.8×10^2			<5.0	<5.0		
Atrazine	4.0×10^2	9.1	12	<5.0	<5.0	<3.01	<3.91
Chloridazon	1.4×10^1	0.12	0.075	<20	<20	<8.93	<3.91
Cyanazine	1.3×10^2			<5.0	<5.0		
Desmetryn	—			<5.0	<5.0		
Fenpropimorph	—			<5.0	<5.0		
Furalaxyl	—			<20	<10		
Metalaxyl	2.9×10^1			<10	<10		
Metamitron	—			<20	<10		
Methabenzthiazuron	—			<10	<10		
Penconazol	—			<5.0	<5.0		
Pendimethalin	—			<5.0	<5.0		
Prochloraz	—			<20	<20		
Prometryn	9.8×10^2			<5.0	<5.0		
Propazine	1.0×10^3			<5.0	<5.0		
Propiconazol	—			<10	<10		
Simazine	1.5×10^2	<2.6	3.4	<5.0	<5.0	<7.81	<1.41
Terbuthylazine	1.1×10^3			<5.0	<5.0		
Terbutryn	3.8×10^3			<5.0	<5.0		
Triademenol	—			<10	<10		
Triadimefon	5.9×10^2			<5.0	<5.0		
Phosphorbiocides							
Azinphosmethyl	4.9×10^2	<1.3	<1.3	<60	<100		
Chlorpyrifos	1.8×10^5			<5.0	<20		
Chlorpyrifos-methyl	2.0×10^4			<5.0	<20		
Cis-mevinphos	5.2×10^1	<0.14	<0.14	<5.0	<5.0		
Diazinon	1.9×10^3	<4.8	<4.8	<5.0	<20		
Dichlorvos	5.2×10^1			<5.0	<20		
Dimethoate	6.0	<0.018	0.020	<10	<50	<2.64	<2.24
Fenitrothion	2.5×10^3	<6.5	<6.5	<5.0	<20		
Malathion	5.0×10^2	2.8	<1.3	<10	<50	<2.02	<1.02
Parathion-ethyl	6.0×10^3	<16	<16	<5.0	<20		
Parathion-methyl	5.2×10^2	<1.5	<1.4	<5.0	<20		
Pirimifos-methyl	1.6×10^4			<5.0	<20		
Sulfotep	—			<5.0	<20		
Trans-mevinphos	5.2×10^1			<10	<50		
Nitrogen PAHs							
4-Azafluorene	—			<4–25	<30–300		
5,6-Benzoquinolin	—			<4–25	<30–300		
7,8-Benzoquinolin	—			<4–25	<30–300		
Acridine	3.2×10^3		<8,400	<4–25	<30–300		
Carbazole	6.9×10^3		<18,000	<4–25	<30–300		
Indole				<4–25	ND		
Isoquinolin	6.6×10^1			<4–25	<30–300		
Quinolin	1.3×10^2			<4–25	<30–300		

[a] For explanation see Appendix 1.