Measured and critical concentrations of accumulative compounds in the Rhine-Meuse delta with emphasis on non-priority substances

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SUMMARY

The return of indigenous species in the rivers Rhine and Meuse is limited by various hydro-morphological and chemical factors, including microcontaminants such as heavy metals and PCBs. This holds especially for sensitive species, hot spots, peak loads and possibly unknown substances.

The present report focuses on the last topic. The last few decades several groups of microcontaminants have been identified as hazardous because of their accumulation in foodchains. Several of them, in particular chlorinated biphenyls, benzenes and biocides have been selected as priority or bench mark chemicals by regulatory agencies. The accumulation and toxic potential of these chemicals has been investigated relatively well. Even more, water quality management on these substances has caused a substantial reduction of their emission, at least in the rivers Rhine and Meuse.

Meanwhile, there is growing concern about the importance of other substances, not selected for priority lists so far. As the concentrations of priority substances decreases, the relative contribution of other chemicals is likely to increase. In addition, priority substances may be substituted by other chemicals in all kinds of applications.

The present report describes two studies on non-priority substances with an accumulation potential. Concentrations of heavy metals and various groups of organic microcontaminants have been measured in zebramussel and eel from the Rhine-Meuse delta. The concentrations measured have been compared to

- concentrations from other areas
- ' concentrations in toxicity studies and
- quality standards.

For non-priority substances it is concluded that:

1. Concentrations of chlordenes, organotins, nitrogen- and phosphorbiocides and nitrogen polycylic aromatic hydrocarbons are below detection limits. Concentrations of chlorophenols, phthalates and individual bromobiphenyl congeners are not reliable and should be regarded as indicative values.
2. Concentrations of bromobiphenyls, bromodiphenylethers, heptachlor, chloroterphenyls in the Rhine-Meuse delta are on 4-200 times above those found in pristine areas.
3. Concentrations of chlorobenzyltoluenes and toxaphenes are close to levels found in remote regions.
4. A limited number of chronic no effect concentrations for mortality, reproduction or growth were identified for some chlorophenols, toxaphenes, chlordanes, heptachlor and several phthalates.
5. Insufficient data exist for bromobiphenyls, bromodiphenylethers, chloronitrobenzenes, tris(4-chlorophenyl)methanol/ane, chloroterphenyls and tetrachlorobenzyltoluenes.
6. The data that are available do not indicate substantial risks of most non-priority substances for avian and mammalian predators.
7. Bromodiphenylether concentrations in eel are at 6 to 50% of a reported generic no effect level. Taking into account corrections for lab-field differences in caloric content of prey- or food-items, this could mean that these residues may be harmful for sensitive predators.
8. Residues of non-priority substances in mussel from the Rhine and Meuse were 1-l 8 times higher than in mussel from the reference location of IJsselmeer.
9. The total body burden of organic microcontaminants varies between 0.05 to 0.07 $mmol \cdot kg^{-1}$ fat weight for 6 out of 7 samples. The largest contribution to the overall organic microcontaminant burden cornes from traditionally monitored chemicals, viz. polycyclic aromatic hydrocarbons, chlorobiphenyls and chlorobiocides. This is far below the critical level of about 2-20 $mmol \cdot kg^{-1}$ fat weight at which non polar narcosis will affect all species. Obviously, effects from compounds with other more specific modes of action cannot be excluded.
10. The total concentration accumulated in mussel and eel is found to be much lower than the total load sorbed to material that mimics accumulation in organisms. This suggests that other substances not identified in the present studies may be important too.

In general, the non-priority pollutants studied in the present investigations appear to be less important because concentrations observed in mussel and eel are lower than those of related priority chemicals. Even more, measured concentrations are substantially lower than critical levels. However, information on non-priority substances is scarce and the studies show that concentrations of e.g. polybromodiphenylethers (PBDEs) are close to a generic no effect level. This indicates that the risk will be negligible for most species but sensitive species may not be protected sufficiently. Thus, some non-priority chemicals may pose similar

risks to (sensitive) species, but the group of non-priority chemicals appear not to have a dramatic impact on the ecological community as a whole. The present studies do not justify an extensive search to *all* kinds of non-priority chemicals with an accumulation potential.

However, water quality management and research should pay attention to *some* non-priority substances, like e.g. the bromodiphenylethers mentioned above. Whether or not the present studies provide sufficient material to add these or other substances to priority lists is a decision to be taken by the appropriate authorities. The methods and results presented here may serve as an indication of the direction to go. However, we would like to emphasize that the present report does not provide more than a first screening on non-priority pollutants, compared to the wealth of data collected for some priority chemicals.

The *other* non-priority substances should be given less attention because their levels were:

1. low compared to those of related substances
2. (well) below critical concentrations if available or
3. close to residues measured in pristine areas.

For the last category, continental background levels and atmospheric transport appear to be responsible for the residues measured in the organisms. As such, reduction of emissions in the Rhine and Meuse basin, if any, are not likely to diminish concentrations in organisms.

CONTENTS

1. GENERAL INTRODUCTION

The return of indigenous species in the rivers Rhine and Meuse is limited by various hydro-morphological and chemicals factors, including microcontaminants such as heavy metals and PCBs. At the moment microcontaminants have been shown to obstruct ecological rehabilitation in the Rhine and Meuse, in particular as far as

1. sensitive species
2. hot spots
3. peak loads or
4. (possibly) unknown substances

are concerned (see Hendriks et al. 1997 for review).

The present report focused on the last topic. The last few decades several groups of misrocontaminants have been identified as hazardous substances because of their accumulation in foodchains. Many of them, in particular chlorinated biphenyls, benzenes and biocides have been selected as priority or bench mark chemicals by regulatory agencies (e.g. EPA 1984, IRC 1987). The accumulation and toxic potential of these chemicals has been investigated in many laboratory, field and modelling studies. In the Rhine and Meuse, priority substances have been shown to obstruct the return of indigenous species such as the otter (Van der 1996, Leonards 1997) while other priority substances disturb the ecological community of hot spots.

The attention of water quality research and management to priority substances has led to a substantial decrease of some of them in the Rhine and Meuse, the two major rivers in the Netherlands (Kalkhoven 1990, IRC 1993). Meanwhile, there is growing concern about the importance of other substances, not selected for priority lists so far. As the level of priority substances decreases, the relative contribution of other chemicals to the overall accumulation and toxicity is likely to increase. In addition, priority substances may be substituted by other chemicals in all kinds of applications.

These theoretical considerations are supported by preliminary studies in the Dutch sections of the Rhine and Meuse. For instance, less than 15% of the toxicity of Rhine water to waterfleas could be attributed to substances identified by chemical analysis (Hendriks et al. 1994). In the Meuse, the fraction toxicity explained by identified substances varied between 1 and 100% (Maas et al. 1994). In both rivers, fat-soluble compounds turned out to be responsible for most of the toxicity observed.

In the rivers Rhine and Meuse, accumulation of priority pollutants is regularly monitored in zebramussel (Dreissena polymorpha) and fish (Anguilla anguilla) at about thirty locations. The number of substances measured is limited to a few heavy metals, seven PCBs and several chlorobiocides (IRC 1992, IRC 1993, Hendriks and Pieters 1993). However, the total body burden of substances measured in mussel and fish was about 10% of the sum of the concentration of individual substances accumulated in a biomimetric system in the same period (Van Loon et al. 1996).

Both types of studies stress the importance of the same group of substances: fat-soluble organic compounds of a recalcitrant nature. Thus, it was considered appropriate to investigate the accumulation and toxic potential of non-priority chemicals in this group.

The purposes of the studies were to:

1. demonstrate the presence of non-priority compounds in zebramussel and eel of the Rhine-Meuse basin.
2. evaluate the risks of these substances by comparing the measured residues to critical levels.

The first objective is met by extensive chemical analysis of zebramussel and eel sampled at the regular monitoring locations Lobith (Rhine) and Eijsden (Meuse). The second objective is accomplished by a literature review on avian and mammalian toxicity data, food quality standards and levels in pristine areas.

The substances selected for the present study are widely recognized as hazardous, or have received increasing attention in the last few years. Polycyclic aromatic hydrocarbons are natural substances with various antropogenous sources, the latter usually associated with organic matter and fuel.
Polybrominated diphenylethers and biphenyls are used as flame retardants in e.g. electronic apparatus 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 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.

The information obtained may help to set future priorities for water quality management in effluent and surface water control. In particular, these data may be useful for the International Rhine Commission, currently in the process of selecting additional priority chemicals.

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