BIOACCUMULATION OF PERSISTENT CHLORINATED BIPHENYLS, BENZENES AND BIOCIDES IN VARIOUS SPECIES COMPARED WITH THAT OF DIOXINS, FURANS AND OTHER AROMATIC HYDROCARBONS: MODELLING AND FIELD VALIDATION

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1. Introduction

Environmental quality management aims to protect thousands of plant and animal species from thousands of contaminants that are released into their environment. Obviously, one cannot study all contaminants and species empirically in detail. To facilitate extrapolation, several models have been developed for concentration kinetics (e.g. Spacie and Hamelink 1982, Thomann and Connolly 1984, Hawker and Connell 1986, Clark et al. 1990, additional references in Hendriks 1995b) and population dynamics (e.g. Barnthouse et al. 1987, Hallam et al. 1990, additional references in Hendriks and Enserink 1996). Yet, the values for the parameters of most models are specific for a compound and a species.

As a result, we developed the model called Optimal Modelling in EcotoxicoloGical Assessments (OMEGA) (Hendriks 1995d). In this model concentration kinetics and population dynamics are described by traditional equations. The parameters of the model however, are related to well-known characteristics of contaminants and species, such as octanol-water partitioning, fat fraction and adult size.

The model is being applied to miscellaneous contaminants. In the present paper, we will focus on the equilibrium bioaccumulation ratio parameter. The aim is to:

1. give an overview of the concentrations of persistent organochlorines in different foodchains and
2. compare these concentrations to those of related but less persistent compounds.

This is achieved by looking at accumulation of:

1. persistent compounds measured in laboratory experiments with miscellaneous species as reported in literature
2. persistent chlorinated biphenyls, benzenes and biocides measured in field surveys on various species from aquatic (river, lake) and terrestrial (floodplains) foodchains.
3. less persistent compounds occasionally measured in field surveys.

The outcome may be helpful for both modelling and monitoring purposes. Modelling experts may find accumulation factors to calibrate or validate their models on. Environmental quality management may use the results for setting priorities on chemicals and species to be

investigated in a cost effective monitoring program. In addition, it may increase our general understanding of accumulation patterns.

2. Methods

For the general overview that we seek here, we used typical values obtained from previous studies. The basic data have been reported in the subsequent papers. The laboratory studies in this paper were collected from literature reviews (given in Hendriks 1995b). The fat contents of species exposed via water, sediment or soil was usually reported but lipid correction for dietary studies was mostly based on an assumed fat fraction for both food and organism.

The field data were taken from miscellaneous studies, carried out in the Rhine-Meuse delta. Invertebrates, fish, shrews, cows, cormorants, diving ducks were sampled at three or more locations (Hendriks 1993, Hendriks and Pieters 1993, Hendriks et al. 1995, Platteeuw 1996, Hendriks et al. 1996, Reinhold et al. 1996). In addition to this, values based on a few measurements were taken from studies on plants, bats and otter (Fuchs 1983, Koelmans and Lyklema 1992, Van Hattum et al. 1993, Reinhold et al. 1996, Broekhuizen and de Ruiter-Dijkman 1988, see also Smit et al. 1996). Residues in field organisms were related to concentrations measured in suspended solids, sediments or soil sampled near the habitat of the species. To verify the link between the organism and the source of contamination, sessile species were sampled next to mobile species and the diet of the species was checked with biologists.

Chemical analysis was performed as indicated in the subsequent papers.

3.Results and discussion

Laboratory bioaccumulation of persistent organochlorines

Laboratory studies showed that the equilibrium concentration in lower organisms C_2 is a function of the concentration in (pore-)water $C_{0,wat}$, the octanol-equivalent fat contents p_{fat} and the octanol-water partition ratio K_{ow} (e.g. Könemann 1980, Mackay 1982, additional references given in Hendriks 1995b). The same holds for the concentration sorbed to organic solids, where p_{fat} expresses the octanol-equivalent fraction of organic matter. The ratio between the concentration in organisms C_2 and organic matter $C_{0,osol}$ can now conveniently be calculated by

Equation 1.

$$\frac{C_2}{C_{0,osol}} = \frac{p_{fat,2} * K_{ow} * C_{0,wat}}{p_{fat,0} * K_{ow} * C_{0,wat}} = \frac{p_{fat,2}}{p_{fat,0}} \qquad \left(10^2 < K_{ow} < 10^7\right)$$

If the concentration in organisms is expressed in fat weight, $p_{fat,2}$ equals 1 by definition. The octanol-equivalent fat fraction for dry weight organic matter $p_{fat,0}$ can be derived to be about 0.3 (see Hendriks 1995b, based on data from Karickhoff et al. 1979 and Sablic et al. 1995). Thus, the ratio between the concentration in organism fat weight C_2 and the concentration in organic solids dry weight $C_{0,osol}$ is expected to be about $1/0.3 \approx 3.3$ (1.7 if expressed on organic

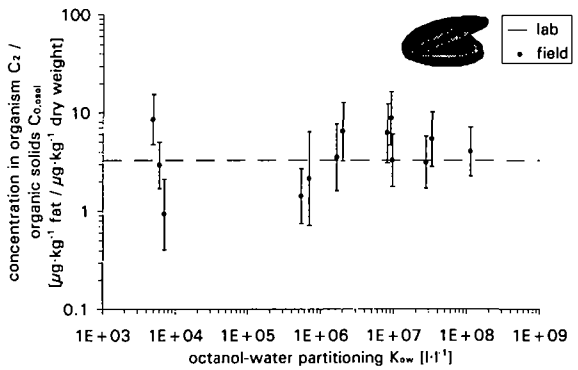
carbon). To facilitate comparison between living and dead biomass, all ratios may be expressed in fat weight. In that case, the ratio between concentrations in organisms and organic matter equals 1.

The ratio of concentrations in organisms C_2 and in their food C_1 can be described by an equation similar to Equation 1 (see Hendriks 1995b for details). Obviously, the quality and quantity of food changes during digestion and the total amount of the octanol-equivalent fat -and with it the capacity to store contaminants- is likely to decrease along the digestive tract. Following a calculation similar to that of Equation 1 indicates that organism-food ratios should be somewhere between 3 and 20, on a lipid weight basis. However, lipid-corrected organism-food ratios rarely exceed 1 in lab studies, probably largely due to short exposure periods. Higher values are occasionally reported, especially for species that are not traditionally used in laboratory experiments (Hendriks 1995b).

Field bioaccumulation of persistent organochlorines

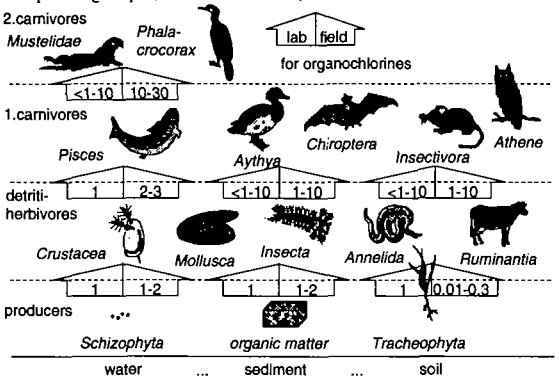
Figure 1. presents the ratios of concentrations in mussel fat weight and organic suspended solids dry weight. One may conclude that the ratios were indeed independent of the octanol-water partitioning ratio of the compound. In addition, most field ratios were only slightly above those reported in laboratory studies.

Figure 1. Bioconcentration ratios $C_2/C_{0,osol}$ of persistent chlorinated biphenyls, benzenes and biocides in zebramussel (Dreisena polymorpha) fat weight and organic suspended solids dry weight in Rhine-Meuse delta surveys (geometric μ±95%-C.I.).



The ratios for the other species are summarized in Figure 2. The species from different trophic levels of the Rhine-Meuse foodweb are separated by dotted lines. The arrows indicate the ratio of lipid-corrected concentrations in adjacent trophic levels. The right panel gives the typical values measured for bioaccumulation of chlorinated biphenyls, benzenes and biocides in field organisms. The higher values of the ranges apply to very persistent compounds, for example PCB153. The lower values apply to slightly less persistent organochlorines. The left panel contains typical values on bioaccumulation in laboratory experiments with more or less related species, as reported in literature.

Figure 2. Typical values for lipid corrected bioaccumulation ratios for persistent organochlorines at different trophic levels. The field data were collected in Rhine-Meuse delta field surveys,whereas the lab data were taken from literature on related species groups (references in text).



From Figure 1 and Figure 2, we may conclude that organochlorine concentrations in the lower end of the aquatic foodchain were about equal. Concentrations of the most persistent compounds in fish were about 3x2=6 times those in organic matter if both are expressed in fat weight (3x2x3.3≈20 if organic matter is expressed in dry weight). The values measured in the field were close to the levels expected from laboratory studies.

At the lower end of the terrestrial food chain, concentrations tended to be much lower than expected from equilibrium partitioning. This indicates that contaminants in soils were less available than those in suspended solids and sediments. This may be attributed to e.g. less intense contact with the water phase or to aging of the soil. In the case of earthworms, field accumulation was also lower than expected from laboratory studies (Belfroid et al.1994). In the case of cows, reduced residues in milk may also attributed to low accumulation in grass. Concentrations in above-ground and above-water parts of plants tended to be much lower than expected from equilibrium partitioning (Briggs et al. 1982, Topp et al. 1986, Travis and Arms 1988). Ingestion of soil -about 5% of the total consumption of cows- apparently could not compensate for this.

At the higher end of the food web, biomagnification ratios of more than 10 were found. This was not expected from laboratory studies which usually produce organism-food ratios of less than 1.

Field bioaccumulation ratios for less persistent compounds.

To reduce costs, less persistent compounds were not measured in all species. Yet, a rough sketch can be given. Field bioconcentration ratios for PAHs in aquatic invertebrates were 10 to 100 times lower than expected from equilibrium partitioning. Concentrations in fish were even lower (Hendriks 1995b, Reinhold et al. 1996). Note that is inconsistent with some short-term laboratory studies on these compounds (e.g. Mackay 1982). Ratios for chlorophenols and chloronitrobenzenes in fish were also lower than expected from equilibrium partitioning. Currently, additional groups of compounds, such as brominated biphenyls, chlorinated terphenyls, nitrobiocides, phosphorbiocides and phtalates are being investigated (Hendriks et al. 1997).

The organism-organic solids ratios for PCDDs and PCDFs in fish and in cows were also lower than expected from equilibrium partitioning. In cows, ratios of PCDDs and PCDFs in milk fat and in soil were even lower than those for isolipophilic PCBs. This may have been caused by additional sources of PCB contamination not taken into account but

biotransformation seems to be a more probable explanation. The ratios for the coplanar congener PCB077 (but not for PCB126 and PCB156) were lower than those for the persistent reference congener PCB153. Despite the lower accumulation of PCDDs, PCDFs and - occasionally- a planar PCB however, total TCDD-equivalents were fairly constant among different species. Per µg of PCB153, TCDD-equivalents ranged from 0.00009 for eel (Anguilla anguilla) to 0.0009 for cattle with intermediate values for mosquito larvae (Chironomidae) and cormorants (Phalacrocorax carbo) (Hendriks 1995c).

Field bioaccumulation ratios that are low in comparison to those for isolipophilic compounds of a more persistent nature indicate the induction of biotransformation. This can be checked by another important parameter in the OMEGA-model: the elimination rate. Whereas persistent compounds are eliminated via physico-chemical pathways only, less persistent chemicals can also be transformed biochemically. Elimination rates of PAHs turned out to be 4.7 higher than those in isolipophilic persistent compounds. For PCDDs and PCDFs a value of 37 was noted (Hendriks 1995a). In the nearby future, bioaccumulation ratios and elimination rates will be compared more closely to verify the consistency of both parameters.

4. Conclusions

In this paper we compared bioaccumulation ratios a fat weight basis.
For persistent organic microcontaminants like chlorinated biphenyls, benzenes and biocides it is concluded that:

1. ratios between concentrations in organisms and in organic matter are (almost) independent of the octanol-water partitioning factor.
   - in the aquatic foodchain, ratios tend to be similar for different compounds, species and conditions (lab, field)
   - in the terrestrial foodchain, ratios tend to be lower than those in the aquatic foodchain with field values being lower than lab values.
2. ratios between concentrations in organisms and in their food tend to be independent of the octanol-water partitioning factor, with field values being higher than lab values.

For less persistent organic microcontaminants like PAHs and PCDDs/PCDFs, it is concluded that:

1. ratios between concentrations in organisms and in organic matter are 10 to more than 1000 times lower than those for isolipophilic persistent compounds
2. elimination rates for these compounds are higher than those for isolipophilic persistent compounds.

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