POPs MONITORING IN FISH:MONITORING DESIGN REQUIREMENTS FOR RISK AND DAMAGE ASSESSMENT

Kurt Seifert[1] and Jamshid Hosseinpour[2]

1 BNGF-Büro für Naturschutz- Gewässer- und Fischereifragen, Gut Hochschloss, D-82396 Pähl
2 Oekometric GmbH, Berneckerstr. 17-21, D-95448 Bayreuth

Introduction

In aquatic eco-toxicology, fish hold an extraordinary position. Many fish species are long living organisms, reach substantial body mass and are, frequently, on top of the aquatic food chain. Compared to terrestrial and other aquatic organisms, fish have special intake-mechanisms and usually very high storage capacities for many groups of contaminants. This is particularly true for persistent organic pollutants (POPs). With lipophilic organic contaminants like polychlorinated biphenyls (PCBs), dioxins, hexachlorobenzene (HCB), lindane (γ-HCH) and other chlorinated hydrocarbons, accumulation factors of 50,000 and more were found in fish, as compared to the concentrations in water[1]. There are two major pathways for intake of lipophilic POPs by fish: penetration through phosphoric lipids of the gills epithelia (bio accumulation) and via food intake (bio magnification)[1]. Considering this, fishes constitute appropriate monitoring organisms for contamination and trend analyses in aquatic systems as well as for source control purposes.

A study by the European Union (2000, 2002)[2,3,4] states that, within the EU, fish and fish products show high levels of dioxins and PCBs if compared with other foods. The contribution of fish to the consumers´ average daily intake of dioxins and dioxin like PCBs varied from country to country between 2% and 63%, with a mean value of around 30%[2]. Also, highly variable levels of contamination with HCB, DDT, tin organic compounds and other POPs were reported in fish from particular fishing grounds[5,6]. Because fishes have a very high potential to gather and store POPs and because they play a considerable role in human nutrition, it is essential for the security of consumers that objective risk assessments are conducted. Also, the knowledge of fish being contaminated will negatively affect sport fishing and tourism. Therefore, fish monitoring is as an important tool in the field of environmental safety, human health, and consumer protection.

Objectives, requirements, design and results of a representative POPs monitoring in fish are presented here as well as measures, imposed by the food administration, which are based on these results. A recent hexachlorobenzene (HCB) contamination in a Southern German part of the Danube is used as a case study.

HCB had been discharged into the river undetected over several years. This was stopped in the beginning of 1999, and in the same year, a fish monitoring program was designed and implemented[7]. The aim of the program was two-fold: to provide for 1) a profound risk assessment with regards to consumers´ health and 2) a precise damage assessment with regards to fisheries, fish commerce, gastronomy, sport fishing and angling tourism. The primary targets of the program were to determine the levels of contamination of fish along the river's axis, to demarcate other sources of contamination, and to monitor the process of HCB decontamination of the fishes after the discharge was stopped.

Methods and Materials

Monitoring design: For selection, out of the almost 60 fish species of the Danube, of target species for the monitoring program, the following criteria were applied: importance of the species as a food fish and as a target of sport fishing, fat contents, habitat and feeding preferences, size of populations, migration behavior and catchability. The following species were chosen: eel (*Anguilla anguilla*), main commercial species, angling target, high fat content, migratory fish; bream (*Abramis brama*), commercial species, medium fat content, limnophilic species; barbel (*Barbus barbus*), commercial species, angling target, medium fat content, rheophilic species; predatory species: pike and pikeperch (*Esox lucius and Sander lucioperca*) commercial species, main angling targets, low fat contents).

To achieve a representative statistical record of contamination levels over time and space, the program followed, in part, experiences gained from studies of other large rivers[8]. 25 specimens of eel, 15 of breams, 15 of barbel, and 10 of predatory fishes were examined per sampling area (SA) and period. To record the geographical expansion of the contamination, six sampling areas (SA 1 – SA 6) along a 257 km long section of the river between river kilometer 2459 (reference area upstream of the place of discharge) and river kilometer 2202 (border of the country) were installed. The fishes were caught from the six sampling areas every year in early summer (May to June). Between 1999 and 2002 a total of approximately 600 individuals of eel, 700 of bream and barbel, 200 of predators and about 90 of other species were analyzed for HCB.

Sampling and analysis: Sampling was carried out with electric fishing gear, supplemented by gillnets and fish traps. Only fishes with body weights between 300 and 500 grams and with a minimum age of five years were tested. After bio-metrical examinations at the catching area, the material to be analyzed (fillets of fish packed separately, cooled and later frosted) was transported to the laboratory. The laboratory analysis was conducted in accordance with standard test procedures: the material was homogenized, mixed with equal amounts of Na_2SO_4 and sea sand and extracted with hexane:acetone (2:1 v:v). Cleanup used a mixed silica column followed by an aluminum oxide column. The HCB analysis was accomplished using a HP 5890 Series II GC-System (Gertsel KAS 2 cold injection system; GC-column: Ultra-2, 25 m, 0.2 mm i.d., 0.33 µm film) coupled with a HP 5970 mass selective detector. Analysis was based on isotope dilution technique using an internal $^{13}C_6$ HCB-standard.

As a base for risk assessment, toxicological data were used (TDI according to IPCS 1997[9]) as well as legal limits of the country, i.e. the allowed maximum HCB-amounts in fish for human consumption: 0.05 mg HCB/kg fresh weight (fish with total fat content $\leq$ 10 %) and 0.5 mg HCB/kg fat (fish with total fat content > 10%).

Results and Discussion

Along the investigated river section of approximately 260 km, the development of the HCB contamination in the eel (*A. anguilla*) within a four years period after the end of HCB discharge (February 1999) is shown in Figure 1. As expected, the highest HCB contamination levels in eels were found in sampling area 2 (SA 2) next to the place of discharge and during the first year (1999) of investigation. Here, eels exceeded the maximum legal concentration of 0.5 mg HCB/kg fat by factor ten. The concentrations there were 70 times higher than in the reference area SA 1, upstream of the source of contamination. Along the axis of the river a successive decrease of the contamination level was measured.

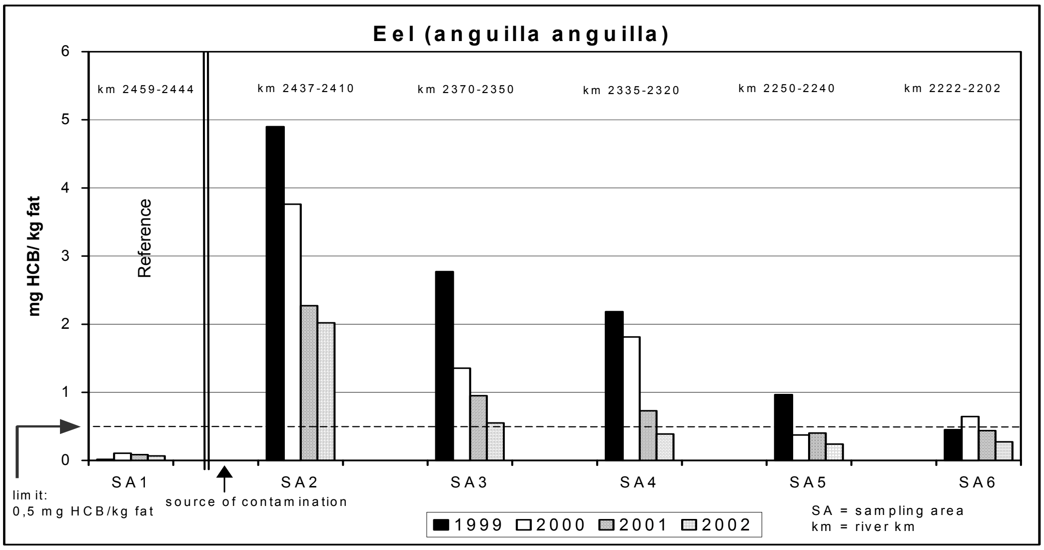

Figure 1: Average HCB contamination in the fat tissue of eels (n = 25 per year and sampling area) along the river's axis in the years 1999-2002

Also, considerable yearly decreases of HCB contamination within the respective sampling areas were found in the course of the four years of examination. An exception from the trend was observed in SA 6, where, from the year 2000, the concentrations of HCB in eels were higher than in SA 5. This was due to another source of contamination coming from a tributary river, which flows into the Danube between SA 5 and SA 6. In breams (*A. brama*) and barbels (*B. barbus*) different patterns of HCB concentrations relating to space and time were found. In these species, the maximum HCB loads were detected in SA 4, which is situated 100 km downriver from the source of contamination. The reason for this is, most likely, the significant higher fat contents of breams and barbels in the sampling area SA 4 as in SA 2.

Table 1: I: Average contamination level of tested fish species in mg HCB/kg fresh weight; areas downstream the point of discharge (SA 2 to SA 6); years 1999 and 2002;
II: Development of exceeding the maximum legal amount of HCB in SA 5 (example) (frequency of exceeding in % of the total sample)

species (medium fat content)	**I (SA 2 to SA 5)**			**II (SA 5)**		
	1999	***2002***	***decrease***	***1999***	***2002***	***decrease***
Eel (25 %)	0,361	0,155	- 57 %	96 %	4 %	- 96 %
Bream (9,5 %)	0,203	0,044	- 78 %	93 %	53 %	- 45 %
Barbel (5 %)	0,128	0,009	- 93 %	100 %	0 %	- 100 %
Predators (1 %)	0,022	0,003	- 86 %	0 %	0 %	-

Table 1 shows the average total HCB contamination of the respective fish species in all of the examined river sections downstream the source of contamination (I) and, as an example, the frequency of cases, where the maximum legally allowed HCB-amounts in SA 5 were exceeded and their developments over time (II). As expected, the levels of HCB-concentration differ significantly according to fish species. Also, a positive correlation between the fat contents of the different species and their HCB loads was verified. The same correlation was stated by KARL et al. (1999) for dioxin concentrations in different sea fish species[10]. However, they did not find, within the same species, a relationship between fat contents and dioxin concentration, whereas our results showed highly significant positive correlations between fat contents and HCB concentrations in eel (correlation coefficient r = 0.67) as well as in bream (r = 0.95) and barbel (r = 0.75). Also, the intensity and speed of decontamination was in dependence to the fat contents of species and individuals.

In SA 5, on the base of these monitoring results, the food administration in 1999 prohibited the traffic and trade of eel, bream and barbel and of other species with similar fat contents. Traffic and trade of predators in SA 5, which, due to minor fat contents, showed only very low HCB-concentrations, were still permitted. From the year 2001 prohibition of trade of barbels and other similar species was discontinued, following the results of the monitoring. In this river section, at the end of 2002, eels were again opened to the traffic and trade as only one sample exceeded very slightly the legal maximum for HCB. Different regulations were applied in the other river sections, due to the specific monitoring results in the respective sampling areas.

Conclusions

During the first four years, the fish monitoring program described above proved to be an effective, reliable and appropriate instrument for consumer protection as well as for damage assessment. On the base of the monitoring results, exact and in-depth risk assessments were conducted for each year and each river section. Thus, it was possible that the traffic and trade of the fishes of the Danube were regulated in specific relation to particular river sections, for particular fish species and groups of fishes as well as following trends of decontamination processes. Trend analyses of monitoring results permitted the timely opening of the market. In addition, assessment and regulation of economic damage was carried out on the base of the yearly results of the program. The economic damage could be assessed and compensated for more than 80 fisheries enterprises and other claimants alongside the river stretch of 260 km. Beyond the primary targets of the program and in view of the necessity for methodical standardization and harmonization in future international POPs monitoring activities[11], comprehensive experiences have been gained during the study, to be considered in future activities.

Acknowledgements

We would like to thank Ms. Becker from Oekometric and her team for excellent analytic work.

References

1. Hofer, R. and Lackner, R.; (1995) Fischtoxikologie, Gustav Fischer Verlag Jena-Stuttgart, ISBN 3-334-60846-8
2. European Commission (2000) Report SCOOP Task 3.2.5 (Dioxins) Final Report
3. Hosseinpour J., Rottler H., Joas R., Potrykus A., Schott R. (2002) Organohal. Comp. 57, 77-79
4. Joas R., Potrykus A., Schott R. Hosseinpour J., Rottler H. (2002) Organohal. Comp. 55, 291
5. Steffen, D., Wunsch, H., Kämmereit, M., Kuballa, J.; (2001) ISSN: 1434-2499
6. Heinisch, E., Marth, P., Ketrup A., Wenzel S.; (1998) in: Proc. Workshop: "POPs in environmental matrices of Bavaria and the Czech Republic", Nov. 28. 1997
7. Seifert, K. and Hartmann, F.; (2001) Wertermittlungsforum 19 (1)
8. Gaumert, T.; (1996) Inf. Fischwirtsch. 43 (4)
9. IPCS (1997) Environmental Health Criteria 195, 1997
10. Karl, H., Blüthgen, A., Ruoff, U., (1999) www.bfa-fish.de/news/news-d/hintergrund.htm
11. Hosseinpour J. (2001) Organohalogen Compounds 54, 332-334