

LEVELS IN BIOTA

Begoña Jiménez¹ and K.W. Schramm²

1. Institute of Organic Chemistry, CSIC. Juan de la Cierva 3, 28006 Madrid, SPAIN.

2. Institute of Ecological Chemistry, Ingolstaedter Landstr. 1, D-85764 Neuherberg, GERMANY.

The main POPs of concern presented in this session were PCDDs, PCDFs, PCBs and PBDEs, and toxaphenes, which were studied both in aquatic and terrestrial environment at different trophic levels and continents.

AQUATIC ENVIRONMENT.

Among the 13 papers presented, different fish species were used as bioindicators, including mostly species for human consumption (herring, breams, dabs, perch, eel, salmon, blue shark, swordfish, etc.) Crustaceans and bivalves were also used in two studies.

Koistinen et al. investigated the contamination of different sites along the coast of Finland using herring samples. It was proven to see whether polluted and less polluted sites along the coast of Finland were reflected in the herring data. Besides, dioxins and PCBs, toxaphene, DDT compounds and PCNs were analysed. This study revealed no clear point sources for most studied organochlorine pollutants, except possibly for toxaphene and PCNs.

Schröter et al. investigated the contamination of fresh water fish with PCDD/Fs and dioxin-like PCBs. Breams are widely distributed in Europe and often used as a monitoring organism for fresh water and sediment contamination due to their small migration radius. Adult breams feed mainly on benthic invertebrates. Thus, they are permanently in direct contact with the sediments. Although bream is less consumed at least in Germany results from this study might facilitate general statements regarding the contamination of other fresh water fish species with PCDD/Fs and dioxin-like PCBs. Bream samples from three sampling sites (Elbe – Blankenese, Rhine – Weil and Bimmen) showed PCDD/F levels that exceed the maximum permitted value of 4 pg WHO-TEQ /g ww set by the European Commission for the muscle meat of fish which is intended for human consumption. In consideration of the WHO-TEQ levels of dioxin-like PCBs all investigated bream samples from German rivers achieved or even exceed the European Commissions limit value.

Munsch et al. determined the contamination levels of dabs from the Eastern Part of the English Channel, France. Dab (*Limanda limanda*) is a benthic flat fish commonly found in European coastal waters, and chosen by the International Council for the Exploration of the Sea (ICES) as a sentinel species. The TEQs calculated were lower than the recommended limit of 3 pg TEQ/g w.w. set by the European Commission for sea products intended for human consumption. However, this limit does not take into account the contribution of PCBs. As the estimation of TEQ is highly dependent upon the TEF used for the calculation, and that the TEF concept includes some uncertainty, authors strongly recommend the communication of data on an individual-congener concentration basis, especially in studies of environmental concern.

Roots et al. presented dioxin and dioxin-like PCB levels in perch (*Perca fluviatilis*) from the north-eastern part of the Baltic Sea. None of the perch samples, collected in 2003, exceeded the limit for the concentration of dioxin, established by the EU. Authors propose that the analysis of six samples of fish should be provisionally satisfying both for testing of dioxin and “dioxin like PCBs” levels in perch and informing the consumers of the amount of toxicants consumed when eating perch.

Voorspels et al. determined PCBs and OCPs in benthic invertebrates and different fish species from both Belgian North Sea (BNS) and Western Scheldt Estuary (SE) in order to evaluate trends in levels, congener distribution, and geographical variation. Apart from the concentration difference between BNS and SE, a correlation was observed between pollutant concentration and the distance to Antwerp. This correlation was highly significant for both PCBs and OCPs in crab, shrimp, sole, and bib.

Van Leeuwen et al. presented the results of a new monitoring program on organic contaminants in fish from the Netherlands started in 2003 for a comprehensive dataset for evaluation of potential risk for consumers. The samples were obtained from the local market (farmed salmon, eel, etc.), caught during stock assessment cruises of the research vessel Isis, from local fishermen or by electro fishery (eel). The levels of PCDD/Fs in the fish samples do not exceed the current European MRL of 4 pg TEQ/g ww.

Erdogrul et al. investigated the levels and distribution of organohalogenated contaminants in several fish species from Sýr Dam Lake (Kahramanmaraş, Turkey), an artificial lake with great economical importance for the region. A total of 83 individual fishes, representing 5 species *Acanthobrama marmid*, *Cyprinus carpio* (carp), *Chondrostoma regium* (nose-carp), *Barbus rajanorum* (barbel), *Siluris glanis* (wels), were analyzed. DDTs were the prevalent organohalogenated contaminants found in the 5 fish species from Sýr Dam Lake. For all species, the PCB profile was dominated by the tri- to penta-CB isomers, which constituted between 53 and 90% of the total PCBs. The PCB levels in the fish species from Sýr Dam Lake are also below the tolerance limits set for freshwater fish from European countries (1.4 ug/g ww in Germany). PBDEs were detected in all muscle and liver samples from the 5 fish species, except few samples of carp liver and nose-carp muscle. The PBDE levels were lower than the PCB levels, but they were at the same level or higher than HCB, HCHs and CHLs.

Azevedo et al. studied PCBs and DDTs in fish high on the food web. Blue shark and swordfish are carnivorous fishes of great economic importance. The study investigated the concentration of PCBs and DDTs in samples of muscle tissues of blue shark (*Prionace glauca*) and swordfish (*Xiphias gladius*) from Brazilian coasts. Authors explain that the low organochlorinated concentrations observed in their study, can be due to the fact that these animals live in open sea, without any punctual pollution sources.

Mola et al. presented a study planned to monitor the dioxin and dioxin-like contaminants in the marine environment of Korea. In general, PCDFs revealed the higher contributions to the total concentrations in comparison with those of PCDDs. Tetra-chlorinated compounds had the highest contribution, while the high chlorinated compounds showed low contribution. Congener profiles of DL-PCBs in marine organism showed the similar patterns. PCB 126 had the highest levels (>70%) in all organism samples analyzed, followed by PCB 169 and PCB 156. Generally, non-ortho PCBs were the major contributors to total DLPCBs concentrations.

Schmid et al. focused on the global transfer of POPs, affected by long-range atmospheric transport. In this study, fish from 7 alpine lakes from the Grisons (Switzerland) situated between 2062 and 2637 m above sea level were investigated.

Karl et al. investigated dioxins, dioxin-like PCBs, marker PCBs and a range of organochlorine pesticides (toxaphene, chlordane, DDT, HCB etc.) in the muscle meat of salmon. Within the context of a study to develop methods for the detection of organically produced products taking salmon as example it was checked if the contaminant levels and/or the contaminant patterns are suitable to differentiate between organically and conventionally farmed salmon. With a market share of 8.4 % in 2001 (approx. 100,000 t) farmed salmon is one of the most important fish species on the German market. In general, levels in farmed salmon were in the same range as in organic salmon. All mean concentrations, ranging between 0.2 and 0.48 ng WHO-PCDD/F-TEQ/kg (w.w.), were far below the EU-limit of 4 ng/kg w.w.. Unlike the dioxin contamination, the dioxin-like PCB contents of conventional farmed salmon were higher, than that of organic salmon. Lowest concentrations were found in wild salmon. The total WHO-TEQ in salmon is dominated by the dioxin-like PCBs. The contribution to the total toxicity equivalents is 4 - 7 times above that of dioxins. The mean WHO-PCDD/F + PCB-TEQ ranged between 1.8 and 3.1 ng/kg w.w. Wild Atlantic salmon was less contaminated than farmed salmon but significantly higher than wild Pacific salmon.

Bodin et al. discussed new data on PCBs, PCDD/Fs and PBDEs in crustaceans. The main objective was to obtain an estimation of the concentration ranges of those contaminants in large crustaceans from the French coast. PCBs, PCDD/Fs and DL-PCBs are much higher in crabs from Antifer compared to other sites which confirms a chronic pollution of the whole Bay of Seine mainly due to contaminant inputs by the Seine River.

The CB138/CB153 ratio decreases from 0.8 in mussels to around 0.6 in crustaceans and unlike mussels, crabs present CB149/CB118 and CB132/CB105 ratios lower than 1. These differences can be explained by specific metabolism capabilities, crustaceans being able to partially biotransform PCBs. The distribution of dioxins in all crustacean species is characterized by the prevalence of the PCDF (45-75%) compared to the PCDD. The main compounds are the OCDD and TCDF. These fingerprints are very similar to those observed in mussels and also look like typical pattern of combustion processes.

Müller et al. reported results from the National Dioxin Program with a particular emphasis on the levels of dioxin-like chemicals in marine bivalves and sediments. The levels, expressed as TEQs, ranged from 0.0068 – 3.4 pg TEQ/Humans/g ww. Overall, levels of dioxin-like chemicals in bivalves were well below the benchmark value of 25

pg/g fresh wt for dioxins in fish set by the U.S. FDA, which was identified as a level with no serious health effects; and therefore also much below the 50 pg/g fresh wt action level set by the US FDA. A general trend of increasing concentration in biota with increasing levels in sediments was found in this study. The data clearly demonstrate a higher accumulation of the lower chlorinated PCBs and PCDD/Fs in biota compared to sediments.

TERRESTRIAL ENVIRONMENT.

Most of the studies presented focused on top predators and birds, in particular. One study focused on the brown bear.

Fernandes et al. reported POPs exposure in grey heron (*Ardea cinerea*). In the United Kingdom recent investigations have detected elevated levels of mortality and bone disease in grey herons at an established colony in Nottinghamshire along the course of the river Trent. The causes of mortality are unclear but deformities recorded in the other birds include multiple fracture of the tarsus, tibia and metacarpal bones. These findings have prompted a pilot study into assessing the level of environmental contaminants in the tissue and eggs of these birds. Authors concluded that the levels of dioxin and PCB WHO-TEQs recorded in dead and deformed nestling tissue at the Nottinghamshire site, compared to unaffected nestlings, are indicative of a relationship between the levels of these contaminants and the deformities observed in the nestlings

Malisch et al. presented a study using eggs of peregrine falcon as suitable bioindicators for different regions of Germany. The relative contribution of PCBs to the total TEQ was on average 84%. It should be remarked that in this study, TEQs were calculated using the WHO TEFs for humans, even if the authors indicate that there are differences for some congeners. In fact, they reported that the sum of WHO TEQs would be increased about 20% when using TEF for birds instead that for humans. Authors recommended that for the purpose of comparison of data from different regions and years it should be considered to present data on dry matter basis, as well. Thus, for old eggs samples (partly dried; rotten; begun to sit on), data on dry matter are considered to provide best comparability. It is recommended to report dry matter and fat content generally to allow recalculations for the required comparison. In comparison to the data for the usual background contamination of hen eggs for human consumption, eggs of birds of prey are extremely high contaminated with PCDD/Fs and PCBs.

Takazawa et al. carried out a sampling survey of pintails at Lake Hyoko, Niigata, Japan. The toxaphene levels among fat, breast muscles, and livers were discussed. This is the first study to show residue levels of toxaphene in Japanese biota. Lipid in breast muscles was shown to be capable of being a final sink for migratory birds; authors conclude that the distribution of toxaphene stems from the motion of breast muscles during migration. In addition to this, the assumption that toxaphene contamination had spread to the Far East, including Japan, has at least been validated.

Corsolini et al. evaluated PCBs, PBDEs and chlorinated pesticides in blood samples of the Adélie penguin, *Pygoscelis adeliae*, the Emperor penguin, *Aptenodytes forsteri* and the South Polar skua, *Cataracta maccormicki* from three sites in the Ross Sea (Antarctica). The detection of BDEs 47, 99 and 100 in Antarctic organisms confirm the global distribution of PBDEs. Presence of low-brominated congeners, tri- to penta-BDEs might suggest that contamination is due to long-range transport. Even the PCB class of isomers patterns could confirm this hypothesis: low chlorinated PCB congeners, from tri- to penta-CBs, constitute 34-62% of the PCB residue. p,p'-DDE is the most persistent metabolite and thus its detection in samples is also due to a high degree of biomagnification in the Antarctic food web.

Bolta et al. focused their study on the brown bear (*Ursus arctos*). Solid scientific evidence on contamination with PCDD/Fs was presented for the polar bear (*Ursus maritimus*), while PCDD/Fs levels in the brown bear (*Ursus arctos*) population, which once lived throughout the entire European continent, has remained undetermined. This investigation on the PCDD/F contents in adipose tissue of the brown bear represents the first information of the PCDD/Fs in the wildlife of Slovenia. Higher PCDD/Fs levels were detected in the kidney fat. Compared to the levels of PCDD/Fs published for the polar bear the analysis results for the brown bear in this study stand in the lower range of the reported values. Lower PCDD/Fs detected in the adipose tissue of the brown bear could be explained through its different nourishment; while the polar bear primarily feeds on meat, brown bear can seasonally consume up to 95% of vegetal food, depending on the availability of the food in the living area.

Nearly all contributions used human TEF values to present their data. Very few authors tried to assess the risk of contamination for the species investigated, based on their TEF. Thus, the link from monitoring to risk assessment and the discussion of the importance of time, season and decade is often missing. With respect to future use of the data produced it is recommended to present data on levels of biota in a format which allows the assessment of the risk for biota and human exposure as well