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POP MONITORING IN FISH

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Introduction:
In implementing the requirements of the Water Framework Directive (WFD)[1)] a biota monitoring was carried out at selected monitoring sites of the Austrian surveillance monitoring program in the year 2013. This monitoring program was based on Directive 2008/105/EC on environmental quality standards (EQS) in the field of water policy as well as amendments or supplements by Directive 2013/39/EC and on the equivalent Austrian law „Gewässerzustandsüberwachungsverordnung" (GZÜV) and aimed to examine EQS and trends for pollutants in biota. In this text the results for PCDD/F, PCB and PBDE are discussed, but within this survey also another 7 parameter groups have been analysed. Further information can be found in the corresponding report [2)].

Material and Methods:
Fish have been sampled at a total of 33 sites (see Figure 1) from the Austrian surveillance monitoring (32 river monitoring sites and one lake-monitoring site). The selection of sites also included areas without or only marginally influenced by anthropogenic activities (reference sites). The sampled fish species were mostly chub (Squalius cephalus), at reference sites mostly trout (Salmo trutta). At 5 sampling sites 3-8 fishes were analysed separately for a possible detection of trends, at the other 28 sampling sites 2-9 fishes of the same species were mixed up to one pool sample for analysis. The results given below are calculated on fresh weight basis (FW).

For analysis the whole fish were homogenized and freeze-dried. An aliquot of the sample has been extracted with toluene in a soxhlet extractor. After a three step liquid column clean up the extracts are analysed by GC-HRMS according to EPA 1613 [3)], EPA 1614 [4)] or EPA 1668 [5)] respectively.

Results and Discussion:
Environmental quality standards (EQS) define the good chemical status of surface water bodies according to article 16 of the WFD. PCDD/F, PCB and PBDE are persistant and lipophilic substances and accumulate in the food chain. Therefore also maximum levels are defined in the EC food legislation[6)]. Since freshwater fish are used for biota monitoring but are also classified as food, it seems useful to compare the results of this study with both reference criteria, i) the EQS and ii) the maximum levels for fish according to the food legislation as well.

For this study, as supposed for checking the water quality, the whole fish has been analyzed. Therefore a direct assessment of the samples according to food law is not possible, because for food control only muscle meat has to be analyzed. However, the measured concentrations may provide information on areas of potential concern.

The EQS for PCDD/F and dioxin-like compounds is 0.0065 µg TEQ/kg FW and thus corresponds to the maximum level of 6.5 pg TEQ/g FW given by the EC food regulation. In addition there is a maximum level of 3.5 pg TEQ/g FW in the EC food regulation for PCDD/F only.

The dioxin-like PCBs are added to the PCDD/F limit in both legislations and therefore no limit exists for DL-PCB only. For the non-dioxin-like PCBs a maximum level of 125 ng/kg FW exists in the food regulation for the sum of PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180.

The EQS for PBDE is 0.0085 ug/kg FW for the sum of 6 congeners (BDE-28, BDE-47, BDE 99, BDE-100, BDE-153 and BDE-154). In the food regulation there is no maximum level, but a Commission recommendation to reach a LOQ of 0.01 ng/g FW.

The measured concentrations of PCDD/F (see Figure 2) are consistently well below the maximum level of 3.5 pg TEQ/g FW. PCDD/F are therefore according to current knowledge neither a risk for the environment nor for the use of fish as food.

For the dioxin-like PCBs higher concentrations could be found in some samples of rivers with industrial influence. Two single fish exceed the maximum level for the sum of PCDD/F and DL-PCBs already due to the DL-PCB levels, one of them by more than twice. Since PCDD/F contribute little to the total TEQ of PCDD/F and DL-PCB the picture for the DL-PCB levels is very similar, as for the sum of PCDD/F and DL-PCBs (see Figure 3).

The non-dioxin-like PCB (NDL-PCB) also show considerable levels in individual fish from industrially influenced rivers, but none of the samples exceeds the maximum level for food. However, there are several samples which contents of NDL-PCBs are more than half the maximum level for food (see Figure 4). An EQS does not exist for this group of substances.

The substance group of polybrominated diphenyl ethers (PBDE) show the least satisfactory results out of the three considered groups of POPs. The analysed concentrations of all samples are above the EQS for these substances, partly several orders of magnitude higher (see Figure 5). Also the proposed LOQ for these substances for food samples is exceeded clearly. Whether the EQS has been set too ambitious for these substances or the toxicity was considered too high is currently being discussed. The EQS is based on the most toxic congener, but for compliance checking several congeners are summed up. Furthermore for these very hydrophobic and lipophilic substances only 10% were allocated to be taken up by food consumption. In combination with a daily fish consumption of 115 g, this very low EQS value is determined. Increasing the EQS would relax the current dramatic image.

Acknowledgements:
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References:

1. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, establishing a framework for Community action in the field of water policy

2. Report of the Austrian Ministry for Agriculture, Forestry, Environment and Water Resources, M.Clara, A.Draxler and K.Deutsch, "FISCH UNTERSUCHUNGS-PROGRAMM 2013; GZÜV-UNTERSUCHUNGEN" (June 2015)

3. EPA Method 1613 Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (1994)

4. EPA Method 1614, Brominated Diphenyl Ethers in Water Soil, Sediment and Tissue by HRGC/HRMS (2007)

5. EPA Method 1668 Revision B, Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS (2008)

6. Commission Regulation (EC) No 1881/2006 of 19 December 2006

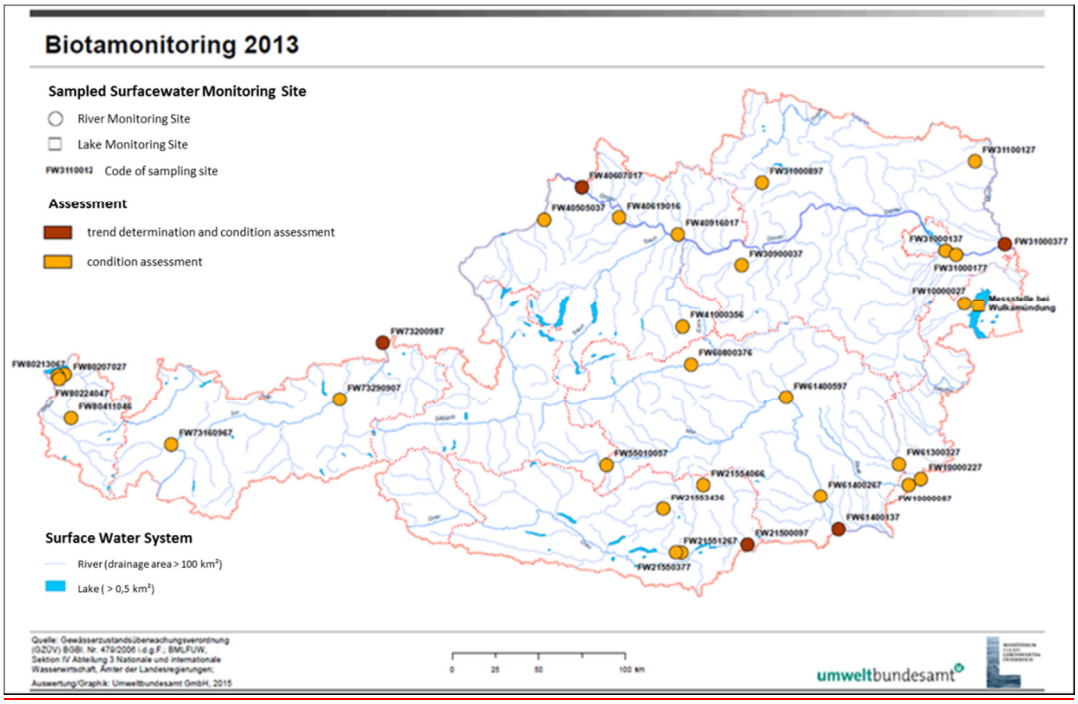

Figure 1:Map of Austria with sampling sites.

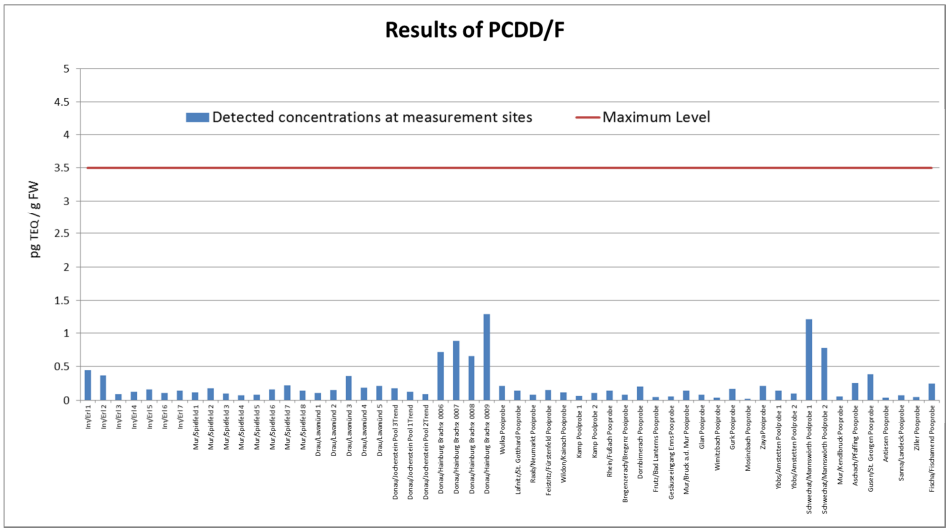

Figure 2: Results of PCDD/F in fish

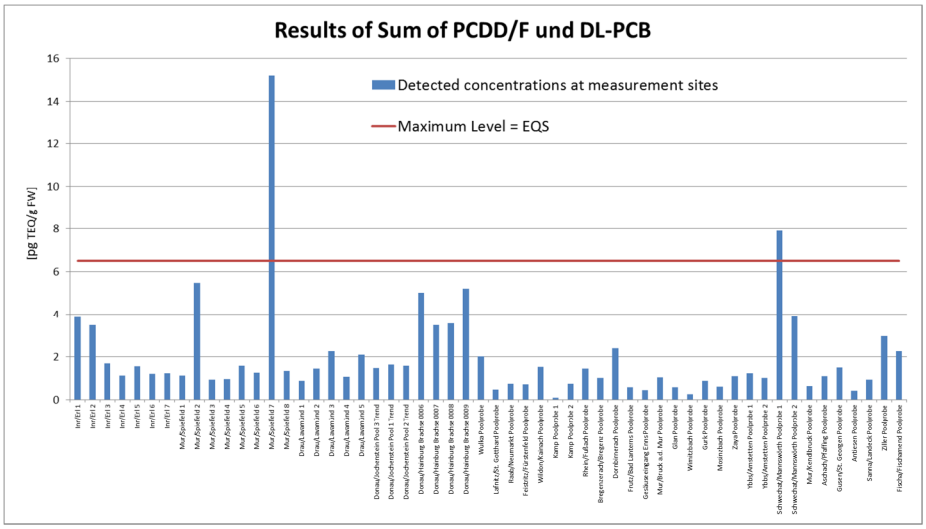

Figure 3:Results of sum of PCDD/Fand DL-PCB in fish

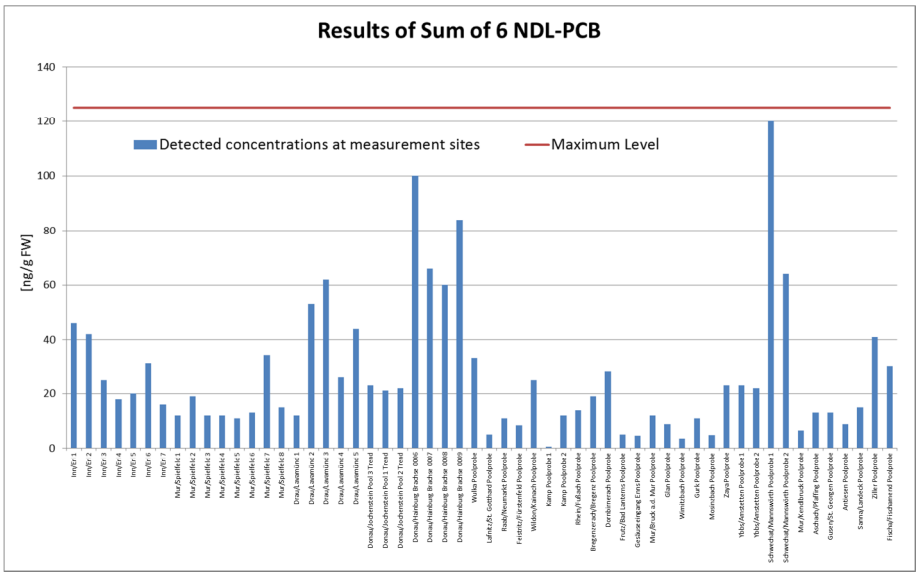

Figure 4:Results of NDL-PCB in fish

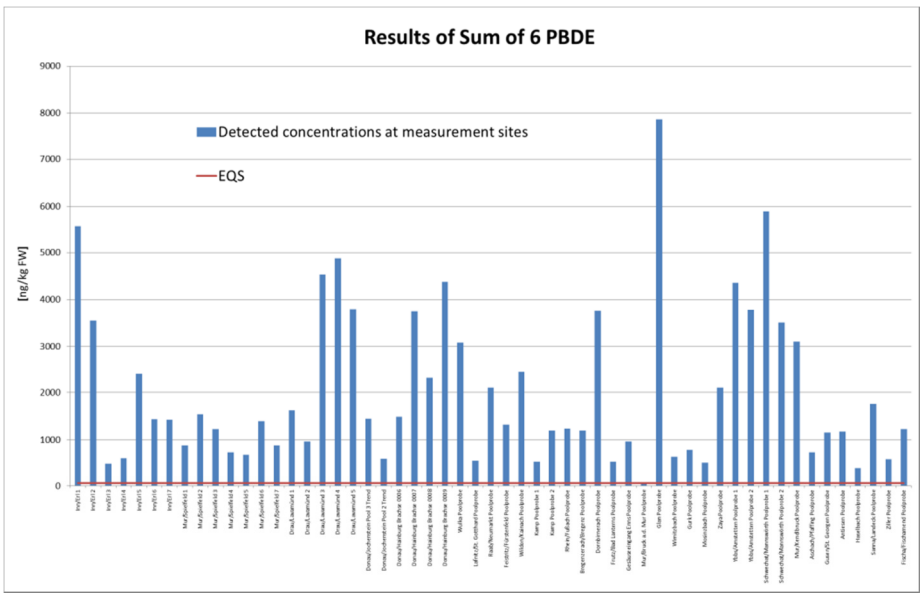

Figure 5: Results of PBDE in fish