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Current levels and trends of selected EU Water Framework Directive priority substances in freshwater fish from the German environmental specimen bank☆

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ABSTRACT

Under the German environmental specimen bank programme bream (*Abramis brama*) were sampled in six German rivers and analysed for the priority hazardous substances dicofol, hexabromocyclododecane (HBCDD), hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), heptachlor + heptachlor epoxide (HC + HCE), polybrominated diphenylethers (PBDEs), polychlorinated dibenzo-p-dioxins and -furans and dioxin-like polychlorinated biphenyls (PCDD/Fs + dl-PCBs), and perfluorooctane sulfonic acid (PFOS). The aim was to assess compliance with the EU Water Framework Directive environmental quality standards for biota (EQS_{Biota}) for the year 2013, and to analyse temporal trends for those substances that are of special concern. General compliance was observed for dicofol, HBCDD and HCBD whereas PBDEs exceeded the EQS_{Biota} at all sites. For all other substances compliance in 2013 varied between locations. No assessment was possible for HC + HCE at some sites where the analytical sensitivity was not sufficient to cover the EQS_{Biota}. Trend analysis showed decreasing linear trends for HCB and PFOS at most sampling sites between 1995 and 2014 indicating that the emission reduction measures are effective. Mostly decreasing trends or constant levels were also observed for PCDD/Fs and dl-PCBs. In contrast, increasing trends were detected for PBDEs and HBCDD which were especially pronounced at one Saar site located downstream of the industries and conurbation of Saarbrücken and Völklingen. This finding points to new sources of emissions which should be followed in the coming years.

1. Introduction

The EU Water Framework Directive (WFD) (Directive, 2000/60/EC) aims at the protection and improvement of the aquatic environment (EC, 2000). This includes the reduction of emissions of hazardous substances and the enhancement of the ecological status of the aquatic environment. Achieving this goal Europe-wide requires common definitions of the chemical status of the water quality. In this context, priority substances were identified that require action at the European Union (EU) level. For these substances environmental quality standards (EQSs) were derived which serve as benchmark concentrations for harmful effects to wildlife and humans. Among the priority substances a group of hazardous substances was identified that represent a significant risk to or via the aquatic environment (EC, 2008, EC, 2013).

Most priority hazardous substances are persistent organic pollutants (POPs) characterized by chemical properties that may significantly affect human health and the environment, i.e. chemical stability, toxicity and a high potential for bioaccumulation. The latter leads to higher concentrations in biota compared to the water phase. Biota monitoring is therefore an alternative to the measurement of these substances in water. In the EU Directive 2013/39/EU for eight of these substances, respectively substance groups, namely dicofol, hexabromocyclododecane (HBCDD), hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), mercury and

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its compounds (Hg), heptachlor + heptachlor epoxide (HC + HCE), polybrominated diphenylethers (PBDEs), and perfluorooctane sulfonic acid (PFOS) a monitoring in fish is advised. For another group of chemicals, i.e. polycyclic aromatic hydrocarbons (PAHs), the monitoring of benzo(*a*)pyrene and fluoranthene in mussels is requested since these compounds are metabolized by fish. For polychlorinated dibenzo-p-dioxins and -furans and dioxin-like polychlorinated biphenyls (PCDD/Fs + dl-PCB) the EQS_{Biota} relates to fish, crustaceans and molluscs. Table S1 (Supplementary material 1) gives an overview on compounds, protections goals and EQSs. For some compounds the EQS_{Biota} is intended to protect the human health (i.e. safe consumption of fish) while for others the main focus is on the prevention of secondary poisoning of fish-eating top predators.

Meanwhile, all of these substances are regulated to reduce their emissions to the environment. Some bans and restrictions go back to the 1970s and 1980s (e.g. for dl-PCBs and HCB) while others have only been banned recently (e.g. PFOS, HBCDD and HCBD). It is therefore of interest to analyse the temporal trends and current environmental concentrations of these POPs with respect to compliance with the EQS_{Biota}.

In this context, the German Environmental Specimen Bank (ESB) is a valuable tool because highly standardized sampling and archiving of environmental samples allows the (retrospective) assessment of temporal and spatial trends of chemicals (www.umweltprobenbank.de/en/). The present study focuses on bream (*Abramis brama*) sampled in three major German stream systems and their tributaries. The aim was to determine the EQS_{Biota} compliance for the eight organic priority hazardous substances and chemicals' groups for which compliance monitoring is requested in fish. Furthermore, temporal trends were analysed for HCB, HBCDD, PBDEs, PCDD/Fs + dl-PCBs, and PFOS to evaluate the success of emission reduction measures.

2. Materials and methods

2.1. Sampling

Sampling and processing under the German ESB programme is highly standardized and follows standard operating procedures (German Environment Agency, 2016; Paulus et al., 1996; Rüdel et al., 2015). In brief, bream are collected every year after spawning between mid-July and early October. Routinely, 20 fish aged 8–12 years are taken at each sampling site (Klein et al., 2012). The muscle tissue (filet) is dissected and immediately shock-frozen in liquid nitrogen as a pooled sample of all bream from one site. In the laboratory, the tissue is pre-crushed, cryo-milled and finally stored in an archive as homogenized powder at temperatures below −150 °C in an inert atmosphere to minimize chemical alterations (Rüdel and Weingärtner, 2008; Rüdel et al., 2009).

Fig. 1 shows the locations of the sampling sites and Table 1 gives a brief description of the sites and a rationale why they were chosen by the ESB. The sites are located in the three main streams in Germany, i.e. the Rhine, Elbe and Danube, as well as in the Elbe tributaries Saale and Mulde and the Rhine tributary Saar. Lake Belau is located in an agricultural region in Schleswig-Holstein and is representative of remote sites with relatively low anthropogenic influence.

2.2. Chemical analysis

Tissue samples of bream muscle were retrospectively analysed

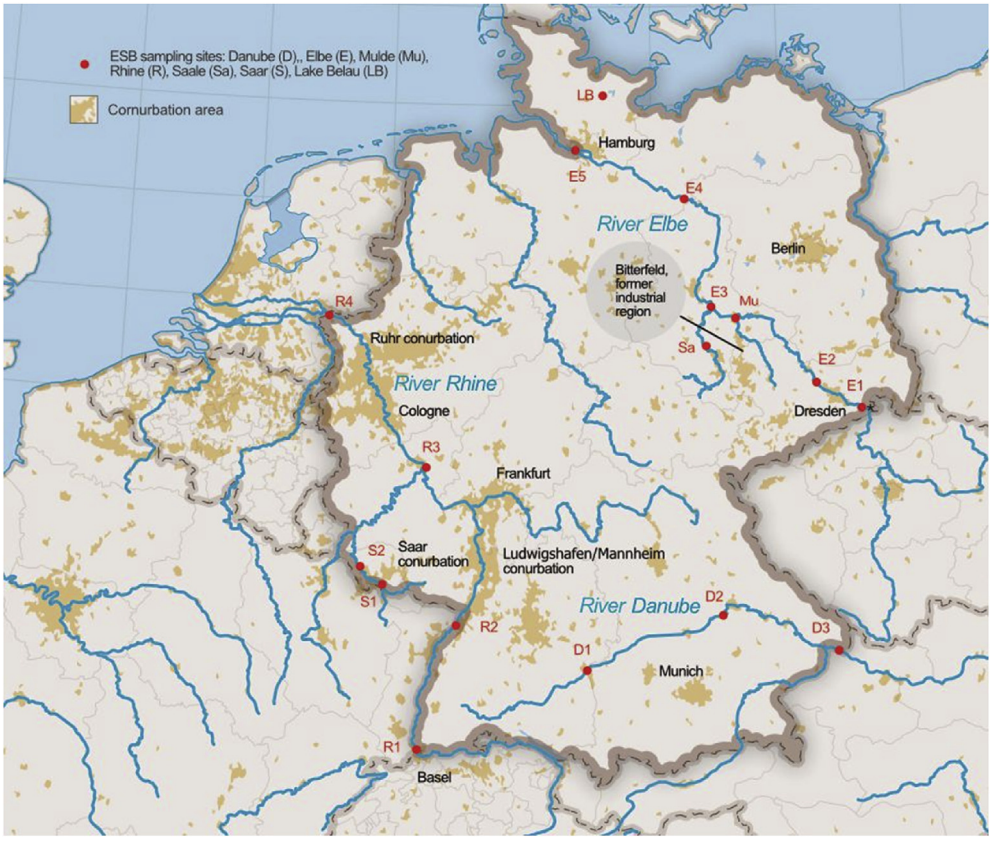

Fig. 1. Freshwater sampling sites of the German environmental specimen bank.