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Retrospective monitoring of mercury in fish from selected European freshwater and estuary sites

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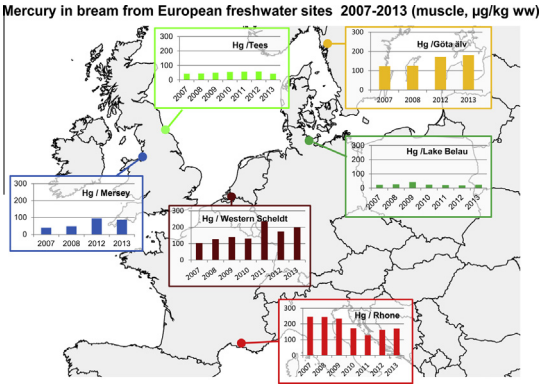
HIGHLIGHTS

- Total Hg and Methyl-Hg were analyzed in bream from five rivers and one lake in Europe.
- Between 2007 and 2013 the environmental quality standard for Hg was exceeded at all riverine sites.
- Highest Hg levels were detected in the Rhône (FR), Göta älv (SE) and Western Scheldt (NL).
- Since 2007 THg and Methyl-Hg significantly decreased in bream from the Rhône estuary.
- The Methyl-Hg fraction of THg was always >80% and comparable at all riverine sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Levels and trends of total mercury (THg) and methylmercury (MeHg) compounds in bream (*Abramis brama*) from different European sites were compared. Bream were collected between 2007 and 2013 in the estuaries of the rivers Scheldt (Netherlands), Rhône (France), Göta älv (Sweden), Tees (United Kingdom), and Mersey (UK), and in Lake Belau (Germany). A direct mercury analyzer was used to determine THg concentrations while MeHg was measured by gas chromatography/inductively coupled plasma-mass spectrometry applying stable isotope dilution. THg and MeHg in annual pool samples of bream ranged between 15.9 and 251 µg kg^{-1} wet weight (ww) with lowest concentrations found at the reference site Lake Belau and highest in samples from the river Rhône. The EU environmental quality standard (EQS) of 20 µg kg^{-1} ww was exceeded at all sites and in all years except at Lake Belau in 2012. Significantly decreasing trends over time were observed only in bream from the Rhône, while THg increased in bream from the Western Scheldt. The MeHg fractions of THg were always >80% and a significant difference between sites was detected only in one case (Rhône *vs.* Lake Belau).

1. Introduction

Mercury (Hg) is in the focus of environmental science since many years because of its ubiquitous presence in the ecosphere and its high toxicity. It exists in a large number of different

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physical and chemical forms of which elemental Hg and monomethylmercury compounds (CH_3HgX, here designated as MeHg) are the most relevant. Especially MeHg is of great concern because of its combination of high toxicity and high potential for bioaccumulation and biomagnification (EQS substance data sheet, 2005; Merian et al., 2004).

A major part of the environmental Hg is of anthropogenic origin and enters aquatic ecosystems via atmospheric deposition (E-PRTR, 2014; Lepom et al., 2012; Merian et al., 2004; Pacyna et al., 2009). Emission reduction is therefore of decisive importance. With the new Minamata Convention on Mercury (UNEP, 2013) a global treaty was agreed upon to protect human health and the environment. It includes, e.g., a ban on new mercury mines, the phase-out of existing ones and control measures on air emissions.

The European Water Framework Directive (WFD, EC, 2000) sets an environmental quality standard (EQS) for Hg at 20 $\mu g\ kg^{-1}$ wet weight (ww) in fish (EC, 2008, 2013). The EQS is intended to protect top predators against secondary poisoning and refers to total Hg (i.e., the sum of inorganic and organic Hg species). However, because of its special environmental relevance, speciation analysis is worthwhile to determine the fraction of MeHg in fish samples and study whether this fraction is constant or differs between years and geographical sites. This approach allows a risk assessment based on the actual present Hg species.

The aim of the present study is the comparison of different freshwater sites in Europe regarding levels and trends of THg and MeHg in fish. To enhance comparability, uniform methods of chemical analysis were used for all samples. Moreover, the study focused on one fish species, namely bream (*Abramis brama*) which is abundant at all selected sites.

2. Materials and methods

2.1. Sampling

In order to ensure a high degree of continuity and consistency, sampling and sample treatment were performed according to standard operating procedures developed for the German Environmental Specimen Bank (ESB, German Federal Environment Agency, 2014; Klein et al., 2012; Paulus et al., 1996; Rüdel et al., 2008). Bream (*A. brama*) was sampled between 2007 and 2013 at six European sites, i.e., in the rivers Scheldt (Netherlands), Rhône (France), Göta älv (Sweden, no sampling 2009–2011), Tees (United Kingdom, UK), and Mersey (UK, no sampling 2009–2011) and in Lake Belau (Germany). The sampling was performed in the context of a project designed to monitor changes of environmental concentrations of hexabromocyclododecane (Rüdel et al., 2012). Briefly, about 15 fish were collected per site and year after the spawning season. After sampling and dissecting the muscle tissues were directly cooled to −150 °C. Pooled annual samples were prepared by a cryomilling procedure (Rüdel et al., 2008) using a Palla VM-KT with titanium milling cylinder and titanium milling rods (manufactured by KHD, Cologne) cooled to <−150 °C with liquid nitrogen before usage. The homogenized sample material was transferred into glass vials and stored above liquid nitrogen.

2.2. Sampling sites

The river sampling sites are located near the river mouths or in the estuary area, the respective geographical coordinates are summarized in Table S1 (Supplementary material).

Scheldt: The River Scheldt flows through France, Belgium and the Netherlands before it enters the North Sea. Its catchment area is about 22,000 km^2 with an average population density of 352 inhabitants km^{-2} (International Scheldt Commission, 2015). The sampling site 'Western Scheldt' is located near Appelzak in the industrialized estuary area of the Scheldt downstream of Antwerp. The water quality here is poor and affected by industrial and urban waste waters. Likely Hg sources are the chloralkali industry, the nonferrous industry, PVC production and phosphate industry located around the harbor of Antwerp or the tributaries of the Scheldt (Baeyens et al., 1998). Sediment contamination is high with reported Hg levels up to 1900 $\mu g\ kg^{-1}$ in the early 1990s (Baeyens et al., 1998; Leermakers et al., 1993). In 2012, Hg emissions in the adjoining river basin district 'Scheldt in Flanders' amounted to 308 kg (air) and 4.05 kg (water) (E-PRTR, 2014, Supplementary material, Table S2).

Rhône: The Rhône originates in Switzerland and runs through Lake Léman and southeastern France. At Arles, shortly before entering the Mediterranean Sea the river divides into two branches, the Grand Rhône and the Petit Rhône. The catchment area of the French Rhône between Lake Léman and the Mediterranean Sea encompasses about 91,000 km^2 with an average population density of 98 inhabitants km^{-2} (Olivier et al., 2008). The sampling site 'Rhône' is located in the Grand Rhône downstream of Arles and is influenced by industrial and urban waste waters as well as by the surrounding agriculture. In the river basin district 'Rhône and Coastal Mediterranean' atmospheric Hg emissions stem mainly from chemical and metal working industry and added up to 758 kg in 2012. The majority of direct Hg emissions are associated with urban waste water treatment plants (WWTPs, E-PRTR, 2014).

Göta älv: The Swedish river Göta älv rises in Lake Vänern in western Sweden and flows into the Kattegat at Gothenburg. Its catchment area comprises approximately 48,000 km^2 with an average population density of about 21 inhabitants km^{-2} (Nilsson, 2006). The sampling site 'Göta älv' is located in the city of Gothenburg shortly upstream of the harbor area. The atmospheric Hg emissions in this area are mainly associated with chemical industry and waste incineration and were relatively low in 2012 (i.e., 32.4 kg). The direct releases into the water were even lower (i.e., 4 kg in 2012) and stem from urban WWTPs and from pulp industry (E-PRTR, 2014, Supplementary material, Table S2).

Mersey: The River Mersey originates from the confluence of the rivers Tame and Goyt in North West England and enters the Irish Sea at Liverpool. Its catchment area covers approximately 4700 km^2 and is densely populated (1070 inhabitants km^{-2}, website of the Mersey Basin Campaign). The adjacent city of Manchester was one of the leading industrial cities in England in the 19th and 20th century and its industrial activities had a major impact on the environment. Heavy industry and textile industry, however, have turned down in the 1960s and the large port of Manchester closed in the 1980s. Since then the water quality of the rivers Irwell and Mersey and of the Manchester Ship Canal have greatly improved but a legacy of former times can still be found in the sediments of the Mersey estuary where average Hg concentrations of 0.84 mg kg^{-1} and 3.16 mg kg^{-1} were detected in the surface sediment (0–10 cm depth) and the 10–50 cm layer, respectively, in 2000–2002. The lower Hg concentrations in the surface sediments are attributed to more stringent emissions controls and diminution in manufacturing since the 1970s (Vane et al., 2009). Nowadays atmospheric Hg emissions as well as direct releases into the water are mostly caused by chemical industry and waste management. Other contributors are mineral industries, thermal power stations, gas and oil refineries and (for direct releases) urban WWTPs. In 2012 atmospheric Hg emissions of 505 kg were reported compared to direct emissions into the water of 42 kg (E-PRTR, 2014, Supplementary material, Table S2). The sampling site 'Mersey' is located near Warrington about 20 km upstream of Runcorn where the Mersey widens into its estuary.