EGU2020-9735
https://doi.org/10.5194/egusphere-egu2020-9735
EGU General Assembly 2020

Mercury contamination in German rivers: Historical trends and current situation

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Mercury (Hg) is a priority pollutant in aquatic ecosystems. In Germany, the chemical status of all large rivers is classified as “not good” due to the exceedance of at least one environmental quality standard (EQS) of the EU Water Framework Directive [1], mostly due to the failure to meet the EQS for Hg in fish of 20 µg kg^{-1}. Mercury has been introduced to rivers in Germany for more than a century from a variety of anthropogenic sources (e.g., industrial effluents, waste water treatment plants). Transport of Hg in river water occurs dominantly associated with suspended particulate matter, while dissolved Hg concentrations are low. Direct Hg releases to surface waters have been greatly reduced over the last decades and today inputs are dominated by diffuse sources (e.g., atmospheric deposition, soil erosion) and the remobilization of Hg previously deposited in bottom sediments. A key factor in controlling the remobilization and transfer of legacy Hg from sediments to water and ultimately into biota is the chemical form in which Hg is present in sediments and suspended particulate matter.

Here, we present (i) historical trends of Hg concentrations in suspended particulate matter in German rivers (e.g., Rhine, Elbe) over several decades compiled from public databases [2] and (ii) first results of a study aiming to characterize the chemical form of Hg in recently collected suspended particulate matter and contaminated sediment samples from German rivers using pyrolytic thermodesorption analysis [3]. The Hg release curves of samples during continuous heating up to 650°C were compared with those of reference compounds. Total Hg concentrations were determined by a direct Hg analyzer (Nippon MA-3000).

The historical records reveal that Hg concentrations in suspended particulate matter have decreased in the large German rivers from the beginning of the 1990s until today. For example, while yearly average values of 500-800 µg kg^{-1} Hg were still common in the lower reaches of the Rhine river in the early 1990s, most values in the last five years have been below 300 µg kg^{-1} Hg. However, the Elbe river, one of the most polluted rivers in Germany, still exhibits Hg values above 1000 µg kg^{-1} in some areas, despite a decreasing trend from even higher historical values. First results from pyrolytic thermodesorption analyses reveal that Hg in suspended particulate matter from Rhine and Elbe is released at temperatures around 300°C, suggesting a dominance of organically-bound and/or sulfide-bound Hg(II) species. Interestingly, a shift to lower Hg release temperatures was observed after aging of wet sample material and for freeze-dried compared

with wet sediments, highlighting the importance of sample preparation and the dynamic nature of Hg binding forms in natural samples.

[1] European Environment Agency (2018) European waters - Assessment of status and pressures 2018.

[2] e.g., http://undine.bafg.de, http://fgg-rhein.bafg.de, https://www.umweltprobenbank.de

[3] Biester H., Scholz C. (1997) Determination of mercury binding forms in contaminated soils: Mercury pyrolysis versus sequential extractions. Environ. Sci. Technol. 31, 233-239.