Mercury contamination in German rivers: Historical trends and current situation

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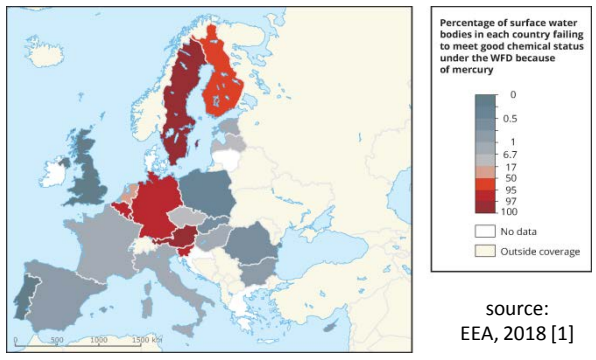
Introduction:

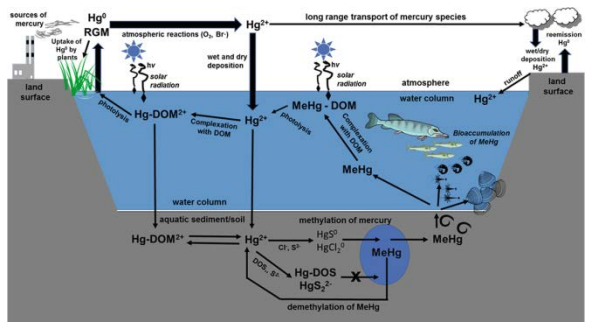
- Chemical status of all large rivers in Germany is "not good" due to exceedance of environmental quality standard of EU Water Framework Directive for mercury (Hg) in fish of 20 µg kg^{-1} [1].
- Large historic Hg emissions into rivers from anthropogenic sources (industry, mining, waste water, …) over > 1 century.
- Strong reduction of direct Hg releases in last decades, but legacy Hg can be remobilized from deposited sediments.
- Hg transport in rivers mostly as suspended particulate matter.
- Chemical form of Hg in sediments and suspended particulate matter controls mobilization to water and uptake into biota.

Mercury problem in surface waters of European countries



source: EEA, 2018 [1]

Environmental behavior and fate of Hg species in aquatic systems

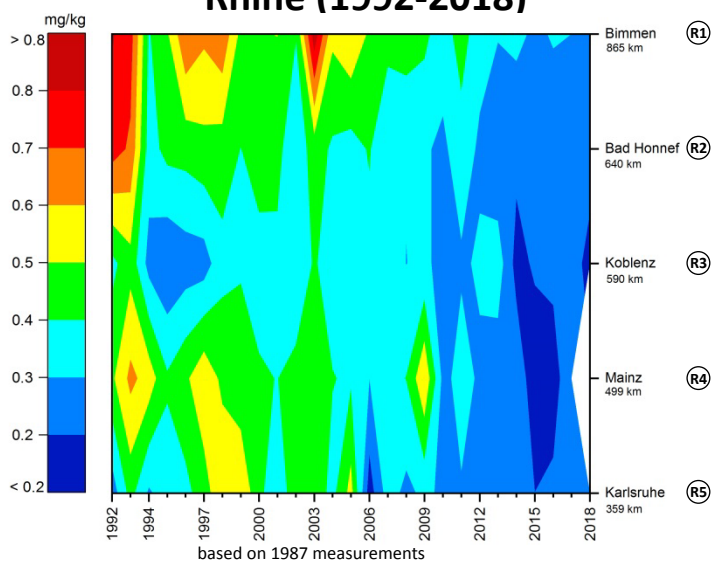


source: Orem et al. (2019) [2]

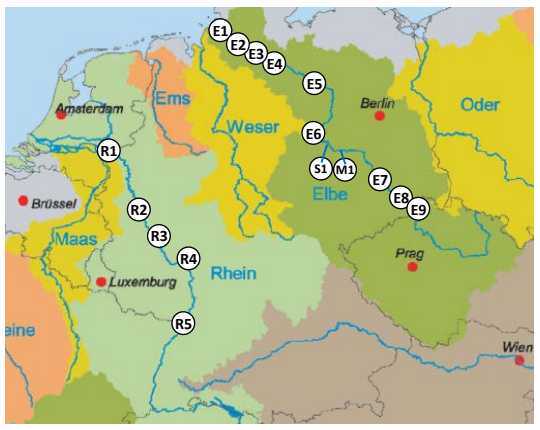
Historical Hg trends in suspended particulate matter

(data sources: federal states FGG-Rhein, FGG-Elbe [3])

Rhine (1992-2018)



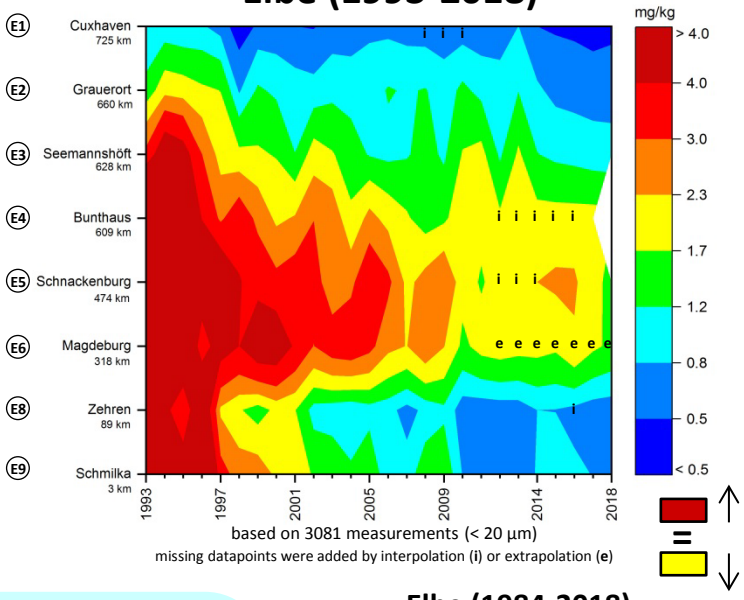
based on 1987 measurements



Note different color scales:

Rhine = Elbe

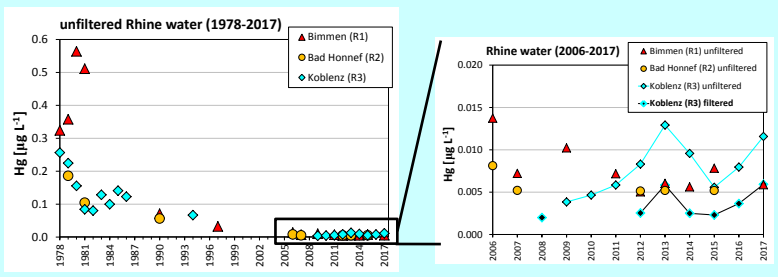
Elbe (1993-2018)



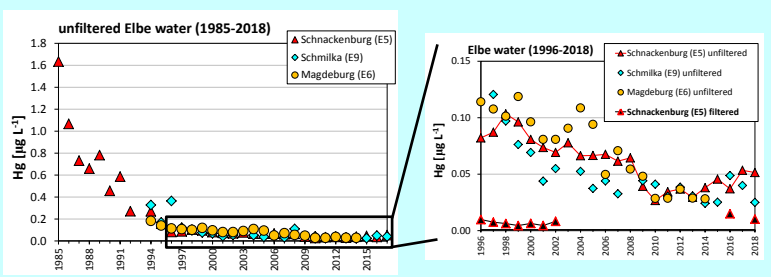
based on 3081 measurements (< 20 µm)

missing datapoints were added by interpolation (**i**) or extrapolation (**e**)

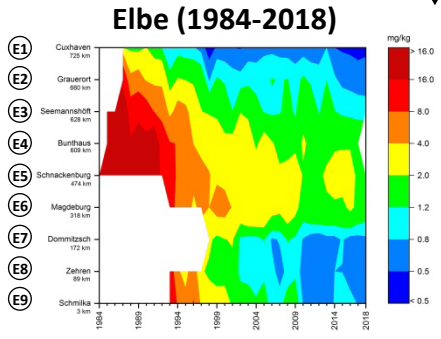
Historical Hg trends in water: Rhine



Historical Hg trends in water: Elbe



Elbe (1984-2018)



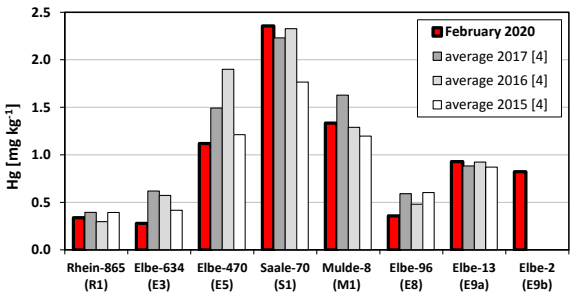
based on 3143 measurements (< 20 µm)

same datapoints added by interpolation or extrapolation as in plot above

white areas: no data available

Current situation: Suspended particulate matter in February 2020

(own measurements)



- High Hg concentrations in the Elbe are strongly influenced by the tributaries Saale and Mulde.
- Drying of samples at 105°C resulted in Hg loss of up to 34%, but variations between samples suggest existing differences in chemical binding forms of Hg.

Methods:

- Historical Hg concentration data was compiled from different public databases [3,4].
- Suspended particulate matter samples were collected in February 2020 at eight sampling sites on rivers in Germany (5x Elbe, 1x Rhine, Saale, Mulde)
- Total Hg concentrations were determined by a direct Hg analyzer (Nippon MA-3000) using combustion, amalgamation, and atomic absorption spectrometry
- Binding forms of Hg in samples are investigated by pyrolytic thermodesorption [5] recording continuous Hg release curves during heating up to 650°C in a N_2 gas flow.

References:

[1] European Environment Agency (2018) Mercury in Europe's environment. EEA Report No 11/2018

[2] Orem et al. (2019) Aquatic Cycling of Mercury. In: Rumbold et al. *„Mercury and the Everglades"*. Springer

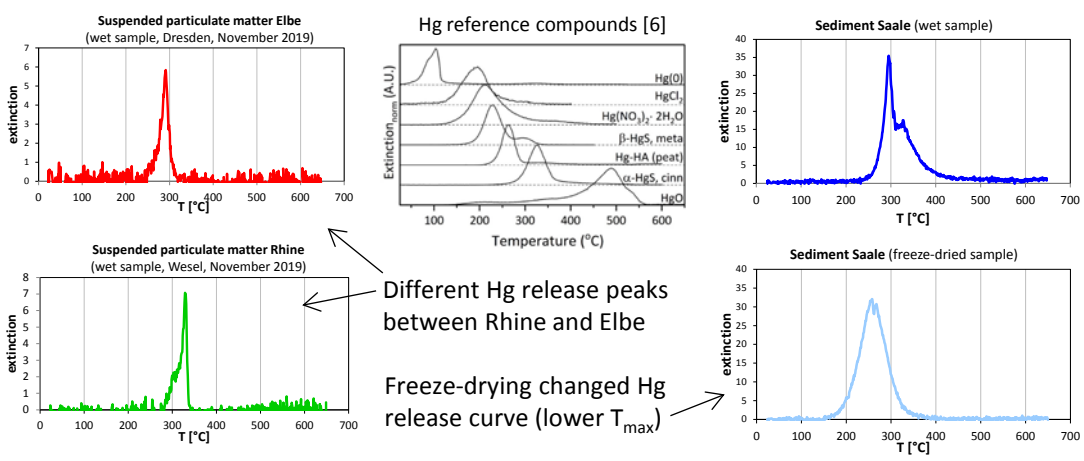
[3] Data sources: http://fgg-rhein.bafg.de, http://fgg-elbe.de, http://undine.bafg.de

[4] Data source: German environmental specimen bank: https://www.umweltprobenbank.de

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

[6] Gilli et al. (2018) Speciation and mobility of mercury in soils contaminated by legacy emissions from a chemical factory in the Rhône valley in canton of Valais, Switzerland. *Soil Systems* 2(3), 44.

Preliminary data from pyrolytic thermodesorption analysis:



Different Hg release peaks between Rhine and Elbe

Freeze-drying changed Hg release curve (lower T_{max})

Summary and Outlook:

- Analysis of historical data reveals strong decreases of Hg concentrations over the last decades in suspended particulate matter and water samples of German rivers.
- Mercury concentrations in river Elbe are still much higher than in river Rhine and partly influenced by Hg inputs from the tributary rivers Saale and Mulde.
- Preliminary results suggest that Hg in suspended particulate matter and sediments is present in different chemical binding forms (organically-bound Hg(II), Hg-sulfides, …), which will presumably influence the release of Hg into water, Hg species transformations (→ methylation), and Hg uptake into organisms (→ Hg in fish).
- Our future work will use a combination of methods for elucidating the dynamics of Hg and its different species to provide new insights into Hg cycling in river systems.