



## Zinc isotopic variation of water and surface sediments from the German Elbe River

T. Zimmermann<sup>a,b</sup>, A.F. Mohamed<sup>c</sup>, A. Reese<sup>a,b</sup>, M.E. Wieser<sup>c</sup>, U. Kleeberg<sup>a</sup>, D. Pröfrock<sup>a,\*</sup>, J. Irrgeher<sup>a,c,1</sup>

<sup>a</sup> Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Marine Bioanalytical Chemistry, Max-Planck Str. 1, 21502 Geesthacht, Germany

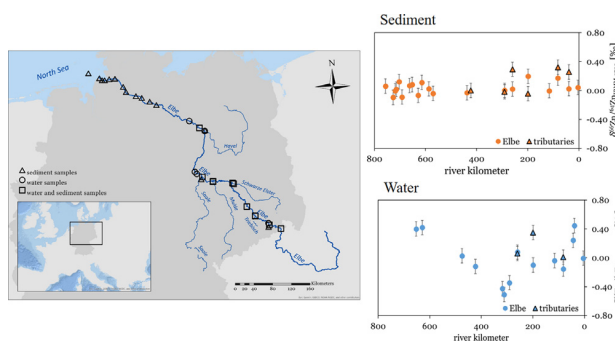
<sup>b</sup> Universität Hamburg, Department of Chemistry, Inorganic and Applied Chemistry, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

<sup>c</sup> University of Calgary, Department of Physics and Astronomy, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

### HIGHLIGHTS

- Zn isotope-amount ratios as a potential tracer for anthropogenic Zn emissions.
- Analysis of water and sediment samples from the Elbe River and its tributaries.
- MC ICP-MS analysis with low blank levels and double spike calibration.
- Enrichment of heavier isotopes in selected anthropogenically impacted tributaries.
- Influence of natural fractionation processes on Zn isotopic composition in water.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 9 August 2019

Received in revised form 24 October 2019

Accepted 24 October 2019

Available online 22 November 2019

Editor: Mae Sexauer Gustin

#### Keywords:

MC ICP-MS

Zn double spike

Isotope tracer

Environment

Isotopic fractionation

Metal pollution

### ABSTRACT

Recent studies suggested the use of the isotopic composition of Zn as a possible tracer for anthropogenic Zn emissions. Nevertheless, studies mainly focused on sampling areas of a few km<sup>2</sup> with well-characterized anthropogenic Zn emissions. In contrast, this study focused on analyzing a large sample set of water and sediment samples taken throughout the course of the Elbe River, a large, anthropogenically impacted river system located in Central Europe. The primary objective was to evaluate the use of the isotopic composition of Zn to trace anthropogenic Zn emission on a large regional scale. In total 18 water and 26 surface sediment samples were investigated, covering the complete course of over 700 km of the German Elbe between the German/Czech border and the German North Sea, including six tributaries. Stable isotope abundance ratios of Zn were assessed by multi-collector inductively coupled plasma mass spectrometry (MC ICP-MS) in water filtrates (<0.45 μm) and total digests of the sieved surface sediment fraction (<63 μm) after analyte/matrix separation using Bio-Rad AG MP-1 resin via a micro-column approach and application of a <sup>64</sup>Zn/<sup>67</sup>Zn double spike. Measured isotopic compositions of  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  ranged from -0.10 ‰ to 0.32 ‰ for sediment samples, and from -0.51 ‰ to 0.45 ‰ for water samples. In comparison to historical data some tributaries still feature high mass fractions of anthropogenic Zn (e.g. Mulde, Triebisch) combined with  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values higher than the lithogenic background. The dissolved  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values showed a potential correlation with pH. Our results indicate that biogeochemical processes like absorption may play a key role in natural Zn isotopic fractionation making it difficult to distinguish between natural and anthropogenic processes.

© 2019 Elsevier B.V. All rights reserved.

\* Corresponding author.

E-mail address: [daniel.proefrock@hzg.de](mailto:daniel.proefrock@hzg.de) (D. Pröfrock).

<sup>1</sup> Present address: Montanuniversität Leoben, Department of General, Analytical and Physical Chemistry, Chair of General and Analytical Chemistry, Franz Josef-Straße 18, 8700 Leoben, Austria.