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

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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

km² 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 19 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 $^{64}Zn/^{67}Zn$ double spike. Measured isotopic compositions of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ ranged from -0.1 ‰ to 0.3 ‰ for sediment samples, and from -0.5 ‰ to 0.4 ‰ for water samples. In comparison to historical data some tributaries still feature high mass fractions of anthropogenic Zn (e.g. Mulde, Triebisch) combined with $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values higher than the lithogenic background. The dissolved $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 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.

Keywords

MC ICP-MS, Zn double spike, isotope tracer, environment, isotopic fractionation, metal pollution

1 Introduction

The analysis of Zn isotope ratios is a rather new field of non-traditional stable isotope analysis. It was not until the early 2000s that significant natural variations in isotopic composition of Zn were reported, even though the first work on Zn isotopic composition based on thermal ionization mass spectrometry (TIMS) dates back to the mid-1950s (Blix et al., 1957). Pioneer work using multi-collector inductively coupled plasma mass spectrometry (MC ICP-MS) was done by Maréchal et al. (1999) who, for the first time, reported significant natural variation in Zn isotopic composition. Further early work covered the analysis of ferromanganese nodules and ocean sediment (Maréchal et al., 2000), deep sea carbonates (Pichat et al., 2003) or higher plants (Weiss et al., 2005).

Since the natural variation of the Zn isotopic composition is rather small (ca. 1 – 2 ‰) (Brand et al., 2014), significant effort had to be put into optimizing MC ICP-MS sample preparation and measurement routines. This included extensive work on instrumental isotopic fractionation corrections, ICP operating conditions or the identification, elimination and control of spectral interferences and blanks (Archer and Vance, 2004; Bermin et al., 2006; Petit et al., 2008). Early studies used an in-house Zn ICP standard purchased from Johnson and Matthey (so called JMC Lyon standard) as 0-anchor (Maréchal et al., 1999). Since this standard is now exhausted, the Commission on Isotopic Abundances and Atomic Weights (CIAAW) suggests the IRMM-3702 (Ponzevera et al., 2006) to be used as new 0-anchor (Brand et al., 2014). A re-evaluation of this material by Moeller et al. (2012) resulted in a $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ value of -0.29 ‰ for the JMC standard. Up to now, the IRMM-3702 is the only standard with published absolute isotope-amount ratios, commercially available and fulfilling all criteria to be used as 0-anchor on an isotope-delta scale as used by CIAAW. The second available isotope standard is the AA-ETH Zn that is so far believed to be isotopically indistinguishable from the IRMM-3702 (Archer et al., 2017).

Zn is a ubiquitous trace metal with an essential role as micronutrient. Furthermore, Zn is widely used in industrial processes for e.g. electroplating, for alloy production and as anti-corrosion coating. With a worldwide production of 11.9 million metric tons (in 2016), Zn is one of the most important metals and therefore a critical source of anthropogenic contamination (Survey, 2017). John et al. (2007b) who investigated the isotopic composition of common forms of anthropogenic Zn, suggested to make use of Zn isotope signatures as potential environmental tracer. Significant isotopic fractionation of Zn metal-based products, which causes the depletion of heavy isotopes in blast furnace emissions ($\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ = -0.36 ‰) (Mattielli et al., 2009) and enrichment in heavy isotopes in effluents ($\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ = 0.41 ‰) (Arnold et al., 2010) and slags ($\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ = 0.18 ‰ to 1.49 ‰) (Sivry et al., 2008) has been described. Other high-temperature processes like coal combustion are also known to induce significant isotopic fractionation leading to the enrichment of heavy Zn isotopes in e.g. fly ash, while flue gases are enriched in lighter Zn isotopes (Gonzalez and Weiss, 2015).

Even though the use of Zn isotopic signatures as a tracer of anthropogenic emissions has been demonstrated and highlighted in various studies, examples on their application to samples from river and coastal environments are still scarce today (Gonzalez et al., 2016; Thapalia et al., 2015). The first studies were published by Petit et al. (2008) who analyzed suspended particulate matter and sediments from the Scheldt estuary, revealing significant differences in isotopic composition of $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ between 0.22 ‰ and 1.13 ‰ for surface sediment samples. Studies by Sivry et al. (2008) and Araújo et al. (2017) focused on relatively small sampling areas (Sivry et al., ca. 10 x 10 km; Araújo et al. ca. 15 x 30 km) with well-known anthropogenic emission by Zn ore treatment plants. In both studies $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ values for sediment samples of up to 1.35 ‰ have been found, which is significantly higher than the corresponding geogenic background. Work by Chen et al. (2008; 2009) are the only studies providing $\delta^{66}Zn/^{64}Zn$ data obtained from a large anthropogenically impacted sampling area, so

far. Their investigation of the Seine River in France showed significant isotopic variations in water samples with $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ ranging from 0.07 ‰ to 0.58 ‰ and a $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ ranging from 0.08 ‰ to 0.30 ‰ for suspended matter, with a distinctly lighter isotopic composition in downstream areas of the Seine. The city of Paris was found to cause a significant input of anthropogenic Zn originating from roadway and roof runoff, resulting in a generally lighter isotopic composition ($\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ = -0.11 ‰ to 0.02 ‰) of the investigated samples.

This study focused on the analysis of the Zn isotopic variation in water and surface sediment samples from one of largest European rivers, the Elbe. With its catchment area of 148 000 km² the Elbe River is the fourth largest river in Central Europe (Bohlich and Strotmann, 2008). For decades, it was considered as one of the most contaminated rivers in Europe. The Elbe and its pollution load have been subject to researchers from several disciplines (Brase et al., 2017; Prange et al., 2001; Prange et al., 1997; Sühring et al., 2015). Since the work of Prange et al. that was conducted in the 1990s, only a limited number of further studies focused on the topic of metal contamination. Only recently, the first work on the use of non-traditional stable isotope ratios as tracers for environmental processes in the study area of the Elbe River was published by Reese et al. (2019). The authors reported stable isotope ratios of Sr, Nd and Pb beside multi-element data of surface sediments from the Elbe estuary. Results clearly proved the potential of "non-traditional" isotope ratio analysis as a valuable tool to describe areas under both, natural and anthropogenic influence. Reese et al. (2019) focused on the interpretation of metal contamination within the context of environmental research related to complex land-river-sea systems.

In this study, we extend the palette of non-traditional stable isotopes used as tracers in the Elbe catchment with stable Zn isotope ratios, in order to further explore the usage of isotopic tools in aquatic ecosystem studies. The main objective of our work was to investigate the variation

123 of natural Zn isotopic composition in water and sediment in a river ecosystem at large scale
124 and evaluate the applicability of Zn isotope ratios as tracer for anthropogenic Zn emissions.
125 Furthermore, this work addressed possible processes that potentially cause natural isotopic
126 fractionation within the river and its catchment.

127 # 2. Experimental

128 ### 2.1 Materials, reagents and reference materials

129 The marine sediment GBW-07313 (National Research Centre for Certified Reference
130 Materials, Beijing, China) and the basalt BCR-2 (U.S. Geological Survey, Reston, USA) were
131 used as reference materials for Zn quantification in sediment digests and the riverine waters
132 SLRS-1 and SLRS-3 (National Research Council of Canada, Ottawa, Canada) were used as
133 reference materials for Zn quantification in water samples. Custom-made multi-elemental
134 standards (Inorganic Ventures, Christiansburg, USA) were used for preparation of external
135 calibrations for quantification via ICP-MS. The isotopic reference material IRMM-3702 (Joint
136 Research Centre, Geel, Belgium) was used for calibration of the double spike.
137 Experimental work was carried out at the Helmholtz-Zentrum Geesthacht and at the University
138 of Calgary. Preparatory laboratory work carried out at the Helmholtz-Zentrum Geesthacht
139 included sieving and digestion of the sediment samples, filtration of the water samples, multi-
140 element quantification measurements and evaporation of the samples to dryness prior to sample
141 preparation for Zn isotopic analysis. The evaporated samples were shipped to the University of
142 Calgary, where column separation and isotopic analysis of Zn were accomplished. Method
143 blanks were processed to monitor the entire procedure including shipping.
144
145 *Helmholtz-Zentrum Geesthacht, Germany*

All sample preparation steps carried out at Department of Marine Bioanalytical Chemistry, Institute of Coastal Research, were performed in a class 10000 clean room inside a class 100 clean bench to minimize blank levels and any risks of contamination. Suprapur® nitric acid (65% *w*/*w*, Merck-Millipore, Darmstadt, Germany) and suprapur® hydrochloric acid (30% *w*/*w*, Merck-Millipore, Darmstadt, Germany) were further purified by double sub-boiling in quartz stills (AHF Analysentechnik, Tübingen, Germany). Tetrafluoroboric acid (38% *w*/*w*) used for sample digestion was purchased from Chem-Lab (Zedelgem, Belgium) and used without any further purification. Ultra-pure water (18.2 MΩ*cm) used for analysis and cleaning was obtained from a Milli-Q ElementQ/QPod Element water purification system (Merck-Millipore, Darmstadt, Germany).

University of Calgary, Canada

All sample preparation steps carried out at the Department of Physics and Astronomy were performed in a class 1000 clean room inside a clean bench to minimize blank levels and any risks of contamination. Aristar® Ultra nitric acid (65% *w*/*w*, VWR International, Radnor, USA) and environmental grad plus hydrochloric acid (32-35% *w*/*w*, VWR International, Radnor, USA) were used. Ultra-pure water used for analysis and cleaning was obtained from a water purification system with a resistivity of 18.2 MΩ*cm. Enriched ^{64}Zn and ^{67}Zn materials used for the preparation of the double spike were purchased in oxide form from Oak Ridge National Laboratory (Oak Ridge, USA). The zinc double spike $n(^{66}Zn)/n(^{67}Zn)$ isotope-amount ratio was ~4.88 in order to achieve the most precise isotope-amount ratios as recommended by Rudge et al. (2009).

2.2 Samples and sample preparation

Surface sediment and water samples from the river Elbe were obtained in the course of a sampling campaign conducted in August and September 2015 between the Elbe estuary

(German Elbe river kilometer 757) and the German Czech border (German Elbe river kilometer 0). The sampling area is shown in Fig. 1. In total 26 sediment and 17 water samples were analyzed in this study.

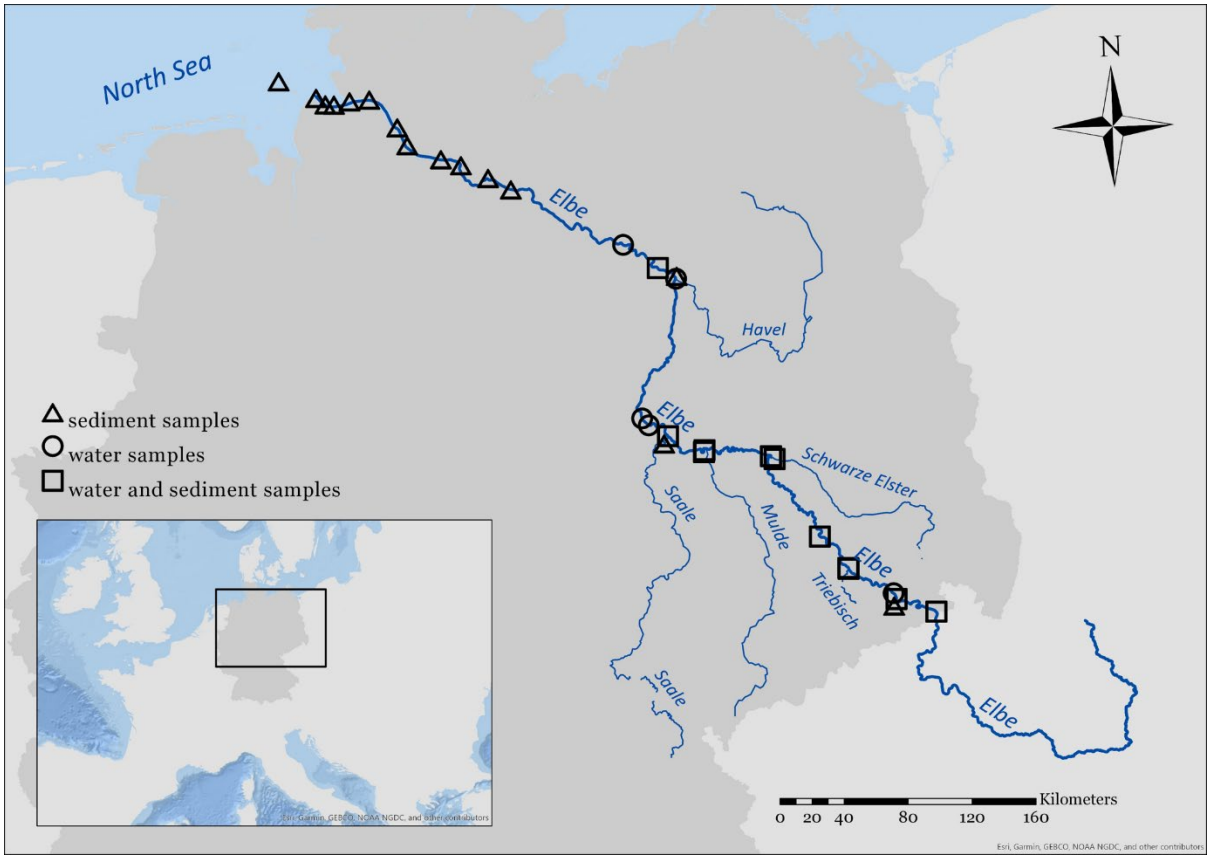

Fig. 1. Map of the Elbe River from the German Czech boarder (river km 0) to the mouth into the North Sea (river km 757). The sampling locations at which sediment samples were taken are marked as triangle, water sampling locations as circle and locations were both, water and sediment samples, were taken are marked as square.

2.2.1 Sampling locations

The part of the Elbe River impacted by the tide starts at river kilometer 757 up to the weir Geesthacht at river kilometer 587. Therefore, within the estuary, the sampling locations S_01 Scharnhörnriff to S_11 Geesthacht were selected. Hamburg is the largest city within the estuary with the third largest port in Europe. Samples upstream of river kilometer 588 up to the

German/Czech boarder at river kilometer 0 were taken between Lauenburg (sample S_12 Lauenburg) and Schmilka (sample S_31 Schmilka). Within this river section, sampling also included locations in the main tributaries, the Havel (S_16 Tb. Havel), the Saale (S_20 Tb. Saale) and the Mulde (S_22 Tb. Mulde), as well as some smaller tributaries, the Schwarze Elster (S_24 Tb. Schwarze Elster), the Triebisch (S_ 27 Tb. Triebisch) and the Müglitz (S_30 Tb. Müglitz). All sampling locations in tributaries are labeled Tb. A detailed description of sampling coordinates including river kilometers can be found in the Supplemental information Table A1.

Sampling locations in this study were selected based on the original locations reported in the 1990s by Prange et al. to allow for direct comparison of data in a time-dependent perspective. However, the impact of tributaries to the Elbe River were considered in the study by Prange et al. by taking samples at the tributary's mouth into the Elbe River only. In this study tributaries were sampled not only at the tributary's mouth but also several kilometers upstream the respective tributary before it discharges into the Elbe River.

2.2.2 Sediment samples

A detailed description of the sediment sample preparation and digestion process, including recoveries of elemental mass fractions of the marine sediment reference material GBW-07313 and the basalt reference material BCR-2 can be found elsewhere (Reese et al., 2019). Both reference materials were quantitatively digested using the presented digestion method resulting in clear, particle free digests. Surface sediment samples were collected by using a custom-made box corer. The top layer (5 to 10 cm) of three or more individual samplings were subsequently homogenized, deep-frozen, freeze dried (Martin Christ Gefriertrocknungsanlagen, Osterode, Germany) and sieved over a cascade of polyamide sieves (Atechnik, Leinburg, Germany) to obtain the <63 µm fraction. About 50 mg of the sieved sediment material was weighed into 55 mL TFM® bombs and 5 mL concentrated double sub-boiled nitric acid, 2 mL concentrated

211 double sub-boiled hydrochloric acid and 1 mL tetrafluoroboric acid were added. The samples
212 were digested for 300 minutes at 180 °C using a MARS 5 Xpress (CEM Corp., Kamp Lintfort,
213 Germany) microwave. Digestion of each sample was carried out in triplicates, quantitatively
214 transferred to 50 mL pre-cleaned DigiTUBEs (SCP Science, Quebec, Canada) and diluted to a
215 final volume of 50 mL with Milli-Q water. Based on the measured Zn mass fraction an amount
216 equivalent to 500 ng Zn was transferred from one of the three digests to a 50 mL pre-cleaned
217 DigiTUBE, evaporated to dryness, sealed and shipped to the University of Calgary. This
218 required the evaporation of up to 15 mL of sample depending on the initial Zn mass fraction.

219 **2.2.3 Water samples**

220 The pH-value of the water samples was measured in an aliquot of the sample before filtration
221 using a portable pH probe (Multi 3430, WTW, Germany). Water samples were filtered in
222 triplicates using a custom built pressure filtration system made of high purity PFA filtration
223 bombs (Savillex, Eden Prairie, USA) and acid washed 0.4 µm polycarbonate filters (Whatman,
224 Maidstone, United Kingdom). The bombs were pressurized with high purity nitrogen or argon.
225 After filtration, the samples were acidified with 500 µL concentrated double sub-boiled nitric
226 acid and stored in 500 mL LDPE Nalgene® bottles (Thermo Fisher Scientific, Schwerte,
227 Germany) at 4 °C. Based on the measured Zn concentration in the individual sample, a sample
228 volume containing an equivalent to 500 ng Zn in total from one sample of each sampling
229 location was transferred to a 50 mL pre-cleaned DigiTUBE, evaporated to dryness and shipped
230 to the University of Calgary. This required the evaporation of up to 150 mL of sample.

231 **2.2.4 Ion extraction of Zn**

232 Prior to ion extraction the evaporated samples were doped with 500 ng of Zn double spike,
233 equilibrated, evaporated again to dryness in a DigiPrep evaporation system under a HEPA-
234 filtered hood (SCP Science, Quebec, Canada) and re-dissolved in 1.5 mL of 1 mol L^{-1}

hydrochloric acid in an ultrasonic bath. Isolation of Zn was accomplished by using the anion exchange resin AG MP-1 (100-200 mesh size, Bio-Rad, Hercules, USA) according to a modified separation scheme published by Moore et al. (2017). Prior to usage, the suspended resin (in 0.5 mol L^{-1} hydrochloric acid) was cleaned with 0.5 mol L^{-1} nitric acid and water. Approximately 250 µL of the resin were packed into leached custom made glass micro columns. After the first ion-extraction cycle, samples with high Ba content were further purified by using Sr Resin (TrisKem International, Bruz, France) in order to remove residual Ba, which could potentially interfere as Ba^{2+} on ^{66}Zn, ^{67}Zn and ^{68}Zn. A detailed description of the ion extraction protocols for both separation cycles can be found in the Supplemental information Table A2.

2.3 Instrumentation and measurement procedures

2.3.1 Elemental analysis

The determination of Zn mass fractions in the sediment digests and Zn concentrations in filtered water samples was performed using an inductively coupled plasma tandem mass spectrometer (ICP-MS/MS) (Agilent 8800, Agilent Technologies, Tokyo, Japan) coupled to an ESI SC-4 DX FAST autosampler (Elemental Scientific, Omaha, Nebraska, USA) at the Helmholtz-Zentrum Geesthacht. For quantification an external calibration, prepared from custom-made multi-elemental standards ranging from 0.1 µg L^{-1} to 100 µg L^{-1} was used. Solutions were prepared on a daily basis. A detailed description of the instrument configuration can be found in the Supplemental information Table A3.

Multi-elemental data were processed using MassHunter version 4.2 and a custom-written Excel® spreadsheet. Recoveries were calculated using the marine reference sediment GBW-07313 and riverine reference waters SLRS-1 and SLRS-3. Combined uncertainties were

calculated using a simplified Kragten (1994) approach taking into account reproducibility, repeatability and measurement precision for amount fractions in sediment samples and reproducibility and measurement precision for concentrations in water samples. Samples were analyzed as triplicates, using three individual digests/filtrates. Recoveries for the used reference materials GBW-07313, SLRS-1 and SLRS-3 are shown in the Supplemental information Table A4.

2.3.2 Isotopic analysis

Zn isotope-amount ratios were measured at the University of Calgary using a Neptune MC ICP-MS (Thermo Fisher Scientific, Bremen, Germany) operated in low mass resolution mode. A 20-mL cyclonic spray chamber (Glass Expansion, Pocasset, USA) fitted with a glass nebulizer (sample uptake of 100 µL min^{-1}) was used as sample introduction system. A detailed description of the instrument configuration can be found in the Supplemental information Table A3.

Faraday cups H2, C, L1, L2, L4 were used to measure the ion beams of ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn. Sample measurements consisted of one block with 30 measurements. In order to correct for potential Ni interferences occurring on ^{64}Zn, one measurement of 8 s integration time prior to the measurement of Zn was used. During this 8 s measurement, ^{60}Ni was monitored on faraday cup C, ^{62}Ni on L2 and ^{64}Zn on L4, respectively. Due to adjusted zoom optic voltages, no magnet jump was needed.

Typical sensitivities were around 8 V for 1 µg mL^{-1} ^{64}Zn with blank values of 2 mV. Instrumental isotopic fractionation correction was achieved with a ^{64}Zn+^{67}Zn double spike, which was calibrated against the certified material IRMM-3702. Sample and standards were

283 doped with equal amounts of double spike (1:1 ratio) leading to a final Zn concentration of 500
284 ng mL^{-1} for each sample.
285 Zn isotopic compositions are reported as $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ expressed as parts per thousand
286 (‰) relative to the Zn IRMM standard IRMM-3702 calculated by Eq. 1.
287
288 $$\delta^{66}Zn/^{64}Zn_{IRMM-3702} = \left(\frac{^{66}Zn/^{64}Zn_{Sample}}{^{66}Zn/^{64}Zn_{IRMM-3702}} - 1\right) \qquad (1)$$
289
290 We refer to $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ throughout the manuscript. A conversion to $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$
291 is available in the Supplemental Information.
292 Data processing of the raw ratios was done offline using a data reduction program written by
293 Alex Tennant (University of Calgary) in Python™. The program employs root finding
294 algorithms to solve the double spike equations as described by Rudge et al. (2009). The code
295 includes blank correction and correction for instrumental isotopic fractionation based on the
296 $^{64}Zn/^{67}Zn$ isotope-amount ratio of the double spike. The double spike was calibrated against
297 IRMM-3702 via internal isotopic fractionation correction using a $^{66}Zn/^{68}Zn$ ratio for IRMM-
298 3702 of 0.66525 (Moeller et al., 2012). The spectral interference of ^{64}Ni on mass ^{64}Zn was
299 found to be negligible and was therefore not corrected. For quality control, IRMM-3702 spiked
300 with the double spike as well as IRMM-3702 following ion extraction were run routinely,
301 multiple times every day. For isotope data combined uncertainties were calculated taking into
302 account measurement precision and reproducibility of the used IRMM-3702 standard. (Note:
303 The 0-anchor material is not assigned with an uncertainty per definition.)

3 Results

3.1 Validation and performance characteristics of the analytical method

The suitability of the modified sample preparation protocol for water and sediment samples was evaluated with respect to different analytical parameters. Recoveries for the IRMM-3702 reference material after ion extraction yielded values of 108% ± 7% (*n*=4), indicating a quantitative recovery of Zn. Furthermore, measured recoveries of the separated water and sediment samples ranged from 88% to 113% (with a mean of 98% ± 6%, *n*=44) based on the measured standard to double spike ratio. Procedural Zn blanks for the ion extraction protocol were 1.0 ng ± 0.2 ng (*n*=6), which was negligible for a total sample amount of 500 ng Zn. Measurements of the IRMM-3702 reference material yielded an external between-run precision of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ = -0.02 ‰ ± 0.10 ‰ (*U*(*k*=1), *n*=22) for a total of 5 measurement days.

3.2 Concentration measurements and isotopic data

All sampling locations, including measured Zn concentrations/mass fractions and Zn isotopic compositions ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$) can be found in the Supplemental information Table A1. Note: Historical samples by Prange et al. had been taken at the same sampling coordinates. Zn mass fractions for historical sediment samples were measured in <20 µm grain size fractions, water samples were filtered via 0.45 µm filters, respectively.

3.3.1 Zn mass fractions and $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ in sediment samples

Zn mass fractions for sediment samples ranged from 42 mg kg^{-1} to 1120 mg kg^{-1} along the course of the Elbe (see Table A1 and Fig. 2A). The average mass fraction of all sediment samples analyzed in this study was 417 mg kg^{-1} ± 294 mg kg^{-1} (1 SD, *n*=26). The lowest measured mass fraction of around 42 mg kg^{-1} was found in the estuary (S_01 Scharhörnriff, km

757). Elevated mass fractions of 879 mg kg^{-1} and 826 mg kg^{-1} were measured for two sampling locations upstream the city of Hamburg (S_10 Billwerder Inseln, km 615 and S_11 Geesthacht, km 587). Mass fractions upstream the weir in Geesthacht were highly variable ranging from 135 mg kg^{-1} for the Havel River (S_16 Tb. Havel, km 423) to 1120 mg kg^{-1} measured in the Elbe River near the mouth of the tributary Triebisch (S_26 Triebisch, km 82). Elevated Zn mass fractions could also be found in two major tributaries of the Elbe River, the Saale (750 mg kg^{-1}, S_20 Tb. Saale, km 291) and the Mulde (593 mg kg^{-1}, S_22 Tb. Mulde, km 260).

Zn isotopic compositions expressed as $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ of sediment samples ranged from -0.10 ‰ to 0.32 ‰. Taking into account the analytical uncertainty of 0.10 ‰ ($U(k=1)$) most of the samples where not significantly different from each other. In addition, three sampling locations with significantly heavier isotopic compositions could be identified. All of them are assigned to tributaries of the Elbe River, namely the Mulde ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.29 ‰ ± 0.10 ‰, S_22 Tb. Mulde, km 260), the Triebisch ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.32 ‰ ± 0.10 ‰, S_27 Tb. Triebisch, km 82) and the Müglitz ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.26 ‰ ± 0.10 ‰, S_30 Tb. Müglitz, km 39).

3.3.2 Zn concentrations and $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ in water samples

Dissolved Zn concentrations for water samples ranged from 3.2 µg L^{-1} to 1680 µg L^{-1}. The average concentration of all water samples of this study (except sample S_27 Tb. Triebisch) was 12.6 µg L^{-1} ± 14.4 µg L^{-1} (1 SD, n=16). Most measured Zn concentrations were found to be lower than 10 µg L^{-1} with only a few exceptions (see Table A1 and Fig. 2B). Concentrations higher than 10 µg L^{-1} were observed for the two sampling locations S_17 Magdeburg at km 318 (17.3 µg L^{-1}) and S_18 Schönebeck at km 311 (35.8 µg L^{-1}) within the Elbe. Significantly elevated concentrations were also found for sampling locations deducted to tributaries, namely the mouth of the Saale (16.4 µg L^{-1}, S_19 Saale, km 291), the tributary Mulde (14.4 µg L^{-1}, S_22 Tb. Mulde, km 260) and the mouth of the tributary Triebisch (58.7 µg L^{-1}, S_26 Triebisch,

km 82). An extremely elevated concentration of dissolved Zn of 1680 µg L^{-1} was observed for the tributary Triebisch (S_27 Tb. Triebisch, km 82).

The Zn isotopic composition of water samples showed higher relative variability compared to the sediment samples with $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ ranging from -0.51 ‰ to 0.45 ‰. For samples taken in the estuary (S_08 Tonne 107, km 653 and S_09 Seemannshöft, km 629) generally higher $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values than those for the riverine samples upstream were observed ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.40 ‰ ± 0.10 ‰, $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.43 ‰ ± 0.10 ‰). A comparable high $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ value was also observed for the tributary Schwarze Elster ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.35 ‰ ± 0.10 ‰, S_24 Tb. Schwarze Elster, km 199). Additionally, a $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ value of 0.45 ‰ ± 0.10 ‰ was observed in the Elbe River near the mouth of the tributary Müglitz (S_29 Müglitz, km 39). In contrast to this, significantly lower $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values of -0.43 ‰ ± 0.10 ‰, -0.51 ‰ ± 0.10 ‰ and -0.34 ‰ ± 0.10 ‰ were observed for the three sampling locations S_17 Magdeburg, S_18 Schönebeck and S_19 Saale (km 291-318), respectively.

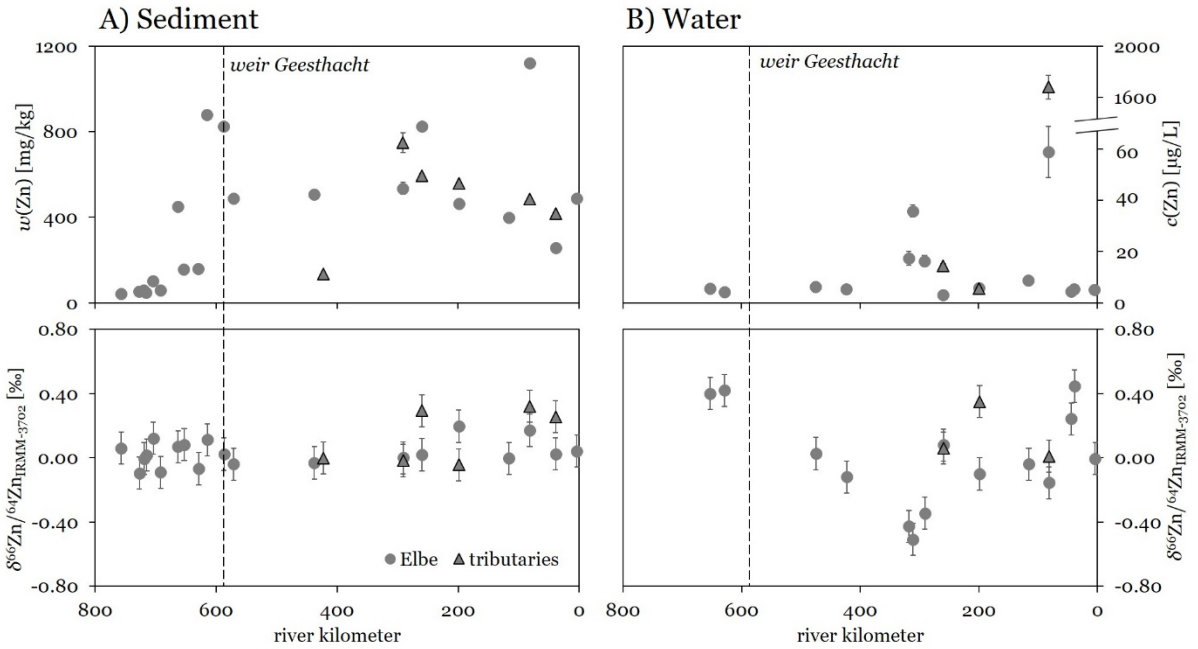

Fig. 2. A) Zn mass fractions and $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values for collected sediment samples in the course of the Elbe River and its tributaries. B) Zn concentrations and $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$

values for collected water samples in the course of the Elbe River and its tributaries. Sampling locations are sorted according to the German Elbe river kilometer. (Error bars correspond to U ($k = 1$) for isotopic data and to U ($k = 2$) for mass fractions and concentrations, respectively (if not visible U = smaller than spotsize)

4 Discussion

4.1 Comparison with historical data published by Prange et al.

When comparing Zn mass fractions in sediment samples from this study to historical data, it has to be noted that Zn mass fractions were measured in different grain size fractions (this study <63 µm, Prange et al. <20 µm). Since heavy metal mass fractions in different grain size fractions can significantly vary, a direct comparison to historical sediment data is challenging (Ackermann et al., 1983). Nevertheless, the historical data can give valuable information about the origin of concentration hotspots within the Elbe River. In contrast to that, concentration data of dissolved Zn in the water phase is directly comparable between both datasets.

4.1.1 Comparison of Zn mass fractions in sediment samples to historical data

Prange et al. published median Zn mass fractions in Elbe sediments for all analyzed samples from the confluence of Mulde and Elbe to the estuary (river kilometer 650 – 260) of 2530 mg kg^{-1} (1992) and 1820 mg kg^{-1} (1995). Historical Zn mass fractions of sampling locations S_19 Saale (3026 mg kg^{-1} (1992), 2452 mg kg^{-1} (1995)), S_21 Mulde (3379 mg kg^{-1} (1992), 4887 mg kg^{-1} (1995)) and S_26 Triebisch (23800 mg kg^{-1} (1992), 8442 mg kg^{-1} (1995)), indicate that the corresponding tributaries carried high loads of Zn at the time. Additionally, published Zn median mass fractions decreased during the study period from 2530 mg kg^{-1} in 1992 to 1420 mg kg^{-1} in 1998, indicating a decrease of Zn emissions into the Elbe River.

The average Zn mass fractions in sediment samples of this study was 417 mg kg^{-1}, which is significantly lower than historical data. In comparison with recent data from other European river systems e.g. the Danube average Zn mass fractions were significantly lower than in the Elbe River (187 mg kg^{-1} ± 25 mg kg^{-1} in <63 µm grain size fraction) (Woitke et al., 2003). Estimated geogenic background concentrations for the Elbe River range between 50 mg kg^{-1} and 200 mg kg^{-1} (only available for <20 µm fraction) (LAWA, 1998). (For some sampling locations, such as S_21 Mulde at km 260 (824 mg kg^{-1} (this study)) and S_26 Triebisch at km 82 (1120 mg kg^{-1} (this study)) Zn mass fractions in the sediment samples are still higher than the average load of the Elbe River. This might still make these tributaries potential sources of anthropogenic Zn emissions into the Elbe River e.g. originating from old mining activities.

4.1.2 Comparison of Zn concentrations in water samples to historical data

The average discharge volume of the Elbe River increases from 315 $m^3 s^{-1}$ at the German/Czech boarder to 877 $m^3 s^{-1}$ at the mouth of the estuary. The most important tributaries are the Havel 115 $m^3 s^{-1}$, the Saale 115 $m^3 s^{-1}$, the Mulde 73 $m^3 s^{-1}$ and the Schwarze Elster 28 $m^3 s^{-1}$ (ATV-DVWK, 2000). During August/September 2015 the average discharge of the Elbe River was approximately 240 $m^3 s^{-1}$ that is considered as a dry period with low water discharge (IKSE, 2017). For water samples taken in September 1995 and 1998 by Prange et al. the discharge volumes were approximately 990 $m^3 s^{-1}$ and 320 $m^3 s^{-1}$, respectively. Historical median concentrations of the dissolved Zn fraction in Elbe water samples between river kilometer 650 and 260 varied between 16.5 µg L^{-1} (1992) and 3.0 µg L^{-1} (1995) respectively. An estimated geogenic background of dissolved Zn in unpolluted German Rivers lies in the range of 1 µg L^{-1} (LAWA, 1998).

Historical data showed significantly higher Zn concentrations for some sampling locations at the confluence of tributaries. This included samples taken at the locations S_19 Saale (50.5 µg L^{-1} (1995), 55.8 µg L^{-1} (1998)), S_21 Mulde (109.9 µg L^{-1} (1995), 3.95 µg L^{-1} (1998)), S_23

Schwarze Elster (47.5 µg L^{-1} (1995), 5.37 µg L^{-1} (1998)), S_26 Triebisch (1490 µg L^{-1} (1995), 1780 µg L^{-1} (1998)) and S_29 Müglitz (32.1 µg L^{-1} (1995), 15.8 µg L^{-1} (1998)). For some of these sampling locations, a decrease of Zn concentrations could be observed over time (S_21 Mulde, S_23 Schwarze Elster), whereas at some sampling locations the measured Zn concentrations remained constant (S_19 Saale, S_26 Triebisch). Our data indicated that even today some tributaries carry significantly higher dissolved Zn amounts than the Elbe River itself, namely the Mulde (14.4 µg L^{-1}, S_22 Tb. Mulde, km 260) and the Triebisch (1680.0 µg L^{-1}, S_27 Tb. Triebisch, km 82) making tributaries a potential source of anthropogenic Zn contamination. Especially, the tributary Triebisch that still contains high amounts of dissolved Zn.

In summary, Zn concentrations in sediment and water clearly decreased during the last three decades indicating a substantial decrease of anthropogenic Zn emissions into the Elbe River, an observation also described by other authors (Vink et al., 1999). Nevertheless, some sampling locations are still characterized by elevated Zn concentrations.

4.2 Zn isotopic signatures of sediment samples

A detailed description of the underlying geology is shown in Fig. 3. Most of the catchment area is characterized by glacial deposits. Nevertheless, the surface geology significantly changes upstream and tributaries originating in the Ore Mountains (e.g. Mulde, Triebisch und Müglitz) feature a significant change in surface geology of their catchments. The catchment area of these tributaries is mainly characterized by metamorphic and igneous bedrock (Rohstoffe, 2006).

Our study revealed no significant changes in isotopic composition of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ for sediment samples taken in the Elbe River with a mean of 0.05 ‰ ± 0.11 ‰. In fact, measured $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ are in accordance to the terrestrial background of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ -0.01 ‰ ± 0.05 ‰ (corresponding to$\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ of 0.28 ‰ ± 0.05 ‰) as published by Chen

et al. (2013). Regarding the Elbe River estuary, a thorough mixing of sediment of marine and fluvial origin can be observed. This is reflected in the measured mass fractions of Zn, as well. Sediment samples S_10 and S_11 with high amounts of Zn (879 mg kg^{-1} and 826 mg kg^{-1} Zn) are rapidly diluted with marine sediment with significantly lower Zn mass fractions. This phenomenon was studied in detail by Reese et al. (2019) using isotope-amount ratio analysis of $n(^{87}Sr)/n(^{86}Sr)$, $n(^{143}Nd)/n(^{144}Nd)$ and multi-elemental mass fraction data. As no significant change in isotopic composition of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ could be observed for samples taken in the Elbe River estuary, it can be assumed that the isotopic composition of Zn, is similar for fluvial as well as for marine sediments in the investigated catchment area.

Three tributaries of the Elbe River, the Mulde ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.29 ‰ ± 0.10 ‰, S_22 Tb. Mulde, km 260), the Triebisch ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.32 ‰ ± 0.10 ‰, S_27 Tb. Triebisch, km 82) and the Müglitz ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.26 ‰ ± 0.10 ‰, S_30 Tb. Müglitz, km 39) are the only samples with significantly heavier isotopic composition. As shown in Fig. 4A, no direct linear correlation of the Zn isotopic composition and Zn mass fraction of sediment samples could be observed.

Other studies reported heavier isotopic composition of sediment samples caused by anthropogenic Zn emissions e.g. by Zn ore treatment plants (Araújo et al., 2017; Sivry et al., 2008, Skierszkan et al., 2016). This is mainly due to the significantly heavier isotopic composition of industrial tailings from Zn production relative to Zn ores, caused by the production processes. In fact, the three tributaries rise in the nearby Ore Mountains, a region in which mining activities started as early as in the Middle Ages. Especially during the 20th century, the catchment of the Freiberger Mulde (as part of the Mulde River), was characterized by Zn ore mining and processing of the ore leading to high, anthropogenic Zn amounts in water and sediment of the Mulde River (Voland B.).

Another explanation may also lie in changes of bedrock geology (see Fig. 3) that may lead to the heavier isotopic composition, as it is known for Zn bearing minerals featuring great variability in Zn isotopic composition with reported $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values of up to 1.10 ‰ (corresponding to $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ value of 1.39 ‰) (Mondillo et al., 2018).

Overall our data indicates anthrophonic Zn sources to contribute to the total Zn load in the tributaries.

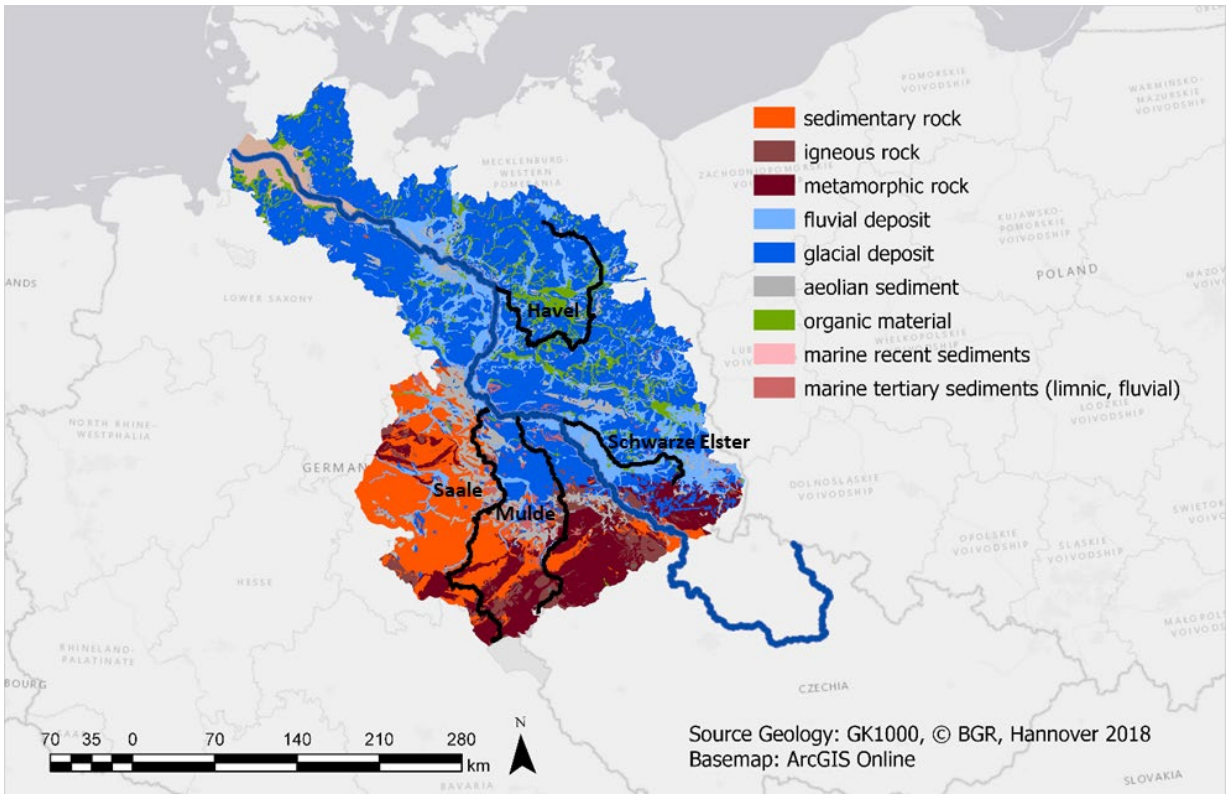

Fig. 3. Surface geology of the Elbe River catchment within Germany (Rohstoffe, 2006)

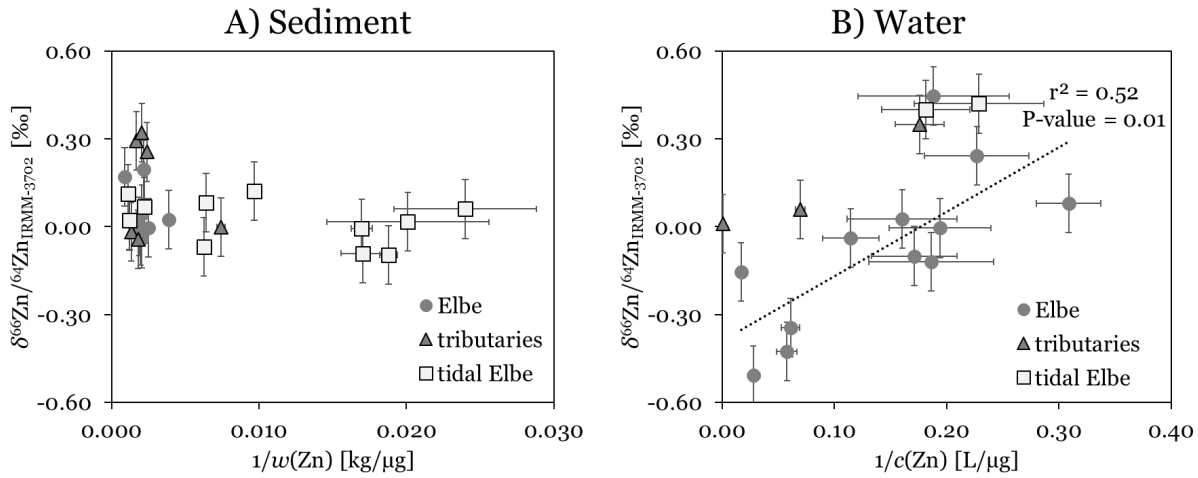

Fig. 4. A) $\delta^{66/64}Zn_{IRMM\text{-}3702}$ of sediment samples compared to inverse Zn mass fractions B) $\delta^{66/64}Zn_{IRMM\text{-}3702}$ of water samples compared to inverse dissolved Zn concentrations. The given trend line does not include values from tributaries and the tidal Elbe. Error bars correspond to U (k = 1) for isotopic data and to U (k = 2) for mass fractions and concentrations, respectively (if not visible U = smaller than spotsize)

4.3 Isotopic signatures of water samples

Measured $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ of Elbe water samples had an average value of 0.02 ‰ ± 0.28 ‰ that is in accordance to the terrestrial background of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ 0.0 ‰ ± 0.05 ‰ (Chen et al., 2013). Although selected samples feature significantly higher, but also lower $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values than the terrestrial background. In fact, a positive correlation between the Zn isotopic composition and the dissolved Zn concentration in the water phase might be possible, as shown in Fig. 4B. In case of the Elbe River generally lower concentrations of dissolved Zn are paired with heavier $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values. An observation which has been described by Little et al. (2014) in a compilation of different water samples from various river systems.

Similar correlations were also observed for the isotopic systems of Cu and Mo (Vance et al., 2008, Archer and Vance, 2008), where isotopic fractionation processes are mainly caused by natural redox processes. Unlike Cu or Mo, Zn has only one oxidation state, neglecting fractionation processes related to redox reactions. Furthermore, lighter as well as heavier isotopic compositions of dissolved $\delta^{66}Zn/^{64}Zn$ than the lithogenic value have been reported in

502 literature (Little et al., 2014), therefore more complex biogeochemical fractionation processes
503 have to be taken into account.
504 A major source of Zn emissions into the environment are effluence of industrial tailings, which
505 potentially change the Zn isotopic composition of water and can therefore be used as a potential
506 tracer for anthropogenic Zn emissions. This raises the question of possible fractionation
507 processes between bedrock and water phase during weathering. In case of the oxidative
508 dissolution of sphalerite at laboratory conditions an initial increase in $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ of 0.2
509 ‰ in the dissolved fraction has been described. However, the observation of significant
510 isotopic fractionation vanished after dissolution of more than 1% of the mineral (Fernandez
511 and Borrok, 2009). Furthermore, analysis of dissolved $\delta^{66}Zn/^{64}Zn$ in waste rock drainage
512 waters varied little, with a $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ of 0.06 ‰ ± 0.08 ‰. This value is in accordance
513 to the natural isotopic composition of bedrock (Matthies et al., 2014). Therefore, it seems
514 possible that natural fractionation between bedrock or mine tailings and dissolved Zn is
515 insignificant once a system reached steady state. Taken into account the significantly heavier
516 isotopic composition of some mine tailings ($\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ of up to 1.49 ‰, corresponding
517 to $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ of 1.20 ‰ (Sivry et al., 2008)) the isotopic composition of dissolved Zn
518 may be influenced by mine tailing effluent water.

519 **4.4 Potential influence of pH and SPM on isotope signatures of dissolved Zn**

520 A pronounced natural fractionation process leading to an isotopic composition enriched in
521 lighter dissolved Zn isotopes is described to be the sorption of preferably heavier isotopes to
522 suspended matter. A process that has been studied e.g. for the sorption of Zn to the surface of
523 iron oxides with a $(\Delta^{66}Zn/^{64}Zn)_{sorbed-aqueous}$ of up to 0.53 ‰ (Juillot et al., 2008) and for the
524 sorption on the surface of kaolinite $(\Delta^{66}Zn/^{64}Zn)_{absorped\text{-}solution}$ of up to 0.49 ‰ (Guinoiseau et
525 al., 2016). These sorption processes are described to be dependent on pH and ionic strength,
526 with potential larger fractionation at higher pH and higher ionic strength (Guinoiseau et al.,

2016, Bryan et al., 2015). Dissolved Zn may also be fractionated by the preferable sorption of heavy isotopes ($(\Delta^{66}Zn/^{64}Zn)_{sorbed-aqueous}$ of up to 0.24 ‰) to humic acid, an analogue of organic matter (Jouvin et al., 2009).

Our data indicate potential fractionation processes of dissolved Zn dependent on the pH-value. As shown in Fig. 5, an increasing pH-value potentially leads to a lighter isotopic signature of dissolved Zn, thus heavier isotopes might be preferably removed from the water phase. Szynkiewicz and Borrock (2016) previously described this process for water samples taken in the Rio Grande watershed, with a maximum of isotopic fractionation happening at pH-values between 8.0 and 8.5. This indicates that the pH-value plays an important role on natural fractionation of dissolved Zn not only for less anthropogenically impacted rivers like the Rio Grande, but also for anthropogenically impacted rivers like the Elbe.

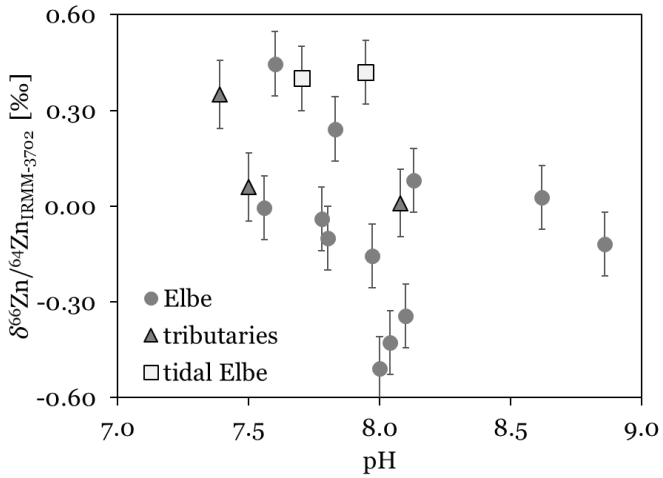

Fig. 5. $\delta^{66}Zn/^{64}Zn_{IRMM-3702}$ of water samples plotted versus the pH-value. Error bars correspond to U (k = 1) for isotopic data.

Nevertheless, natural processes might also lead to an enrichment of heavy Zn isotopes in the water phase. The preferable uptake of light Zn by organisms might represent another key factor of possible natural fractionation processes leading to a heavier isotopic composition of the water phase. This process is also thought to play an important role in the oceanographic mass balance of Zn, as dissolved Zn in the oceans is isotopically heavier ($\delta^{66}Zn/^{64}Zn_{IRMM-3702}$ of 0.21

548 ‰ corresponding to $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ of 0.50 ‰,) than the riverine input of Zn (Little et al.,
549 2014). Experimental work on the uptake of Zn by marine diatom cells showed a preferable
550 uptake of light Zn by the cells, with a $\Delta^{66}Zn/^{64}Zn_{cell-aqueous}$ of up to -0.8 ‰ (John et al., 2007a).
551 Analysis of lake settling particles proved a significant isotope fractionation of $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ -0.95 ‰ ± 0.08 ‰ (corresponding to $\delta^{66}Zn/^{64}Zn_{JMC\text{-}Lyon}$ -0.66 ‰ ± 0.08 ‰), caused by the
553 preferable uptake of lighter Zn isotopes by algae associated to the suspended particular matter
554 (SPM). The largest isotope fractionation was found during summer period with highest algae
555 production (Peel et al., 2009), a process likely to happen also for samples in this study, as
556 sampling was done during the high summer period. It should be mentioned that the degree of
557 possible isotopic fractionation for dissolved Zn in the water phase depends on the amount of
558 Zn taken up by algae. If this is insignificant in comparison to the amount of dissolved Zn in the
559 water phase, no changes in the isotopic composition of dissolved Zn will be observed.
560

561 ## 5. Summary and conclusion

562 Stable Zn isotope abundance ratios and Zn concentrations/mass fractions were assessed in 19
563 water and 26 surface sediment samples from the German Elbe between the German/Czech
564 border and the German North Sea, including the main tributaries the Havel, the Saale and the
565 Mulde. Measured $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values of the sediment samples are in good accordance
566 to the terrestrial background ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ of 0.0 ‰ ± 0.05 ‰), except for the tributaries
567 Mulde, Triebisch and Müglitz, which feature significantly heavier isotopic compositions.
568 Potential sources are discussed to be either of anthropogenic origin or caused by changes in
569 bedrock geology. $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values of the water samples showed larger variability
570 ($\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ ranging from -0.51 ‰ to 0.45 ‰) and a potential linear correlation with
571 dissolved Zn concentrations. Generally lower concentrations of dissolved Zn are paired with
572 heavier $\delta^{66}Zn/^{64}Zn_{IRMM\text{-}3702}$ values and vice versa, indicating complex fractionation processes

of dissolved Zn even for an anthropogenically impacted river like the Elbe. Furthermore, the pH-value may play another important role for natural fractionation processes. Our results indicate that even though Zn isotope abundance ratio analysis has been successfully applied in order to trace anthropogenic Zn emissions, natural fractionation processes play an important role in the biogeochemistry of Zn, making it challenging to distinctly trace anthropogenic Zn emissions in large river systems. Until today, only few publications have reported Zn isotopic composition in river systems at a large regional scale. Therefore, our work will help to better understand biogeochemical fractionation processes, as well as possible anthropogenic influences on the isotopic composition of Zn in such systems. However, this study does not provide any data regarding the seasonal changes of natural fractionation processes, especially for dissolved Zn. Future studies should also include the analysis of SPM, as SPM reflects an important link between the sediment and the dissolved Zn of the water phase. This study also demonstrates once more that profound knowledge of the biogeochemical fractionation processes are a prerequisite for correct data interpretation, processes that are not fully understood yet.

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Competing interests declaration

The authors have no competing interests to declare.

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