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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

25 km<sup>2</sup> with well-characterized anthropogenic Zn emissions. In contrast, this study focused on  
26 analyzing a large sample set of water and sediment samples taken throughout the course of the  
27 Elbe River, a large, anthropogenically impacted river system located in Central Europe. The  
28 primary objective was to evaluate the use of the isotopic composition of Zn to trace  
29 anthropogenic Zn emission on a large regional scale. In total 19 water and 26 surface sediment  
30 samples were investigated, covering the complete course of over 700 km of the German Elbe  
31 between the German/Czech border and the German North Sea, including six tributaries. Stable  
32 isotope abundance ratios of Zn were assessed by multi-collector inductively coupled plasma  
33 mass spectrometry (MC ICP-MS) in water filtrates (<0.45 μm) and total digests of the sieved  
34 surface sediment fraction (<63 μm) after analyte/matrix separation using Bio-Rad AG MP-1  
35 resin via a micro-column approach and application of a <sup>64</sup>Zn/<sup>67</sup>Zn double spike. Measured  
36 isotopic compositions of  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  ranged from -0.1 ‰ to 0.3 ‰ for sediment  
37 samples, and from -0.5 ‰ to 0.4 ‰ for water samples. In comparison to historical data some  
38 tributaries still feature high mass fractions of anthropogenic Zn (e.g. Mulde, Triebisch)  
39 combined with  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values higher than the lithogenic background. The  
40 dissolved  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values showed a potential correlation with pH. Our results  
41 indicate that biogeochemical processes like absorption may play a key role in natural Zn  
42 isotopic fractionation making it difficult to distinguish between natural and anthropogenic  
43 processes.

44

## 45 **Keywords**

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

## 48 **1 Introduction**

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

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

73 Zn is a ubiquitous trace metal with an essential role as micronutrient. Furthermore, Zn is widely  
74 used in industrial processes for e.g. electroplating, for alloy production and as anti-corrosion  
75 coating. With a worldwide production of 11.9 million metric tons (in 2016), Zn is one of the  
76 most important metals and therefore a critical source of anthropogenic contamination (Survey,  
77 2017). John et al. (2007b) who investigated the isotopic composition of common forms of  
78 anthropogenic Zn, suggested to make use of Zn isotope signatures as potential environmental  
79 tracer. Significant isotopic fractionation of Zn metal-based products, which causes the  
80 depletion of heavy isotopes in blast furnace emissions ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}} = -0.36 \text{ ‰}$ ) (Mattielli  
81 et al., 2009) and enrichment in heavy isotopes in effluents ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}} = 0.41 \text{ ‰}$ )  
82 (Arnold et al., 2010) and slags ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}} = 0.18 \text{ ‰}$  to  $1.49 \text{ ‰}$ ) (Sivry et al., 2008) has  
83 been described. Other high-temperature processes like coal combustion are also known to  
84 induce significant isotopic fractionation leading to the enrichment of heavy Zn isotopes in e.g.  
85 fly ash, while flue gases are enriched in lighter Zn isotopes (Gonzalez and Weiss, 2015).  
86 Even though the use of Zn isotopic signatures as a tracer of anthropogenic emissions has been  
87 demonstrated and highlighted in various studies, examples on their application to samples from  
88 river and coastal environments are still scarce today (Gonzalez et al., 2016; Thapalia et al.,  
89 2015). The first studies were published by Petit et al. (2008) who analyzed suspended  
90 particulate matter and sediments from the Scheldt estuary, revealing significant differences in  
91 isotopic composition of  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$  between  $0.22 \text{ ‰}$  and  $1.13 \text{ ‰}$  for surface sediment  
92 samples. Studies by Sivry et al. (2008) and Araújo et al. (2017) focused on relatively small  
93 sampling areas (Sivry et al., ca.  $10 \times 10 \text{ km}$ ; Araújo et al. ca.  $15 \times 30 \text{ km}$ ) with well-known  
94 anthropogenic emission by Zn ore treatment plants. In both studies  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$  values  
95 for sediment samples of up to  $1.35 \text{ ‰}$  have been found, which is significantly higher than the  
96 corresponding geogenic background. Work by Chen et al. (2008; 2009) are the only studies  
97 providing  $\delta^{66}\text{Zn}/^{64}\text{Zn}$  data obtained from a large anthropogenically impacted sampling area, so

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

105 This study focused on the analysis of the Zn isotopic variation in water and surface sediment  
106 samples from one of largest European rivers, the Elbe. With its catchment area of 148 000 km<sup>2</sup>  
107 the Elbe River is the fourth largest river in Central Europe (Bohlich and Strotmann, 2008). For  
108 decades, it was considered as one of the most contaminated rivers in Europe. The Elbe and its  
109 pollution load have been subject to researchers from several disciplines (Brase et al., 2017;  
110 Prange et al., 2001; Prange et al., 1997; Sühling et al., 2015). Since the work of Prange et al.  
111 that was conducted in the 1990s, only a limited number of further studies focused on the topic  
112 of metal contamination. Only recently, the first work on the use of non-traditional stable isotope  
113 ratios as tracers for environmental processes in the study area of the Elbe River was published  
114 by Reese et al. (2019). The authors reported stable isotope ratios of Sr, Nd and Pb beside multi-  
115 element data of surface sediments from the Elbe estuary. Results clearly proved the potential  
116 of “non-traditional” isotope ratio analysis as a valuable tool to describe areas under both,  
117 natural and anthropogenic influence. Reese et al. (2019) focused on the interpretation of metal  
118 contamination within the context of environmental research related to complex land-river-sea  
119 systems.

120 In this study, we extend the palette of non-traditional stable isotopes used as tracers in the Elbe  
121 catchment with stable Zn isotope ratios, in order to further explore the usage of isotopic tools  
122 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*

146 All sample preparation steps carried out at Department of Marine Bioanalytical Chemistry,  
147 Institute of Coastal Research, were performed in a class 10000 clean room inside a class 100  
148 clean bench to minimize blank levels and any risks of contamination. Suprapur<sup>®</sup> nitric acid  
149 (65% w/w, Merck-Millipore, Darmstadt, Germany) and suprapur<sup>®</sup> hydrochloric acid (30% w/w,  
150 Merck-Millipore, Darmstadt, Germany) were further purified by double sub-boiling in quartz  
151 stills (AHF Analysentechnik, Tübingen, Germany). Tetrafluoroboric acid (38% w/w) used for  
152 sample digestion was purchased from Chem-Lab (Zedelgem, Belgium) and used without any  
153 further purification. Ultra-pure water (18.2 MΩ\*cm) used for analysis and cleaning was  
154 obtained from a Milli-Q ElementQ/QPod Element water purification system (Merck-Millipore,  
155 Darmstadt, Germany).

156

157 *University of Calgary, Canada*

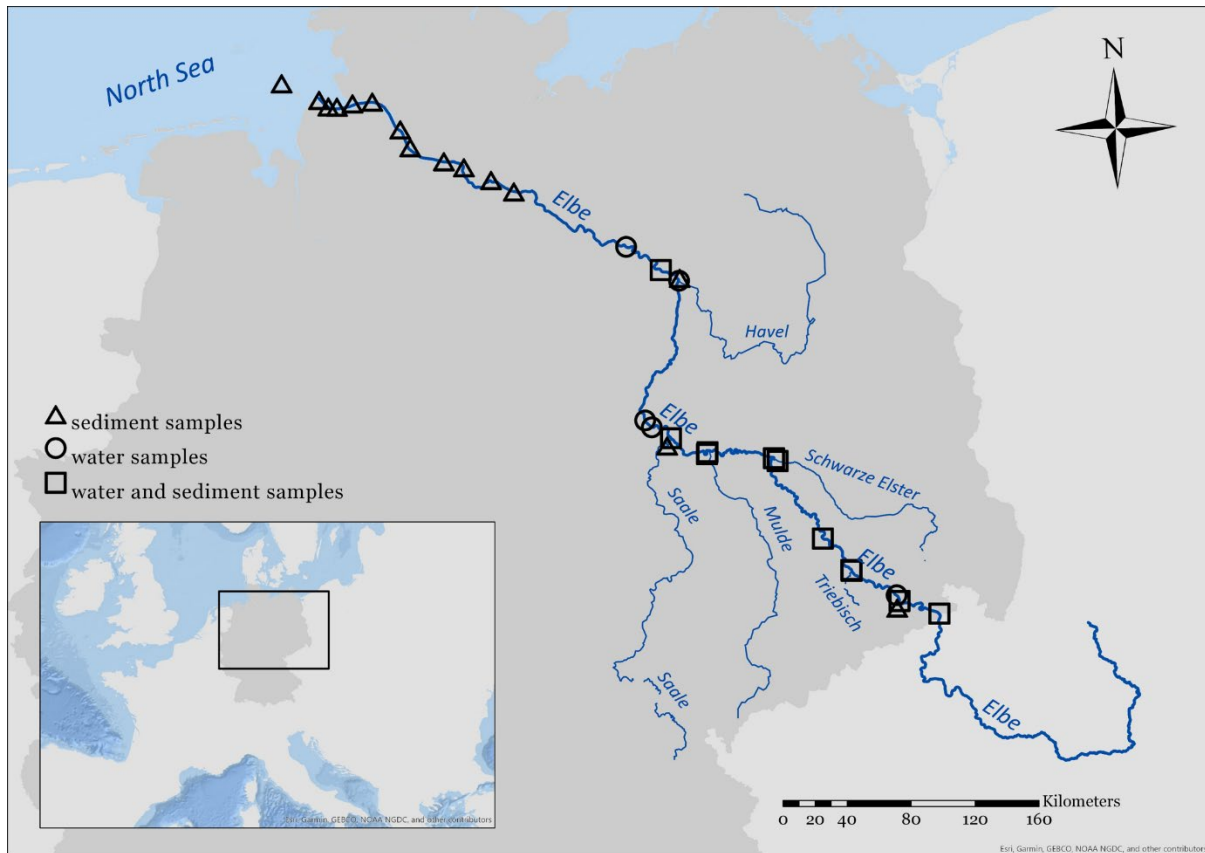
158 All sample preparation steps carried out at the Department of Physics and Astronomy were  
159 performed in a class 1000 clean room inside a clean bench to minimize blank levels and any  
160 risks of contamination. Aristar<sup>®</sup> Ultra nitric acid (65% w/w, VWR International, Radnor, USA)  
161 and environmental grad plus hydrochloric acid (32-35% w/w, VWR International, Radnor,  
162 USA) were used. Ultra-pure water used for analysis and cleaning was obtained from a water  
163 purification system with a resistivity of 18.2 MΩ\*cm. Enriched <sup>64</sup>Zn and <sup>67</sup>Zn materials used  
164 for the preparation of the double spike were purchased in oxide form from Oak Ridge National  
165 Laboratory (Oak Ridge, USA). The zinc double spike  $n(^{66}\text{Zn})/n(^{67}\text{Zn})$  isotope-amount ratio was  
166 ~4.88 in order to achieve the most precise isotope-amount ratios as recommended by Rudge et  
167 al. (2009).

## 168 **2.2 Samples and sample preparation**

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

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

174



175

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

180

### 181 2.2.1 Sampling locations

182 The part of the Elbe River impacted by the tide starts at river kilometer 757 up to the weir  
183 Geesthacht at river kilometer 587. Therefore, within the estuary, the sampling locations S\_01  
184 Scharnhörnriff to S\_11 Geesthacht were selected. Hamburg is the largest city within the estuary  
185 with the third largest port in Europe. Samples upstream of river kilometer 588 up to the



186 German/Czech boarder at river kilometer 0 were taken between Lauenburg (sample S\_12  
187 Lauenburg) and Schmilka (sample S\_31 Schmilka). Within this river section, sampling also  
188 included locations in the main tributaries, the Havel (S\_16 Tb. Havel), the Saale (S\_20 Tb.  
189 Saale) and the Mulde (S\_22 Tb. Mulde), as well as some smaller tributaries, the Schwarze  
190 Elster (S\_24 Tb. Schwarze Elster), the Triebisch (S\_27 Tb. Triebisch) and the Müglitz (S\_30  
191 Tb. Müglitz). All sampling locations in tributaries are labeled Tb. A detailed description of  
192 sampling coordinates including river kilometers can be found in the Supplemental information  
193 Table A1.

194 Sampling locations in this study were selected based on the original locations reported in the  
195 1990s by Prange et al. to allow for direct comparison of data in a time-dependent perspective.  
196 However, the impact of tributaries to the Elbe River were considered in the study by Prange et  
197 al. by taking samples at the tributary's mouth into the Elbe River only. In this study tributaries  
198 were sampled not only at the tributary's mouth but also several kilometers upstream the  
199 respective tributary before it discharges into the Elbe River.

### 200 **2.2.2 Sediment samples**

201 A detailed description of the sediment sample preparation and digestion process, including  
202 recoveries of elemental mass fractions of the marine sediment reference material GBW-07313  
203 and the basalt reference material BCR-2 can be found elsewhere (Reese et al., 2019). Both  
204 reference materials were quantitatively digested using the presented digestion method resulting  
205 in clear, particle free digests. Surface sediment samples were collected by using a custom-made  
206 box corer. The top layer (5 to 10 cm) of three or more individual samplings were subsequently  
207 homogenized, deep-frozen, freeze dried (Martin Christ Gefriertrocknungsanlagen, Osterode,  
208 Germany) and sieved over a cascade of polyamide sieves (Atechnik, Leinburg, Germany) to  
209 obtain the <63  $\mu\text{m}$  fraction. About 50 mg of the sieved sediment material was weighed into 55  
210 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<sup>-1</sup>

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

245

## 246 **2.3 Instrumentation and measurement procedures**

### 247 **2.3.1 Elemental analysis**

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

256 Multi-elemental data were processed using MassHunter version 4.2 and a custom-written  
257 Excel<sup>®</sup> spreadsheet. Recoveries were calculated using the marine reference sediment GBW-  
258 07313 and riverine reference waters SLRS-1 and SLRS-3. Combined uncertainties were

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

265

### 266 **2.3.2 Isotopic analysis**

267

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

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

280 Typical sensitivities were around 8 V for  $1 \mu\text{g mL}^{-1}$   $^{64}\text{Zn}$  with blank values of 2 mV.  
281 Instrumental isotopic fractionation correction was achieved with a  $^{64}\text{Zn}+^{67}\text{Zn}$  double spike,  
282 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<sup>-1</sup> for each sample.

285 Zn isotopic compositions are reported as  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  expressed as parts per thousand  
286 (‰) relative to the Zn IRMM standard IRMM-3702 calculated by Eq. 1.

287

$$288 \quad \delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} = \left( \frac{^{66}\text{Zn}/^{64}\text{Zn}_{\text{Sample}}}{^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}} - 1 \right) \quad (1)$$

289

290 We refer to  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  throughout the manuscript. A conversion to  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$   
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  $^{64}\text{Zn}/^{67}\text{Zn}$  isotope-amount ratio of the double spike. The double spike was calibrated against  
297 IRMM-3702 via internal isotopic fractionation correction using a  $^{66}\text{Zn}/^{68}\text{Zn}$  ratio for IRMM-  
298 3702 of 0.66525 (Moeller et al., 2012). The spectral interference of  $^{64}\text{Ni}$  on mass  $^{64}\text{Zn}$  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.)

## 304 **3 Results**

### 305 **3.1 Validation and performance characteristics of the analytical method**

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

### 316 **3.2 Concentration measurements and isotopic data**

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

#### 322 **3.3.1 Zn mass fractions and $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$ in sediment samples**

323 Zn mass fractions for sediment samples ranged from  $42 \text{ mg kg}^{-1}$  to  $1120 \text{ mg kg}^{-1}$  along the  
324 course of the Elbe (see Table A1 and Fig. 2A). The average mass fraction of all sediment  
325 samples analyzed in this study was  $417 \text{ mg kg}^{-1} \pm 294 \text{ mg kg}^{-1}$  (1 SD,  $n=26$ ). The lowest  
326 measured mass fraction of around  $42 \text{ mg kg}^{-1}$  was found in the estuary (S\_01 Scharhörnriff, km

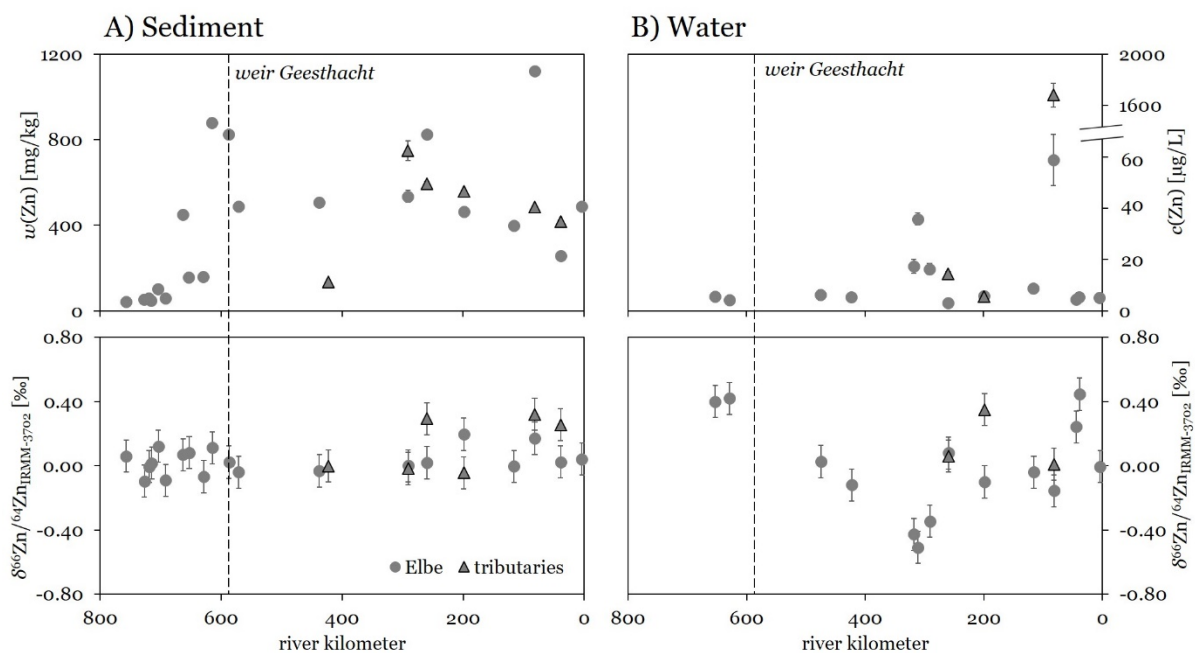
327 757). Elevated mass fractions of 879 mg kg<sup>-1</sup> and 826 mg kg<sup>-1</sup> were measured for two sampling  
328 locations upstream the city of Hamburg (S\_10 Billwerder Inseln, km 615 and S\_11 Geesthacht,  
329 km 587). Mass fractions upstream the weir in Geesthacht were highly variable ranging from  
330 135 mg kg<sup>-1</sup> for the Havel River (S\_16 Tb. Havel, km 423) to 1120 mg kg<sup>-1</sup> measured in the  
331 Elbe River near the mouth of the tributary Triebisch (S\_26 Triebisch, km 82). Elevated Zn  
332 mass fractions could also be found in two major tributaries of the Elbe River, the Saale (750  
333 mg kg<sup>-1</sup>, S\_20 Tb. Saale, km 291) and the Mulde (593 mg kg<sup>-1</sup>, S\_22 Tb. Mulde, km 260).  
334 Zn isotopic compositions expressed as  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  of sediment samples ranged from -  
335 0.10 ‰ to 0.32 ‰. Taking into account the analytical uncertainty of 0.10 ‰ ( $U(k=1)$ ) most of  
336 the samples were not significantly different from each other. In addition, three sampling  
337 locations with significantly heavier isotopic compositions could be identified. All of them are  
338 assigned to tributaries of the Elbe River, namely the Mulde ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  0.29 ‰  $\pm$  0.10  
339 ‰, S\_22 Tb. Mulde, km 260), the Triebisch ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  0.32 ‰  $\pm$  0.10 ‰, S\_27 Tb.  
340 Triebisch, km 82) and the Müglitz ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  0.26 ‰  $\pm$  0.10 ‰, S\_30 Tb. Müglitz,  
341 km 39).

### 342 **3.3.2 Zn concentrations and $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$ in water samples**

343 Dissolved Zn concentrations for water samples ranged from 3.2  $\mu\text{g L}^{-1}$  to 1680  $\mu\text{g L}^{-1}$ . The  
344 average concentration of all water samples of this study (except sample S\_27 Tb. Triebisch)  
345 was 12.6  $\mu\text{g L}^{-1} \pm 14.4 \mu\text{g L}^{-1}$  (1 SD,  $n=16$ ). Most measured Zn concentrations were found to  
346 be lower than 10  $\mu\text{g L}^{-1}$  with only a few exceptions (see Table A1 and Fig. 2B). Concentrations  
347 higher than 10  $\mu\text{g L}^{-1}$  were observed for the two sampling locations S\_17 Magdeburg at km  
348 318 (17.3  $\mu\text{g L}^{-1}$ ) and S\_18 Schönebeck at km 311 (35.8  $\mu\text{g L}^{-1}$ ) within the Elbe. Significantly  
349 elevated concentrations were also found for sampling locations deducted to tributaries, namely  
350 the mouth of the Saale (16.4  $\mu\text{g L}^{-1}$ , S\_19 Saale, km 291), the tributary Mulde (14.4  $\mu\text{g L}^{-1}$ ,  
351 S\_22 Tb. Mulde, km 260) and the mouth of the tributary Triebisch (58.7  $\mu\text{g L}^{-1}$ , S\_26 Triebisch,

352 km 82). An extremely elevated concentration of dissolved Zn of  $1680 \mu\text{g L}^{-1}$  was observed for  
 353 the tributary Triebisch (S\_27 Tb. Triebisch, km 82).  
 354 The Zn isotopic composition of water samples showed higher relative variability compared to  
 355 the sediment samples with  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  ranging from  $-0.51 \text{‰}$  to  $0.45 \text{‰}$ . For samples  
 356 taken in the estuary (S\_08 Tonne 107, km 653 and S\_09 Seemannshöft, km 629) generally  
 357 higher  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values than those for the riverine samples upstream were observed  
 358 ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} 0.40 \text{‰} \pm 0.10 \text{‰}$ ,  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} 0.43 \text{‰} \pm 0.10 \text{‰}$ ). A comparable  
 359 high  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  value was also observed for the tributary Schwarze Elster  
 360 ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} 0.35 \text{‰} \pm 0.10 \text{‰}$ , S\_24 Tb. Schwarze Elster, km 199). Additionally, a  
 361  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  value of  $0.45 \text{‰} \pm 0.10 \text{‰}$  was observed in the Elbe River near the mouth  
 362 of the tributary Müglitz (S\_29 Müglitz, km 39). In contrast to this, significantly lower  
 363  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values of  $-0.43 \text{‰} \pm 0.10 \text{‰}$ ,  $-0.51 \text{‰} \pm 0.10 \text{‰}$  and  $-0.34 \text{‰} \pm 0.10 \text{‰}$   
 364 were observed for the three sampling locations S\_17 Magdeburg, S\_18 Schönebeck and S\_19  
 365 Saale (km 291-318), respectively.

366  
 367



368  
 369 **Fig. 2.** A) Zn mass fractions and  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values for collected sediment samples in  
 370 the course of the Elbe River and its tributaries. B) Zn concentrations and  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$



371 values for collected water samples in the course of the Elbe River and its tributaries. Sampling  
372 locations are sorted according to the German Elbe river kilometer. (Error bars correspond to  $U$   
373 ( $k = 1$ ) for isotopic data and to  $U$  ( $k = 2$ ) for mass fractions and concentrations, respectively (if  
374 not visible  $U =$  smaller than spotsize)  
375

## 376 **4 Discussion**

### 377 **4.1 Comparison with historical data published by Prange et al.**

378 When comparing Zn mass fractions in sediment samples from this study to historical data, it  
379 has to be noted that Zn mass fractions were measured in different grain size fractions (this study  
380  $<63 \mu\text{m}$ , Prange et al.  $<20 \mu\text{m}$ ). Since heavy metal mass fractions in different grain size  
381 fractions can significantly vary, a direct comparison to historical sediment data is challenging  
382 (Ackermann et al., 1983). Nevertheless, the historical data can give valuable information about  
383 the origin of concentration hotspots within the Elbe River. In contrast to that, concentration  
384 data of dissolved Zn in the water phase is directly comparable between both datasets.

385

#### 386 **4.1.1 Comparison of Zn mass fractions in sediment samples to historical data**

387 Prange et al. published median Zn mass fractions in Elbe sediments for all analyzed samples  
388 from the confluence of Mulde and Elbe to the estuary (river kilometer 650 – 260) of  $2530 \text{ mg kg}^{-1}$   
389  $\text{kg}^{-1}$  (1992) and  $1820 \text{ mg kg}^{-1}$  (1995). Historical Zn mass fractions of sampling locations S\_19  
390 Saale ( $3026 \text{ mg kg}^{-1}$  (1992),  $2452 \text{ mg kg}^{-1}$  (1995)), S\_21 Mulde ( $3379 \text{ mg kg}^{-1}$  (1992),  $4887 \text{ mg}$   
391  $\text{kg}^{-1}$  (1995)) and S\_26 Triebisch ( $23800 \text{ mg kg}^{-1}$  (1992),  $8442 \text{ mg kg}^{-1}$  (1995)), indicate that the  
392 corresponding tributaries carried high loads of Zn at the time. Additionally, published Zn  
393 median mass fractions decreased during the study period from  $2530 \text{ mg kg}^{-1}$  in 1992 to  $1420$   
394  $\text{mg kg}^{-1}$  in 1998, indicating a decrease of Zn emissions into the Elbe River.

395 The average Zn mass fractions in sediment samples of this study was  $417 \text{ mg kg}^{-1}$ , which is  
396 significantly lower than historical data. In comparison with recent data from other European  
397 river systems e.g. the Danube average Zn mass fractions were significantly lower than in the  
398 Elbe River ( $187 \text{ mg kg}^{-1} \pm 25 \text{ mg kg}^{-1}$  in  $<63 \mu\text{m}$  grain size fraction) (Woitke et al., 2003).  
399 Estimated geogenic background concentrations for the Elbe River range between  $50 \text{ mg kg}^{-1}$   
400 and  $200 \text{ mg kg}^{-1}$  (only available for  $<20 \mu\text{m}$  fraction) (LAWA, 1998). (For some sampling  
401 locations, such as S\_21 Mulde at km 260 ( $824 \text{ mg kg}^{-1}$  (this study)) and S\_26 Triebisch at km  
402 82 ( $1120 \text{ mg kg}^{-1}$  (this study)) Zn mass fractions in the sediment samples are still higher than  
403 the average load of the Elbe River. This might still make these tributaries potential sources of  
404 anthropogenic Zn emissions into the Elbe River e.g. originating from old mining activities.

#### 405 **4.1.2 Comparison of Zn concentrations in water samples to historical data**

406 The average discharge volume of the Elbe River increases from  $315 \text{ m}^3 \text{ s}^{-1}$  at the German/Czech  
407 boarder to  $877 \text{ m}^3 \text{ s}^{-1}$  at the mouth of the estuary. The most important tributaries are the Havel  
408  $115 \text{ m}^3 \text{ s}^{-1}$ , the Saale  $115 \text{ m}^3 \text{ s}^{-1}$ , the Mulde  $73 \text{ m}^3 \text{ s}^{-1}$  and the Schwarze Elster  $28 \text{ m}^3 \text{ s}^{-1}$  (ATV-  
409 DVWK, 2000). During August/September 2015 the average discharge of the Elbe River was  
410 approximately  $240 \text{ m}^3 \text{ s}^{-1}$  that is considered as a dry period with low water discharge (IKSE,  
411 2017). For water samples taken in September 1995 and 1998 by Prange et al. the discharge  
412 volumes were approximately  $990 \text{ m}^3 \text{ s}^{-1}$  and  $320 \text{ m}^3 \text{ s}^{-1}$ , respectively. Historical median  
413 concentrations of the dissolved Zn fraction in Elbe water samples between river kilometer 650  
414 and 260 varied between  $16.5 \mu\text{g L}^{-1}$  (1992) and  $3.0 \mu\text{g L}^{-1}$  (1995) respectively. An estimated  
415 geogenic background of dissolved Zn in unpolluted German Rivers lies in the range of  $1 \mu\text{g L}^{-1}$   
416 (LAWA, 1998).

417 Historical data showed significantly higher Zn concentrations for some sampling locations at  
418 the confluence of tributaries. This included samples taken at the locations S\_19 Saale ( $50.5 \mu\text{g}$   
419  $\text{L}^{-1}$  (1995),  $55.8 \mu\text{g L}^{-1}$  (1998)), S\_21 Mulde ( $109.9 \mu\text{g L}^{-1}$  (1995),  $3.95 \mu\text{g L}^{-1}$  (1998)), S\_23

420 Schwarze Elster (47.5  $\mu\text{g L}^{-1}$  (1995), 5.37  $\mu\text{g L}^{-1}$  (1998)), S\_26 Triebisch (1490  $\mu\text{g L}^{-1}$  (1995),  
421 1780  $\mu\text{g L}^{-1}$  (1998)) and S\_29 Müglitz (32.1  $\mu\text{g L}^{-1}$  (1995), 15.8  $\mu\text{g L}^{-1}$  (1998)). For some of  
422 these sampling locations, a decrease of Zn concentrations could be observed over time (S\_21  
423 Mulde, S\_23 Schwarze Elster), whereas at some sampling locations the measured Zn  
424 concentrations remained constant (S\_19 Saale, S\_26 Triebisch). Our data indicated that even  
425 today some tributaries carry significantly higher dissolved Zn amounts than the Elbe River  
426 itself, namely the Mulde (14.4  $\mu\text{g L}^{-1}$ , S\_22 Tb. Mulde, km 260) and the Triebisch (1680.0  $\mu\text{g}$   
427  $\text{L}^{-1}$ , S\_27 Tb. Triebisch, km 82) making tributaries a potential source of anthropogenic Zn  
428 contamination. Especially, the tributary Triebisch that still contains high amounts of dissolved  
429 Zn.

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

434

#### 435 **4.2 Zn isotopic signatures of sediment samples**

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

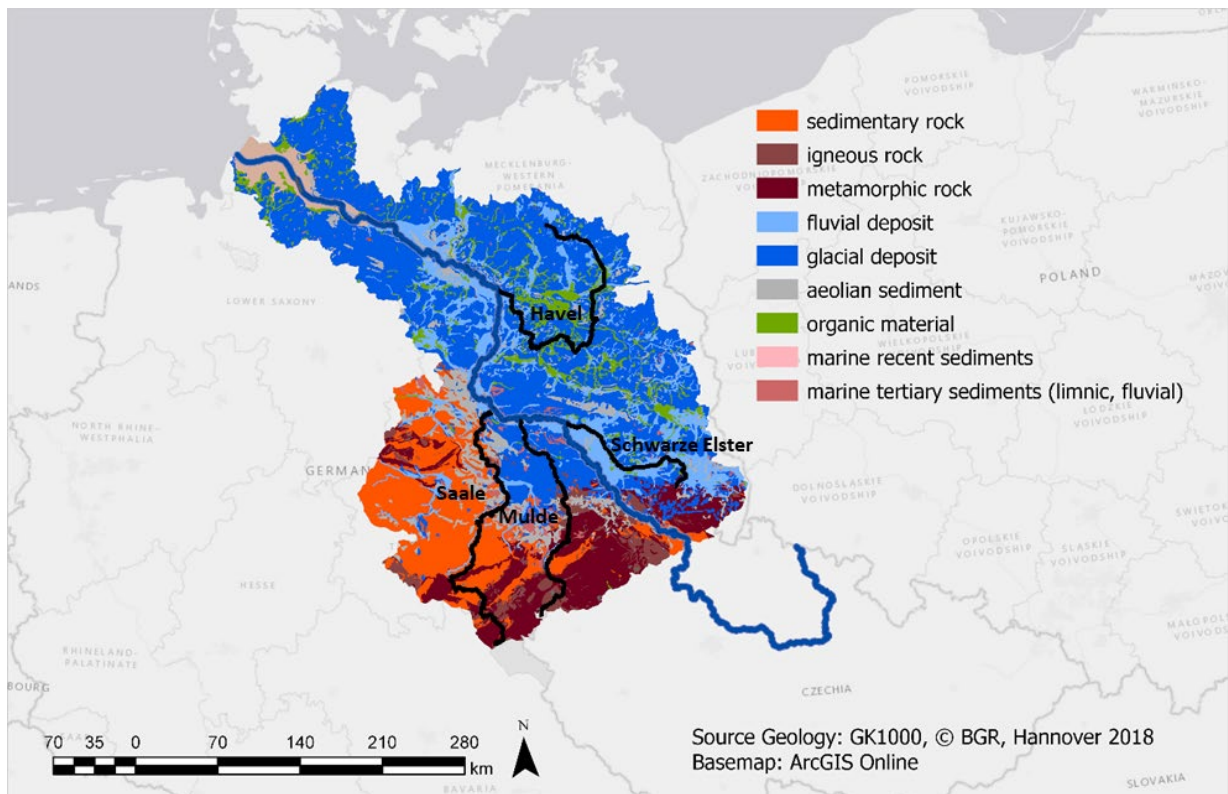
441 Our study revealed no significant changes in isotopic composition of  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  for  
442 sediment samples taken in the Elbe River with a mean of  $0.05\text{‰} \pm 0.11\text{‰}$ . In fact, measured  
443  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$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

445 et al. (2013). Regarding the Elbe River estuary, a thorough mixing of sediment of marine and  
446 fluvial origin can be observed. This is reflected in the measured mass fractions of Zn, as well.  
447 Sediment samples S\_10 and S\_11 with high amounts of Zn ( $879 \text{ mg kg}^{-1}$  and  $826 \text{ mg kg}^{-1}$  Zn)  
448 are rapidly diluted with marine sediment with significantly lower Zn mass fractions. This  
449 phenomenon was studied in detail by Reese et al. (2019) using isotope-amount ratio analysis  
450 of  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ ,  $n(^{143}\text{Nd})/n(^{144}\text{Nd})$  and multi-elemental mass fraction data. As no significant  
451 change in isotopic composition of  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  could be observed for samples taken in  
452 the Elbe River estuary, it can be assumed that the isotopic composition of Zn, is similar for  
453 fluvial as well as for marine sediments in the investigated catchment area.

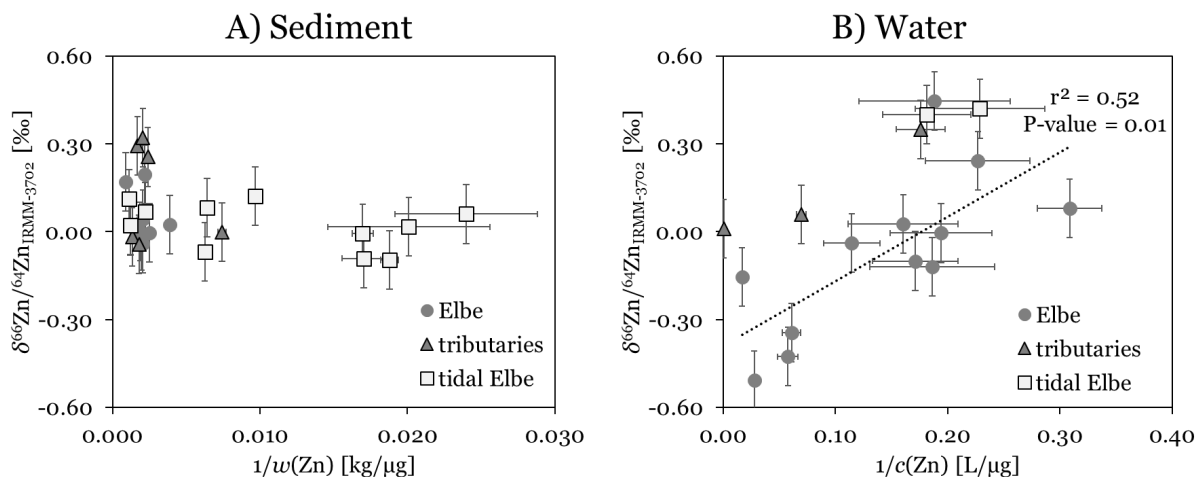
454 Three tributaries of the Elbe River, the Mulde ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} 0.29 \text{ ‰} \pm 0.10 \text{ ‰}$ , S\_22 Tb.  
455 Mulde, km 260), the Triebisch ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} 0.32 \text{ ‰} \pm 0.10 \text{ ‰}$ , S\_27 Tb. Triebisch, km  
456 82) and the Müglitz ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}} 0.26 \text{ ‰} \pm 0.10 \text{ ‰}$ , S\_30 Tb. Müglitz, km 39) are the  
457 only samples with significantly heavier isotopic composition. As shown in Fig. 4A, no direct  
458 linear correlation of the Zn isotopic composition and Zn mass fraction of sediment samples  
459 could be observed.

460 Other studies reported heavier isotopic composition of sediment samples caused by  
461 anthropogenic Zn emissions e.g. by Zn ore treatment plants (Araújo et al., 2017; Sivry et al.,  
462 2008, Skierszkan et al., 2016). This is mainly due to the significantly heavier isotopic  
463 composition of industrial tailings from Zn production relative to Zn ores, caused by the  
464 production processes. In fact, the three tributaries rise in the nearby Ore Mountains, a region  
465 in which mining activities started as early as in the Middle Ages. Especially during the 20<sup>th</sup>  
466 century, the catchment of the Freiburger Mulde (as part of the Mulde River), was characterized  
467 by Zn ore mining and processing of the ore leading to high, anthropogenic Zn amounts in water  
468 and sediment of the Mulde River (Volland B.).

469 Another explanation may also lie in changes of bedrock geology (see Fig. 3) that may lead to  
470 the heavier isotopic composition, as it is known for Zn bearing minerals featuring great  
471 variability in Zn isotopic composition with reported  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values of up to 1.10 ‰  
472 (corresponding to  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$  value of 1.39 ‰) (Mondillo et al., 2018).  
473 Overall our data indicates anthropogenic Zn sources to contribute to the total Zn load in the  
474 tributaries.



476 **Fig. 3.** Surface geology of the Elbe River catchment within Germany (Rohstoffe, 2006)  
477  
478  
479



480  
 481 **Fig. 4.** A)  $\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$  of sediment samples compared to inverse Zn mass fractions B)  
 482  $\delta^{66/64}\text{Zn}_{\text{IRMM-3702}}$  of water samples compared to inverse dissolved Zn concentrations. The given  
 483 trend line does not include values from tributaries and the tidal Elbe. Error bars correspond to  
 484  $U(k=1)$  for isotopic data and to  $U(k=2)$  for mass fractions and concentrations, respectively  
 485 (if not visible  $U$  = smaller than spotsize)  
 486

### 487 4.3 Isotopic signatures of water samples

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

497 Similar correlations were also observed for the isotopic systems of Cu and Mo (Vance et al.,  
 498 2008, Archer and Vance, 2008), where isotopic fractionation processes are mainly caused by  
 499 natural redox processes. Unlike Cu or Mo, Zn has only one oxidation state, neglecting  
 500 fractionation processes related to redox reactions. Furthermore, lighter as well as heavier  
 501 isotopic compositions of dissolved  $\delta^{66}\text{Zn}/^{64}\text{Zn}$  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.

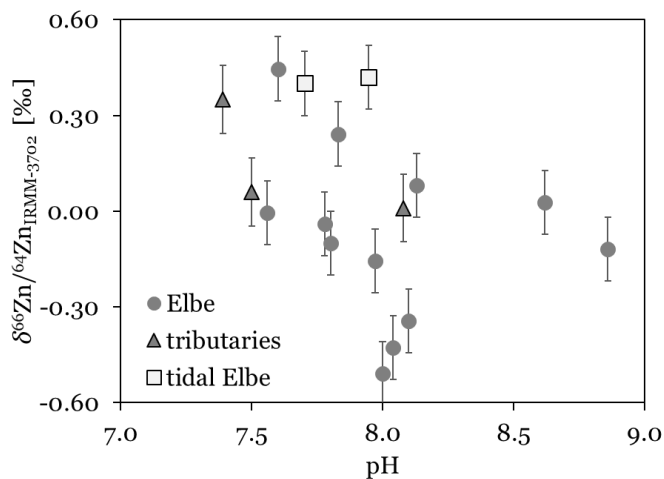
504 A major source of Zn emissions into the environment are effluence of industrial tailings, which  
505 potentially change the Zn isotopic composition of water and can therefore be used as a potential  
506 tracer for anthropogenic Zn emissions. This raises the question of possible fractionation  
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  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  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  $\delta^{66}\text{Zn}/^{64}\text{Zn}$  in waste rock drainage  
512 waters varied little, with a  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  of  $0.06 \text{ ‰} \pm 0.08 \text{ ‰}$ . 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 ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$  of up to 1.49 ‰, corresponding  
517 to  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  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  $(\Delta^{66}\text{Zn}/^{64}\text{Zn})_{\text{sorbed-aqueous}}$  of up to 0.53 ‰ (Juillot et al., 2008) and for the  
524 sorption on the surface of kaolinite  $(\Delta^{66}\text{Zn}/^{64}\text{Zn})_{\text{absorped-solution}}$  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 ( $(\Delta^{66}\text{Zn}/^{64}\text{Zn})_{\text{sorbed-aqueous}}$  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. Szykiewicz 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.**  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  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 ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  of 0.21



548 ‰ corresponding to  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$  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  $\Delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{cell-aqueous}}$  of up to -0.8 ‰ (John et al., 2007a).  
551 Analysis of lake settling particles proved a significant isotope fractionation of  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-}}$   
552 3702  $-0.95 \text{ ‰} \pm 0.08 \text{ ‰}$  (corresponding to  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon}}$   $-0.66 \text{ ‰} \pm 0.08 \text{ ‰}$ ), 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  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values of the sediment samples are in good accordance  
566 to the terrestrial background ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  of  $0.0 \text{ ‰} \pm 0.05 \text{ ‰}$ ), 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.  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values of the water samples showed larger variability  
570 ( $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  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  $\delta^{66}\text{Zn}/^{64}\text{Zn}_{\text{IRMM-3702}}$  values and vice versa, indicating complex fractionation processes

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

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## 594 **Competing interests declaration**

595 The authors have no competing interests to declare.

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