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Zinc isotope composition as a tool for tracing sources and fate of metal contaminants in rivers

³ A review

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- 7

8 Abstract

9 Zinc is a ubiguitous metal, acting both as an essential and a toxic element to organisms depending on its concentration and speciation in solution. Human activities mobilize and 10 spread large quantities of zinc broadly in the environment. Discriminating the natural and 11 various anthropogenic zinc sources in the environment and understanding zinc's fate at a 12 catchment scale are key challenges in preserving the environment. This review presents the 13 state of the art in zinc isotope studies applied to environmental purposes at a river-basin 14 15 scale. Even though the study of zinc isotopes remains less developed than more "traditional" lead isotopes, we can assess their potential for being a relevant tracer of zinc in the 16 environment. We present the principles of zinc isotope measurements from collecting 17 18 samples to mass spectrometry analysis. To understand the fate of zinc released in the 19 environment by anthropogenic activities, we summarize the main processes governing zinc distribution between the dissolved and solid phases, with a focus on the isotope fractionation 20 effects that can modify the initial signature of the various zinc sources. The signatures of zinc 21 isotopes are defined for the main natural sources of zinc in the environment: bulk silicate 22 23 earth (BSE), zinc sulfide ore deposits, and coal signatures. Rivers draining natural 24 environments define the "geological background for surface water", which is close to the BSE value. We present the main anthropogenic sources (metallurgical waste, effluents, fertilizers, 25 etc.) with their respective isotope signatures and the main processes leading to these 26 specific isotope characteristics. We discuss the impact of the various anthropogenic zinc 27

emissions based on the available studies based on zinc isotopes. This literature review points out current knowledge gaps and proposes future directions to make zinc isotopes a relevant tracer of zinc (and associated trace metals) sources and fate at a catchment scale.

31 Keywords

32 Zinc isotopes, metals, contamination, source tracer, catchment.

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37 1. Introduction

38 Zinc (Zn) is ubiquitous, being present in soils, plants and biota, acting both as an essential and a toxic element to organisms depending on its concentration and speciation in solution 39 (e.g. Campbell, 1995; Whitton, 1970). For instance, zinc depletion produces nutrient 40 limitation in the sea, whereas excess zinc can cause a range of reproductive, developmental, 41 behavioral, and toxic responses in a variety of aquatic organisms and insects (e.g. Muyssen 42 et al., 2006; Schmidt et al., 2011). Concerning human health, a surplus of zinc is associated 43 with oxidative stress and is a contributing factor in many chronic diseases (e.g. Walsh et al., 44 45 1994). Many human activities make and mobilize widespread large quantities of zinc in the 46 environment. Industries and wastewater treatment plants expel their zinc-rich liquid effluents directly into rivers. Emissions from metal processing (mining and smelting) are a major 47 source of zinc in the atmosphere and soil (Nriagu and Pacyna, 1988). Coating steel by "hot 48 49 dip" galvanization or zinc electroplating (also called "electrogalvanization") is a common use 50 of zinc, and zinc in these products may be easily released into the environment through 51 corrosion. Other sources of zinc contamination include the disposal of fertilizers and crop protection treatments in cultivated areas (Eriksson, 2001). Zinc is also transferred to the 52 atmosphere and soil through coal combustion and waste incineration (Abanades et al., 2002; 53 54 Xu et al., 2004). Non-combustion traffic emissions relative to vehicles (tires and brakes) and road furniture (galvanized parts and railings) also spread this metal into the environment 55 (Councell et al., 2004; Legret and Pagotto, 1999; Zarcinas and Rogers, 2002). These various 56 zinc contributions, deposited in the environment in particulate form or in larger deposits, are 57 leached by rainfall, forming water runoff with high Zn concentrations. These releases then 58 join rivers, polluting riverbed sediments and the water itself. River basins play a key role in 59 the water cycle, capturing and storing enormous quantities of water, which ultimately supply 60 61 a large part of the available freshwater on Earth. Thus, controlling Zn concentrations in surface water is a major environmental and public health issue. 62

The European Union (EU) Water Framework Directive (2000/60/EC) aims to deliver 63 integrated river basin management for the whole of Europe. The member states of the EU 64 are required to prepare a list of specific pollutants and their environmental quality standards 65 (EQS) in the aquatic environment for evaluating the ecological status of water. Metal zinc, 66 regulated by 22 EU member states, is the river basin-specific pollutant most often monitored 67 in the EU (Arle et al., 2016). The predicted no-effect concentration (PNEC) from the EU Risk 68 Assessment Reports varies depending on the water hardness, with the lowest EQS at 69 70 7.8 µg/L (Kos Durjava et al., 2015). In France, an acceptable ecological status for a water body is reached, without a hardness condition, when the bioaccessible zinc content is below 71 7.8 µg/L (Statute of 27 July 2015, https://substances.ineris.fr/fr/page/9). In the USA, the 72 water quality criterion recommended by the United States Environmental Protection Agency, 73 below which significant risks to the majority of species in a given environment are not 74 expected, is 66.6 µg/L at a hardness of 50 mg/L (United States Environmental Protection 75 Agency, 1996). For good management of water bodies, defining numerical limits for zinc in 76 77 the environment below which unacceptable effects are not expected is not enough. Indeed, the multiplicity of pollution sources, the presence of variable "naturally" occurring background 78 concentrations, the existence of a number of chemical species with various toxicity, and how 79 the abundance of those species changes in response to changes of the water's physical and 80 chemical conditions must be considered. 81

82 Within the last twenty years, developments in mass spectrometry (TIMS, thermal ionization mass spectrometry and MC-ICP-MS, multicollector-inductively coupled plasma-mass 83 spectrometry) have allowed the high-precision measurement of isotope compositions of 84 transition metals and post-transition metals such as zinc (e.g. Maréchal et al., 1999; 85 86 Schoenberg and Von Blanckenburg, 2005; Schönbächler et al., 2007). Zinc has five stable isotopes, ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn, and ⁷⁰Zn, with natural abundances of 49.2, 27.8, 4.0, 18.4, 87 and 0.6% respectively. Since the pioneering work of Maréchal et al. (1999), the application of 88 Zn isotope biogeochemistry has rapidly expanded, and Zn isotope compositions have been 89

90 used in various domains and already discussed in review papers (Albarède, 2004; Cloquet et 91 al., 2008; Moynier et al., 2017; Yin et al., 2015). This review is specifically dedicated to the 92 use of Zn isotopes as tracers to determine the sources of anthropogenic pollution and how 93 they were transported into rivers. This review compiles and discusses currently available 94 data from these previous studies, together with unpublished data from the Loire River Basin 95 (France). From this compilation we have evaluated the ability of Zn isotope compositions to 96 trace metal sources at the catchment scale, in both dissolved and solid phases.

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98 2. Materials and methods

99 The mass of zinc typically required for mass spectrometry analysis (at least 4 replicates) is 100 1 μg (e.g. Chen et al., 2009a; Guinoiseau et al., 2017). Several steps (i.e. collection, 101 preparation and measurement) are necessary to acquire the isotope composition of natural sample. Because metals are everywhere in field and laboratory equipment, costly and time-102 103 consuming procedures are required to minimize zinc contaminations during these steps. All 104 reagents are prepared with 18.2 MΩ.cm (at 25 °C) water and commercial acid purified in 105 laboratory by sub-boiling distillation (e.g. Araújo et al., 2017a; Bermin et al., 2006). All materials, including PFA vessels, pipette tips, columns, and bottles, are previously cleaned in 106 a laboratory with nitric and/or hydrochloric acid and then rinsed thoroughly with 18.2 MQ.cm 107 108 water prior to use (e.g. Balistrieri et al., 2008; Bryan et al., 2015). According to previous studies (Bryan et al., 2015; Nelson et al., 2017), polyvinyl gloves, which are commonly 109 manufactured using zinc stearate as a mold release compound, must not be used when 110 handling samples and hardware. Total procedural blanks (from field to mass spectrometry 111 analysis) must be regularly measured to verify the cleaning procedure. Procedural blanks are 112 generally lower than 10 ng, which represented less than 1% of the mass of zinc analyzed 113 (e.g. Chen et al., 2009a; Guinoiseau et al., 2017). 114

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2.1 Sampling requirements for zinc isotope analyses in water and sediments

We have seen that all materials used in the field to collect samples must be previously 118 cleaned in the laboratory. To determine Zn isotope compositions in solution in liquid samples 119 (surface water, effluent, etc.) the sample volume taken in the field varies between a few tens 120 of milliliters to several liters according to the concentration of the medium. Samples are taken 121 122 using plastic containers, then generally filtered at 0.20 µm or 0.45 µm and placed in plastic bottles rinsed several times with water filtered from the sample (e.g. Aranda et al., 2012; 123 Borrok et al., 2008; Chen et al., 2008; Petit et al., 2015; Szynkiewicz and Borrok, 2016; 124 Wanty et al., 2013). Water samples are preserved with sub-boiled concentrated nitric or 125 126 hydrochloric acid to a pH of approximately 2 (e.g. Aranda et al., 2012; Chen et al., 2014).

Recently, passive diffusive gradients in thin film samplers (DGT samplers) have been also
used successfully for Zn isotope measurements in surface water (Desaulty et al., 2017;
Desaulty and Millot, 2017). DGT can pre-concentrate metals in situ and provide an isotope
composition of water integrated over time.

131 For solid samples, the quantity of materials sampled is not governed by the concentration of 132 solid metals (generally a few hundred mg/kg), which is high compared with the quantity necessary for isotope analysis (1 µg of Zn), but usually considers the need for representative 133 samples. Stream sediments are sampled from the middle of water courses with sampling 134 135 media (shovels, augers, etc.) not containing zinc and not coated with painted surfaces that contain metal-based pigments (Bullen, 2012). The sediment cores are generally taken using 136 acrylic tubes (Araújo et al., 2017a; Sivry et al., 2008). To obtain the required mass of 137 suspended particulate matter (SPM) for isotope and chemical analyses (>50 mg) a large 138 volume of water is collected (often more than 1 L) and then filtered or centrifuged to recover 139 all SPM (Araújo et al., 2017b; Chen et al., 2009b; Guinoiseau et al., 2017; Petit et al., 2015, 140 2008). 141

143 **2.2 Chemical separation and analysis of zinc isotopes**

Prior to isotope analyses, preparation (e.g. solid dissolution) and chemical purification are necessary to separate zinc from coexisting matrix elements. Sample preparation takes place in a cleanroom under positive pressure of filtered air, under a laminar airflow, allowing all phases of sample preparation to be performed under clean conditions (e.g. Borrok et al., 2008; Petit et al., 2015). The chemical purification is generally performed with anionexchange chromatography in concentrated HCl on macro-porous, pre-cleaned resin (AG-MP1, BioRad®) (e.g. Borrok et al., 2007; Maréchal et al., 1999).

While Zn isotope compositions were initially measured by TIMS (Thermal-ionization mass 151 spectrometry) (Rosman, 1972), it is high-precision measurement by MC-ICP-MS (Maréchal 152 153 et al. (1999)) that led to the rapid expansion of Zn isotopes into a variety of environmental applications. Several methods are used for correcting isotope discrimination in the instrument 154 during analysis. Zn isotope data can be acquired by MC-ICP-MS, either by standard-sample 155 bracketing or by the double-spike method. Standard-sample bracketing involves analyzing a 156 157 standard solution directly before and after a sample. This method is often associated with 158 external normalization, which consists, prior to the analysis, of adding to the sample another element having an atomic mass close to that of the element of interest. Zinc data are 159 generally externally normalized to copper (Cu) using an exponential mass-fractionation law 160 161 (Archer and Vance, 2004; Maréchal et al., 1999). Standard-sample bracketing needs complete recovery of the element during chemical preparation to avoid mass discrimination 162 leading to analysis that would not be representative of the bulk sample. In the double-spike 163 method, before chemical preparation, a mixture of two isotopes of the element (generally 164 ⁶⁴Zn-⁶⁷Zn) with a non-natural isotopic composition are added (Arnold et al., 2010a; Bermin et 165 al., 2006). The advantage of using a double-spike method is that the complete recovery of 166 the element during chemical preparation is not necessary. Moreover, since the mass bias is 167 corrected using an isotope ratio of the analyte element, this method is little affected by matrix-168 induced mass bias effects. The double-spike method is particularly well adapted for samples 169

that only contain small amounts of zinc (a few μ g/L) in a matrix with much higher concentrations of other elements such as seawater and biological materials (e.g. Arnold et al., 2015; Zhao et al., 2014). In spite of the advantages of the double-spike method, due to its straightforward approach the standard-sample bracketing method is still in widespread use in recent MC-ICP-MS Zn isotope studies (e.g. Araújo et al., 2019; Gelly et al., 2019).

175 Zn isotope compositions are reported as a classical δ -notation (parts per thousand, ‰) with 176 the ⁶⁶Zn/⁶⁴Zn ratio relative to zinc standard:

$$\delta^{66/64} Zn (\%_0) = \left[\frac{({}^{66}Zn/{}^{64}Zn)_{sample}}{({}^{66}Zn/{}^{64}Zn)_{standard}} - 1 \right] \times 1000$$
177

After the standard used in the original work by Maréchal et al. (1999) i.e. JMC 3-0749C (usually called JMC-Lyon) a number of different reference standards have been developed and used in a routine manner in different laboratories (SRM NIST 683, IMC 12053, PCIGR-1, IRMM-3702, Imperial) (e.g. Moeller et al., 2012; Yang et al., 2018). Despite JMC-Lyon having not been available for many years, data are generally normalized to this standard. All data presented in this review were recalculated referring to JMC-Lyon for easy comparison.

The precision of Zn isotopic measurements depends on the quality of the chemical preparation (total procedural blanks relative to content in sample, quantitative recovery of the element) and on the operating parameters and corrections applied during MC-ICP-MS measures. In recent studies, typical analytical precision for $\delta^{66/64}$ Zn measurements verified by repeated runs of samples and standards is generally around $\pm 0.05\%$ (2 σ) for environmental samples regardless of the method used to correct the instrumental bias (e.g. Araújo et al., 2019; Vance et al., 2016).

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192 **2.3 Additional data from the Loire River Basin**

The corpus of samples coming from the Loire River Basin was composed of liquid and solid 193 samples described in supplementary Tables S1, S2, and S3. Liquid effluents coming from 194 195 various industries and wastewater treatment plants (WWTP) that are usually directly discharged into the Loire river were analyzed (Table S1). Other samples containing high Zn 196 contents were also analyzed (organic fertilizers and brake pads) (Table S1). Pig slurry and 197 manure samples were sampled in Brittany and Pays de la Loire (France) and brake pad 198 199 linings commercially available in France were purchased (Valeo®). Dissolved loads were 200 sampled from the Loire River Basin in an upstream/downstream transect, as well as the Furan River draining various sulfide mineralizations (Table S2). SPM was collected in the 201 Loire River before the estuary (Montjean-sur-Loire) (Table S3). SPM and sediments were 202 collected in the watershed mainly occupied by intensive farming (Argos, Vilaine, Couesnon) 203 (AELB, 2013) (Table S3). The sampling and analysis protocols were in line with these 204 205 described above (sections 2.1. and 2.2.) and detailed in supplementary materials.

206

3. Impact of natural physical and chemical processes on zinc isotope

208 compositions

209 Various processes control metal distribution between the dissolved and particulate phases in surface water. The main mechanisms causing a new Zn isotope distribution between the 210 phases (i.e. isotope fractionation) are equilibrium isotope distribution between dissolved 211 aqueous species and equilibrium and kinetic effects due to the interactions between minerals 212 or live organisms and aqueous solutions (adsorption, precipitation, uptake, etc.). The goal of 213 this article is not to make an exhaustive study of the fractionation that affects Zn isotope 214 compositions in the environment, but to highlight the main processes that govern zinc 215 216 distribution between dissolved and particulate phases and to evaluate how they affect the initial $\delta^{66/64}$ Zn signatures of anthropogenic zinc sources. Isotope fractionation between zinc 217 bound, fixed or adsorbed on a solid organic or inorganic phase and zinc in solution is defined 218 as follows: 219

$\Delta^{66/64} Zn_{solid-dissolved} = \delta^{66/64} Zn_{solid} - \delta^{66/64} Zn_{dissolved}$

Laboratory experimental studies investigated the mechanisms that potentially fractionate Zn 221 222 isotopes (Fernandez and Borrok, 2009; Guinoiseau et al., 2016; Veeramani et al., 2015). These various mechanisms (adsorption, dissolution, precipitation etc.) and their impact on 223 isotope signatures as described in the literature are summarized in Fig. 1. These 224 experiments can be also coupled with X-ray absorption spectroscopy, which provides the 225 226 metal's local structural information (i.e., coordination number, bond distance) allowing to make the link between changes in crystal-chemical parameters and the isotope 227 fractionations. This technique is mainly used to study the chemical environment of zinc 228 during adsorption onto several minerals (Gou et al., 2018; Juillot et al., 2008; Nelson et al., 229 230 2017).

Several theoretical studies used *ab initio* and density functional methods to determine equilibrium stable isotope partitioning between various zinc species by calculating their reduced partition function ratios (RPFR or β). The fractionation between two species A and B is then defined as the ratio of their β -factors $\alpha^{66/64}_{A-B}=\beta^{66/64}_{A}/\beta^{66/64}_{B}$ and a simple relation allows the comparison of these theoretical equilibrium isotopic fractionations and $\delta^{66/64}Zn$ values, which are commonly reported on natural samples:

237 10³ln $\alpha^{66/64}_{A-B} \sim \Delta^{66/64}Zn_{A-B} = \delta^{66/64}Zn_{A-} \delta^{66/64}Zn_{B}$

By calculating β-factors we identify some of the crystal-chemical parameters controlling 238 isotopic properties. In particular, the proprieties of bonds between zinc and its neighbors is 239 240 an important crystal-chemical parameter controlling isotopic fractionation between phases. General theoretical considerations suggest that the lower coordination states and bond 241 lengths should prefer the heavy isotope (Schauble, 2004). Equilibrium stable isotope 242 partitioning between aqueous zinc complexes including aqueous sulfate, chloride, and 243 carbonate species are determined by previous studies (Black et al., 2011; Fujii et al., 2014, 244 2011, 2010). Zinc complexes (Zn phosphates, citrates and malates) were also modeled to 245

discuss the Zn isotope fractionation in roots and leaves of plants (Fujii and Albarède, 2012). 246 247 In their review study, Moynier et al. (2017) summarized the calculated β -factors available in 248 the literature for aqueous solutions and molecules relevant for zinc in biogeochemistry. Their 249 study also provides unpublished data for various molecules (e.g. oxalate species). Ducher et 250 al. (2018, 2016) used also ab initio calculations to determine equilibrium Zn isotope fractionation factors in Zn-bearing minerals (e.g. sphalerite, hydrozincite) and between 251 hexaaquo zinc complexes and minerals. Although a straightforward comparison between the 252 various theoretical data available in the literature is difficult since the β -factors have been 253 determined with different types of input data and methods (Black et al., 2011: Ducher et al., 254 2016; Fujii et al., 2010), these data provide a theoretical basis for the interpretation of Zn 255 isotopic measurements. The β -factors for various dissolved species, organic ligands, Zn-256 bearing minerals and zinc metal are represented in supplementary Fig. S1 (Black et al., 257 258 2011; Ducher et al., 2018, 2016; Fujii et al., 2014; Fujii and Albarède, 2012; Moynier et al., 2017). To compare the β -factors and evaluate the isotope fractionation between phases, in 259 this publication we considered an ambient temperature of 25°C. 260

Distribution between dissolved aqueous species. In aqueous solutions, stable Zn 261 262 complexes depend on the dominant ligands (Albarède, 2004). At increasing chlorine and sulfate concentrations, the hexaaquo zinc complex $Zn(H_2O)_6^{2+}$ gives zinc-chloro complexes 263 264 (e.a. $ZnCl(H_2O)_5)^+$, $ZnCl_2(H_2O)_4$) and zinc-sulphato complexes (e.g. $ZnSO_4(H_2O)_6$, $ZnSO_4(H_2O)_5$). Ab initio calculations showed that aquo-ion and zinc chloride complexes have 265 close isotope signatures (Fujii et al., 2014), whereas zinc sulfates are enriched in ⁶⁶Zn with a 266 value of $\Delta^{66/64}$ Zn ~+0.5‰ relative to aquo-ions (Moynier et al., 2017) (Fig. S1). With 267 increasing pH, carbonate $(ZnCO_3(H_2O)_3)$ and hydroxide $(Zn(OH)_2(H_2O)_4)$ become the 268 dominant species with $\Delta^{66/64}$ Zn enrichment until +1‰ for zinc carbonates relative to aqua-ion 269 (Fujii et al., 2014). 270

Organic complexation. A major part of "dissolved" zinc in rivers is organically complexed
 rather than free and inorganically complexed; this part of organically complexed Zn increases

greatly in estuary zones (e.g. Montgomery and Santiago, 1978; van den Berg and 273 Dharmvanij, 1984). Experiments dedicated to complexation on organic compounds' humic 274 275 acid (an organic matter analog) showed that below pH 6 isotope fractionation is not measurable, while at higher pH the complexed organic Zn is heavier than free Zn^{2+} ($\Delta^{66/64}Zn$ 276 =+0.24‰) (Jouvin et al., 2009). The authors explained this difference by changes in Zn 277 speciation with pH, with higher complexation constants and shorter bond lengths for organic 278 complexed Zn compared to the free Zn²⁺. Ban et al. (2002) measured similar fractionation 279 $(\Delta^{66/64}Zn = +0.20\%)$ between EDTA complexed Zn and Zn²⁺. Theoretical equilibrium isotopic 280 factors seem to confirm these experimental results. β-factor for citrate, another analog for 281 humic acids, showed that the predominant species present in solutions at pH between 4 and 282 8, $Zn(cit)(H_2O)_3$, is enriched in ⁶⁶Zn compared to the hexaaquo zinc complex with 283 $\Delta^{66/64}$ Zn=+0.16‰ (Fujii et al., 2014; Fujii and Albarède, 2012) (Fig. S1). 284

Adsorption onto mineral particles. Adsorption of zinc onto mineral particles (oxides, oxide-285 hydroxides, clay, carbonate and silicates) causes a drop in the $\delta^{66/64}$ Zn_{dissolved} value with 286 $\Delta^{66/64}$ Zn fractionation around +0.30‰. This depends on the nature of the mineral and the 287 solution conditions (pH, ionic strength) (Balistrieri et al., 2008; Bryan et al., 2015; Dong and 288 289 Wasylenki, 2016; Gou et al., 2018; Guinoiseau et al., 2016; Juillot et al., 2008; Nelson et al., 290 2017; Pokrovsky et al., 2005). In most cases, the fractionation is driven by a decrease of 291 coordination number and bond lengths between aqueous Zn (six-coordinate octahedral) and adsorbed Zn (four-coordinate tetrahedral) complexes. 292

Precipitation. While synthetic hydrozincites $(Zn_5(CO_3)_2(OH)_6)$ produced by Wanty et al., 2013 have $\delta^{66/64}Zn$ identical to the dissolved Zn, Veeramani et al. (2015) showed that hydrozincite and hopeite $(Zn_3(PO_4)_2.4H_2O)$ precipitation tends to reduce the $\delta^{66/64}Zn_{dissolved}$ value $(\Delta^{66/64}Zn = +0.18\%)$ and +0.25% respectively). The $\delta^{66/64}Zn_{dissolved}$ value in a river draining a Zn-Pb mining district in Sardinia and containing a consortium of a microalga and a cyanobacterium, which facilities the biomineralization of hydrozincite, is also significantly 299 depleted in heavy isotopes compared to hydrozincite ($\Delta^{66/64}Zn = +0.35\%$) (Wanty et al., 2013). Data obtained by Veeramani et al. (2015) (and also Wanty et al. (2013) for natural 301 samples) are in agreement with the theoretical fractionation value calculated by Ducher et al. 302 (2018) between hydrozincite precipitate and hexaaquo zinc complex ($\Delta^{66/64}Zn \sim +0.30\%$, Fig. 303 S1).

Laboratory experiments with and without bacteria showed that sphalerite (ZnS) precipitation increases $\delta^{66/64}$ Zn_{dissolved} relative to the precipitate ($\Delta^{66/64}$ Zn fractionation of -0.30‰) (Archer et al., 2004; Jamieson-Hanes et al., 2017; Veeramani et al., 2015). This isotope fractionation is consistent with *ab initio* calculations that predict a fractionation of -0.50‰ between sphalerite precipitate and hexaaquo zinc complex (Ducher et al., 2018) (Fig. S1).

309 Dissolution. Using the same calculation, sphalerite dissolution should lead to fractionation between solid and aqueous Zn of $\Delta^{66/64}$ Zn ~ -0.50‰, whereas during oxidative weathering 310 experiments of sphalerite-rich rocks Fernandez and Borrok (2009) measured only a little 311 initial fractionation ($\Delta^{66/64}$ Zn = -0.20‰) that quickly dissipated to give a $\delta^{66/64}$ Zn_{dissolved} close to 312 sphalerite ($\Delta^{66/64}$ Zn = 0.0‰). The initial fractionation can be explained by the transient 313 formation of a surface coating on sphalerite composed of Zn sulfates (Fernandez and Borrok, 314 2009). The theoretical β -factor for Gunningite (ZnSO₄. H₂O) showed that this phase 315 preferentially incorporates the heavier Zn isotopes compared to sphalerite ($\Delta^{66/64}$ Zn ~ 316 +0.30%) and is weakly deleted in heavy isotope compared to Zn^{2+} ($\Delta^{66/64}Zn \sim -0.20\%$), 317 Ducher et al., 2018) (Fig. S1). 318

According to the β -factor values, the dissolution of metallic zinc leads to an enrichment in ⁶⁶Zn for hexaaquo zinc complex with $\Delta^{66/64}$ Zn ~ -1.5‰ (Black et al., 2011) (Fig. S1).

Adsorption onto biological surfaces. Adsorption of zinc onto microorganisms (bacteria, diatoms, plankton, phototrophic biofilm) generally increases the $\delta^{66/64}$ Zn_{adsorbed} value with $\Delta^{66/64}$ Zn fractionation between +0.30 and +1.20‰ that depends on the nature of microorganisms and the solution conditions (pH, ionic strength) (Coutaud et al., 2014;

Gélabert et al., 2006; John and Conway, 2014; Kafantaris and Borrok, 2014). In most cases,
the fractionation seems driven by a mechanism similar to a Zn complexation to organic
functional groups on organisms' external surfaces.

Biological uptake. The uptake by plants (rice, tomato, etc.) and microorganisms (diatom, 328 bacteria, plankton, phytoplankton) may increase or decrease the $\delta^{66/64}$ Zn_{dissolved} value 329 according the uptake process involved (high or low affinity pathway), which depends on the 330 concentration of free ions in the nutrient solution (Arnold et al., 2015, 2010b; Aucour et al., 331 2015, 2011; Caldelas et al., 2011; Couder et al., 2015; Coutaud et al., 2014; Gélabert et al., 332 2006; Houben et al., 2014; John et al., 2007a; Jouvin et al., 2012; Kafantaris and Borrok, 333 2014; Samanta et al., 2018; Smolders et al., 2013; Tang et al., 2016; Viers et al., 2007; 334 Weiss et al., 2005). The uptake of heavy isotopes by microorganisms and plants is favored in 335 low Zn concentration media (~1-10 µg/L). The mechanism is the active uptake by a 336 337 membrane transport protein Zn-ion-permease or by a chelating organic complex Znphytosiderophore (high affinity uptake) (e.g. Arnold et al., 2010b; Tang et al., 2016). 338 Microorganisms and plants preferentially take up the lighter isotopes of zinc when the 339 340 mechanism is diffusive transport across the cell membrane and through the boundary layer of the root (low affinity uptake) (e.g. John et al., 2007a; Jouvin et al., 2012). For plants, we do 341 342 generally see a higher $\delta^{66/64}$ Zn value in roots than in the nutrient medium with a preferential translocation of light isotopes into the upper parts (Fig. 3). Fujii and Albarède (2012) 343 explained these results using ab initio calculations and proposed that the fractionation is 344 345 driven by the difference in Zn speciation between the root system (isotopically heavy Zn phosphates) and the upper parts, rich in isotopically light citrates and malates (Fig. S1). 346

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4. Isotope composition of natural zinc sources

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4.1 The Upper Continental Crust

The average Zn content in the upper continental crust calculated by Taylor and McLennan (1985) is 71 mg/kg. For rocks in the continental crust, analysis of Zn isotope compositions ($\delta^{66/64}$ Zn) in granite shows values between +0.21 and +0.47‰ (n=4, Araújo et al., 2017a; Chen et al., 2009b; Chen et al., 2016; Viers et al., 2007). Based on basaltic and ultramafic sample analyses from different geologic settings, Chen et al. (2013) estimated the average Zn isotope composition of bulk silicate earth (BSE) to be $\delta^{66/64}$ Zn = +0.28 ± 0.05‰ (2 σ).

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4.2 Sulfide and non-sulfide ore deposits

The main zinc ore exploited is sphalerite or blende (ZnS). It represents 90% of current world 357 358 zinc production (Gordon et al., 2003); various zinc minerals such as smithsonite (ZnCO₃) also called calamine, account for the rest (Gordon et al., 2003). Since zinc is present in ores 359 in only a single oxidation state (+II), the variety of isotope compositions in the various 360 361 mineralizations is limited compared to other metal elements like copper (between -3 and +7‰ e.g. Braxton and Mathur, 2011; Maréchal et al., 1999) (Fig. 2). However, the fact that 362 zinc is in various crystallographic environments and coordination numbers (ranging from 4 to 363 6) in Zn-bearing minerals lead to a significant theoretical fractionation between ores until 364 $\Delta^{66/64}$ Zn ~ +1.5‰ (Ducher et al., 2016) (Fig. S1). For silicate and carbonate minerals, in 365 accordance with the general rule of short bonds concentrating heavy isotopes (Schauble, 366 367 2004), a general decrease in β -factors is observed when the bond lengths and coordination numbers increase (Ducher et al., 2016). The highest β -factor value is found for hemimorphite 368 (Zn₄Si₂O₇(OH)₂.H₂O) where Zn atoms are four-fold coordinate with O atoms. The β-factor for 369 willemite (Zn₂SiO₄) is not calculated by Ducher et al. (2016). However, Zn being tetrahedrally 370 371 coordinated with oxygen in willemite like in hemimorphite, it is likely that the β-factors for these phases would be comparable (Mondillo et al., 2018). In hydrozincite (Zn₅(CO₃)₂(OH)₆) 372 the β-factor is lower relative to hemimorphite due to the fact that Zn is found in both 373 tetrahedral and octahedral sites. Smithsonite where Zn is octahedrally coordinated have the 374 lowest β -factor. With β -factor close to smithsonite and Zn tetrahedrally coordinated, 375

sphalerite is out of this general trend because Zn-S bond properties differ from Zn-O bonds(Fig. S1).

For sphalerite and other sulfur-containing minerals like galena (PbS) and chalcopyrite 378 (CuFeS₂) sampled worldwide, the Zn isotope variations ($\delta^{66/64}$ Zn) are relatively low with an 379 interquartile range (IQR) of between +0.05 and +0.26‰ and a mean and median of +0.16‰ 380 (n = 294) (Aranda et al., 2012; Chapman et al., 2006; Deng et al., 2017; Duan et al., 2016; 381 Gagnevin et al., 2012; John et al., 2008; Kelley et al., 2009; Maréchal et al., 1999; Mason et 382 383 al., 2005; Mattielli et al., 2009; Mondillo et al., 2018; Novak et al., 2016; Pašava et al., 2014; Shiel et al., 2010; Sivry et al., 2008; Skierszkan et al., 2016; Sonke et al., 2008; Voldrichova 384 et al., 2014; Wanty et al., 2013; Weiss et al., 2007; Wilkinson et al., 2005; Zhou et al., 2014) 385 (Fig. 2; supplementary Fig. S2). The variability of $\delta^{66/64}$ Zn signatures for sphalerite within a 386 387 deposit is likely due to a kinetic fractionation and Rayleigh distillation during progressive sphalerite precipitation from hydrothermal fluids (Wilkinson et al., 2005). Theory predicts that 388 kinetically controlled reactions favor the incorporation of isotopically light zinc in mineral 389 precipitates relative to the bulk ore-forming fluid (Wilkinson et al., 2005), which likely explains 390 the mean and median value for $\delta^{66/64}$ Zn values in sulfide ore deposits, depleted in heavy 391 isotopes compared to the BSE value (+0.28 $\pm 0.05\%$, 2 σ). 392

Secondary minerals, such as willemite, smithsonite, hydrozincite, and hemimorphite, formed 393 through low-temperature hydrothermal and/or supergene oxidation of primary sulfide 394 deposits, have more variable Zn isotope compositions than primary sulfide ores with $\delta^{66/64}$ Zn 395 values generally between +0.05 and +0.48% and a median value of +0.28% (n = 23, IQR) 396 (Araújo et al., 2017a; Mondillo et al., 2018; Pašava et al., 2014; Voldrichova et al., 2014) 397 (Fig. 2; Fig. S2). These minerals form through the total or partial release of zinc by 398 dissolution from a precursor phase (primary sphalerite or an earlier secondary phase). The 399 400 complete breakdown of primary sulfides/minerals and quantitative reprecipitation of zinc leads to low fractionation, whereas partial dissolution and incorporation causes high 401 402 fractionation between phases. Pašava et al. (2014) studied Zn isotope composition in

403 minerals at La Florida mine (Spain), where an intense supergene alteration of sphalerite leads to the formation of secondary minerals like hydrozincite that are significantly enriched 404 in heavy isotopes relative to sphalerite ($\Delta^{66/64}$ Zn = +0.60‰). For ores coming from the Czech 405 Republic, Voldrichova et al. (2014) showed a strong enrichment in heavy isotopes for 406 hemimorphite relative to sphalerite ($\Delta^{66/64}$ Zn = +0.80‰). These fractionations are consistent 407 with β-factors calculated between hydrozincite, hemimorphite and aqueous Zn by Ducher et 408 al. (2018) ($\Delta^{66/64}$ Zn=+0.30% and $\Delta^{66/64}$ Zn=+0.90% respectively). Mondillo et al. (2018) 409 410 studied Zn isotope compositions in secondary zinc minerals collected from Zn deposits in Ireland, Belgium, Poland, Namibia, and Zambia, formed during low-temperature 411 412 hydrothermal and/or supergene oxidation of primary sulfide deposits. Most of the data observed on minerals can be explained as described above by an isotopic fractionation 413 model in which the partial dissolution of primary sphalerite is followed by the precipitation of 414 415 an initial secondary phase that preferentially incorporates light Zn isotopes (smithsonite) or 416 heavy Zn isotopes (hemimorphite, willemite, hydrozincite) (Fig. S1). However, Mondillo et al (2018) observed also strong negative isotopic shifts for late crystallizing phases ($\Delta^{66/64}$ Zn = -417 0.50% for Willemite and $\Delta^{66/64}$ Zn=-0.66% for hemimorphite relative to a precursor phase). 418 419 Authors explained these low Zn isotope signatures for late crystallizing phases relative to the 420 precursor mineral by the progressive precipitations from fluids that form phases enriched in heavy Zn isotopes leading to a gradual decrease in the $\delta^{66/64}$ Zn values of such phases, and 421 the fluids involved, in time and space. In conclusion, the variability of $\delta^{66/64}$ Zn values in 422 423 secondary ores (between +0.05 and +0.48%, n = 23, IQR), higher than for primary sulfides (between +0.05 and +0.26‰, n = 294, IQR), can be explained by a combination of 424 equilibrium isotope fractionation and open system Rayleigh distillation during incomplete 425 dissolution-reprecipitation reactions. 426

427

4.3 Coal

In coal, the Zn content can reach several hundreds of mg/kg (Novak et al., 2016). Zn isotope compositions in coal vary very widely with $\delta^{66/64}$ Zn values generally between -0.10 and +1.35‰ (n = 14, IRQ) for samples taken in Spain, the Czech Republic, Germany and the USA (Borrok et al., 2010; Novak et al., 2016; Ochoa Gonzalez and Weiss, 2015; Voldrichova et al., 2014) (Fig. S2). The wide variability of coal isotope compositions is related to diagenetic processes (uptake by plants, exchange with pore waters) that occur in peat, a coal precursor (Ochoa Gonzalez and Weiss, 2015).

435 **4.4 Natural water**

436 In rivers that are largely unaffected by human activity, Zn concentrations in solution (dissolved load) are generally between 1 and 2 µg/L (Gaillardet et al., 2003). For rivers with 437 little human impact, the Zn concentrations in solution are substantially lower than the 438 European (7.8 µg/L) and US (66.6 µg/L) EQS values. The particulate phase (sediment & 439 SPM) in rivers generally contains higher quantities of zinc, at around 200 mg/kg for rivers 440 with little human impact (Martin and Meybeck, 1979; Viers et al., 2009). In waters with little 441 human impact ($[Zn]_{dissolved} \le 2 \mu g/L$), the isotope compositions of Zn in solution are generally 442 between $\delta^{66/64}$ Zn = +0.29 and +0.57‰ (n=63, IQR) (Chen et al., 2014, 2008; Little et al., 443 2014; Petit et al., 2015; this study) (Fig. S2). However, we note great variability in $\delta^{66/64}$ Zn 444 values in estuaries. A study on the Garonne estuary (France) showed that in the turbidity 445 zone the dissolved $\delta^{66/64}$ Zn values varied from +0.19 to +0.90‰ from upstream to 446 downstream unlike $\delta^{66/64}$ Zn in SPM, which remained constant (+0.37 ± 0.05‰, 2 σ , n=10) 447 (Petit et al., 2015) (Fig. 3). Although not consistent with fractionation experiments at isotopic 448 equilibrium (Fig. 1), the authors explained this enrichment by kinetically driven adsorption 449 due to strongly increasing sorption sites in the turbidity zone (Petit et al., 2015). The $\delta^{66/64}$ Zn 450 values for zinc in solution in the estuary of the river Kalix (Sweden) and the Amazon estuary 451 (Brazil), between +0.36 and +0.80‰ (n = 7, Little et al., 2014), are also high compared to the 452 453 BSE level (+0.28 \pm 0.05‰, 2 σ) (Fig. 3). As shown previously (see section 3) the part of

"dissolved" Zn complexed to organic ligands relative to free and inorganically complexed Zn 454 increases widely in estuaries compared to upstream. The organic complexed Zn enriched in 455 456 ⁶⁶Zn compared to the free Zn²⁺ (Fig. 1), could participate in the enrichment in heavy isotopes of dissolved Zn in the estuary zone compared to upstream. At the river-sea interface, in 457 addition to physical and chemical processes, mixing between fresh water and seawater 458 $(\delta^{66/64}Zn \sim +0.50\%;$ Boyle et al., 2012; Zhao et al., 2014) may also explain part of the 459 variability observed. If we do not consider estuaries, the variation in $\delta^{66/64}$ Zn in solution in 460 rivers with little human impact ([Zn]_{dissolved} $\leq 2 \mu g/L$) is quite small, with values between +0.28 461 and +0.43‰ (n=46, IQR) and a median value of +0.33‰ close to the BSE value (+0.28 ± 462 0.05%, 2σ) (Fig. 3). Most of the sediments and SPM taken from lakes and rivers with little 463 human impact ($[Zn]_{particulate} \leq 200 \text{ mg/kg}$) have Zn isotope compositions varying from 464 δ^{66/64}Zn=+0.14 to +0.32‰ (n= 129, IQR, Araújo et al., 2017a, 2017b, 2019, 2018; Chen et al., 465 466 2009b; Guinoiseau et al., 2018, 2017; Petit et al., 2015, 2008; Sivry et al., 2008; Thapalia et 467 al., 2010, 2015; this study) (Fig. S2). SPM generally has isotope compositions similar to or slightly lower than the associated dissolved phase (Chen et al., 2009b, 2008). This result 468 469 suggests that adsorption processes are not the dominant process by which Zn enrichment in 470 SPM occurs (Chen et al., 2009b), and that the organic matter in both the sediment and 471 aqueous phase likely plays a crucial role in the distribution of Zn isotopes between these phases. In Fig. 3 where $\delta^{66/64}$ Zn values are shown for sediments and SPM of lakes and rivers 472 with little human impact ($[Zn]_{particulate} \le 200 \text{ mg/kg}$) we see that the Amazon and its tributaries, 473 474 including the Rio Negro, have a considerably lower isotope signature (+0.07 \pm 0.30‰, 2 σ , n 475 = 48) compared to the BSE value (+0.28 \pm 0.05‰, 2 σ). This specific isotope composition is related to the presence in Rio Negro SPM of kaolinite in which zinc is structurally 476 477 incorporated (Guinoiseau et al., 2018). If we do not consider this watershed, Zn isotope compositions in SPM and sediments for lakes and rivers with little human impact ([Zn]_{particulate} 478 \leq 200 mg/kg) have quite a narrow variation with values between +0.23 and +0.40‰ (n=81, 479 IQR) and a median value of +0.30‰, similar to the BSE value (+0.28 \pm 0.05‰, 2 σ) (Fig. 3). 480

These data on $\delta^{66/64}$ Zn values in the dissolved phase (between +0.28 and +0.43‰, n=46, IQR) and the particulate phase (between +0.23 and +0.40‰, n=81, IQR) for lakes and rivers let us define a composition for the geological background for surface water (GBSW) with values between +0.24 and +0.41‰ (n=127, IQR) and a median value +0.30‰, similar to the BSE value (+0.28 ± 0.05‰, 2 σ) (Fig. S2).

486

5. Isotope composition of anthropogenic zinc sources

Considerable quantities of zinc are emitted into the environment by industry, urbanization 487 and agriculture. A summary of major anthropogenic zinc flows emitted into the environment 488 in France is presented in supplementary Table S4. Industries and urban WWTP discharge 489 490 effluents rich in zinc directly into river. Large quantities of zinc-rich solid waste are also emitted into soils and the atmosphere by industry, urbanization and agriculture. The runoff 491 and erosion from industrial, urban, and agricultural soils and atmospheric deposits releases 492 large quantities of zinc into surface freshwater. As well as natural physical and chemical 493 processes (see section 3), the processes used by humans to concentrate, extract or treat the 494 zinc contained in natural materials will impact their $\delta^{66/64}$ Zn value. In particular, high-495 temperature industrial processes, involving evaporation and condensation reactions with 496 kinetic isotope effects, can induce significant isotopic fractionation between industrial and 497 498 natural samples.

499

500 5.1 Mining and industrial activities

Zinc is widely dispersed in soils and the atmosphere because of past and current mining and industrial activity (supplementary Fig. S3). For example, according to IREP (Registre Français des Emissions Polluantes), 502 metric tons of zinc are emitted by industrial activity into soils and the atmosphere each year in France (2010-2017 average; http://www.irep.ecologie.gouv.fr/IREP/index.php). The main emitting activities are the production and smelting of metal, but also power plants (Gouzy and Brignon, 2014). Industries also discharge metal-rich effluents directly into surface water. In France according
to the IREP, 94 metric tons of zinc are emitted directly into surface water each year (20102017 average; http://www.irep.ecologie.gouv.fr/IREP/index.php). These come mainly from
the metallurgy, surface treatment (e.g. electroplating, chemical deposit), and chemical
industries.

512 **5.1.1 Mining activities**

513 Mining operations, in particular related to the extraction of sulfide minerals, cause enormous stocks of waste rock piles that contain notable residual Zn quantities. Samples collected in 514 waste rock piles at sulfide mineral mines in the USA (Fe-Zn-Cu mine) and Peru (Cu-Zn-Mo 515 516 mine) contained large quantities of zinc (up to 0.4% by mass)(Aranda et al., 2012; 517 Skierszkan et al., 2016). The water percolating through these waste rock piles (i.e. effluent) can be also rich in zinc. Skierszkan et al. (2016) showed that experimental waste-rock 518 weathering can produce effluents with high Zn content (up to 16 mg/L). The $\delta^{66/64}$ Zn values 519 for these samples are shown in Fig. S4. The Zn isotope compositions of various samples 520 (solid waste and effluent) generally had values between +0.18 and +0.28‰ (n = 34, IQR, Fig. 521 S3), which are consistent with those of sulfide mineralizations (+0.05 and +0.26‰, n = 294, 522 IQR). 523

This similarity in $\delta^{66/64}$ Zn values between mining residue and ores is because these residues have an isotope signature similar to the mineralizations that they accompany and the zinc in solution in effluents results from the dissolution of zinc-rich minerals, so this process only causes low enrichment of the isotope composition of the solution relative to the solid (Fig. 1).

528

5.1.2 Industrial activities

529 **Metallurgical processes.** The extraction of non-ferrous metals produces enormous 530 quantities of waste called tailings. This solid waste can contain several % by mass of zinc 531 (Bigalke et al., 2010; Juillot et al., 2011; Sivry et al., 2008). The particles emitted by smelter 532 chimneys contain several hundreds of mg/kg of zinc (Mattielli et al., 2009). In general, for

high-temperature zinc pyrometallurgy processes in smelters, the zinc recovery yield is close 533 to 100%, so the isotope fractionation between the ore and the resulting metal is low (Shiel et 534 535 al., 2010; Sonke et al., 2008). John et al. (2007b) showed that the zinc in diverse metal parts (money, raw metals, etc.) has a range of isotope variations (between +0.09 and +0.31‰, n = 536 14) similar to that of ores (between +0.05 and +0.26%, n = 294, IQR). Shiel et al. (2010) also 537 showed by analyzing refined zinc alloy produced in Zn-Pb refining that the fractionation 538 539 between the ore used (+0.17 \pm 0.06‰) and the alloy produced (+0.22 \pm 0.06‰) is low. Using these data for zinc metal, a signature for "common zinc" is defined between +0.15 and 540 +0.22‰, and a median value of +0.19‰ (n = 15, IQR) (Fig. S3 and Fig. S4). Because of 541 evaporation and condensation reactions that occur during the extraction process, waste from 542 the operations (slags) have a considerably higher isotope signature (up to +1.5%) (Bigalke et 543 al., 2010; Couder et al., 2008; Juillot et al., 2011; Sivry et al., 2008; Yin et al., 2018), and 544 particles emitted have a very low signature (up to -0.7%) (Mattielli et al., 2009) compared to 545 ores (between +0.05 and +0.26‰, n = 294, IQR) (Fig. S4). From analyzing various waste 546 547 and products in metallurgic sites in France, a kinetic fractionation factor has been calculated 548 for Rayleigh evaporation of zinc during refining ($\alpha_{solid-vapor}$) that is generally between 1.0001 549 and 1.0004 (Mattielli et al., 2009; Sivry et al., 2008). By following a Rayleigh model (Wiederhold, 2015), simulating the $\delta^{66/64}$ Zn variations in separated and accumulated vapor 550 551 and solid residue, it is possible to estimate the Zn isotope composition in waste produced during the smelting operations: 552

553
$$\partial_{slag} = \partial_{ore} + \varepsilon_{vapor-solid} lnf; \ \partial_{cumul vapor=} = \partial_{ore} + \varepsilon_{vapor-solid} lnf - \frac{\varepsilon_{vapor-solid} lnf}{1-f}$$
 (1)

554 Where $\varepsilon_{vapor-solid}$ is the isotope enrichment factor (‰) with $\varepsilon_{vapor-solid} \approx -1000 \ln \alpha_{solid-vapor}$ and *f* 555 the fraction remaining.

For a starting composition of $\delta^{66/64}$ Zn in ores between +0.05 and +0.26‰ (n=294, IQR), a $\alpha_{solid-vapor}$ fractionation factor between 1.0001 and 1.0004 and assuming a recovery of 98% for pure zinc production in smelting processes, the estimated $\delta^{66/64}$ Zn values are between +0.44

and +1.82‰ for slags and -0.34 and +0.16‰ for particles (Fig. S4). These values are 559 consistent with slags and particles reported in previous studies (Bigalke et al., 2010; Couder 560 561 et al., 2008; Juillot et al., 2011; Mattielli et al., 2009; Sivry et al., 2008; Yin et al., 2018). Water that percolates through slag tailings (between +0.51 and +1.40‰, n=4, Fig. S4) has a 562 similar isotope signature to slags (between +0.50 and +0.78‰, n=12, IQR, Fig. S3) (Shiel et 563 al., 2010; Sivry et al., 2008). These similar signatures for slag and effluents are related to the 564 565 fact that dissolution processes only cause low isotope fractionation of dissolved fraction 566 relative to the solid (Fig. 1). However, metallurgical slags are very heterogeneous materials, composed of many mineral phases: mainly glassy phases but also crystalline phases like 567 spinels (franklinite (ZnFe₂O₄), gahnite (ZnAl₂O₄)), silicates (willemite (Zn₂SiO₄)) and zinc 568 metal (Yin et al., 2018). Theoretical equilibrium isotopic factors show that the dissolution of 569 these phases leads to a wide range of Zn fractionation between aqueous Zn and minerals 570 phases (Fig. S1). Moreover, weathering experiments on slags with different pH, atmospheres 571 and contact times showed that because of the slags' heterogeneity (various amorphous 572 573 glassy and crystalline phases), and because of multiple low-temperature inorganic chemical 574 reactions (precipitation of secondary phase, coprecipitation, adsorption) that take place while they are altered, the $\delta^{66/64}$ Zn values between the slags and the leachate may vary 575 considerably from one experiment to another (up to 3‰) (Yin et al., 2018). 576

577 Since zinc is a chalcophile element, it is found as an impurity in other sulfide minerals like galena (PbS) and chalcopyrite (CuFeS₂). For instance, in the Cubatão industrial region in 578 Brazil, which holds various metallurgical industries, the particles present in the atmosphere 579 have a very low signature ($\delta^{66/64}$ Zn between -0.59 and -0.06‰, n = 10, Souto-Oliveira et al., 580 581 2019, 2018) compared to that of mineralizations (between +0.05 and +0.26%, n = 294, IQR) and similar to that of particles emitted by zinc smelters (between -0.38 and +0.05%, n = 17, 582 IQR, Fig. S3). Zinc is also present in slags produced during lead production (up to 9% by 583 mass) (Gelly et al., 2019). In their study of a former lead smelter in the south of France, Gelly 584 et al. (2019) showed that Zn isotope compositions in slags have low values (between -0.04 585

and +0.18‰, n=8) compared to those of the slags analyzed in previous studies on zinc 586 smelters (between +0.50 and +0.78‰, n=12, IQR) (Fig. S4). The same applies for the slags 587 588 produced in a lead blast furnace in the north of France, whose Zn isotope composition (+0.13 \pm 0.06‰, Yin et al., 2018) is similar to those in the tailings analyzed by Gelly et al., 2019. 589 This depletion is likely not due to the starting material, i.e. galena that has a mean $\delta^{66/64}$ Zn 590 value (+0.23 \pm 0.12‰, 2 σ , n=8) close to that of other sulfide ores (+0.16 \pm 0.48‰, 2 σ , n=294) 591 592 (Fig. 2). This is likely related to a different yield for this process, whose aim was not to recover the zinc. 593

594 Galvanization. Zinc is also used widely to protect metallic parts from corrosion. Zinc can be deposited on the part by submerging it in a liquid bath of molten zinc ("hot-dip" galvanization) 595 or by electrolytic deposit (electroplating). John et al., (2007b) showed that galvanized objects 596 have an isotope signature (between +0.12 and +0.58‰, n=3) similar to the levels in ores 597 (between +0.05 and +0.26‰, n=294, IQR) and "common zinc" (between +0.15 and +0.22‰, 598 n=15, IQR), whereas the parts with an electrolytic deposit have a strongly depleted signature 599 600 (up to -0.60‰) (Fig. S4). This result was confirmed by laboratory experiments, which also showed depletion of the metal deposited that leads to enrichment of liquid bath with kinetic 601 fractionation (a_{solution-metal}) between 1.0010 and 1.0020 (Black et al., 2014; Kavner et al., 602 603 2008). This fractionation is likely due to that fact that not all the zinc present in the electrolytic 604 bath is electrodeposited during this process (60% recovery) and that the light isotopes are 605 preferably electrodeposited (Black et al., 2014; Kavner et al., 2008). By following a Rayleigh 606 model (see equation 1), using a starting isotope composition close to that of ores (between +0.05 and + 0.26‰, n = 294, IQR), kinetic fractionation ($\alpha_{solution-solid}$) between 1.0010 and 607 1.0020 and a 60% recovery yield, the estimated values for $\delta^{66/64}$ Zn in the electrodeposited 608 metal are between -1.17 and -0.35‰, which is similar to the $\delta^{66/64}$ Zn values obtained for 609 commercial electrodeposited (screw and chain) zinc-coated articles (between -0.34 and -610 0.20‰, n = 3, John et al., 2007b) (Fig. S4). 611

Coal and waste combustion in power plants. The combustion of coal and waste in 612 power plants releases high Zn contents into the atmosphere. Fly ash and flue gases sampled 613 614 in coal-fired power plants and waste incineration plants contain large proportions of zinc (up to 3% by mass, Cloquet et al., 2006; Novak et al., 2016). While smelters operate between 615 616 600 °C and 700 °C, in coal-fired power plants, coal is combusted at higher temperatures 617 (from 1200 to 1500 °C). At those temperatures, most of the zinc evaporates and condenses 618 onto the fly ash particles, which are removed in electrostatic precipitators (ESPs) (Ochoa 619 Gonzalez and Weiss, 2015). Although ESPs exhibit good retention for large particles, their efficiency is significantly lower for particles smaller than 0.8 µm remaining in flue gases and 620 621 about 50% of the starting zinc is emitted through the stack (Ochoa Gonzalez and Weiss, 622 2015). The signatures in the fly gas are controlled by condensation processes with isotope fractionation kinetic factors ($\alpha_{solid-vapor}$) ranging between 1.0003 and 1.0007 (Ochoa Gonzalez 623 and Weiss, 2015). From the analysis of fly ash and bottom ash samples coming from three 624 625 power plants in Spain, Ochoa Gonzalez and Weiss (2015) predicted that the incineration of coal and pet coke with $\delta^{66/64}$ Zn between +1.05 and +1.50‰ leads to zinc emission through 626 the plant stack between +0.96 and +1.27‰. By following a Rayleigh model (see equation 1), 627 for a starting composition of $\delta^{66/64}$ Zn in coal between -0.10 and +1.35‰ (n=14, IQR), an 628 $\alpha_{solid-vapor}$ factor between 1.0003 and 1.0007 and assuming a loss of 50% of zinc in the flue 629 gas, $\delta^{66/64}$ Zn values are estimated between -0.31 and +1.26‰ for zinc emission (Fig. S4). 630 The Zn isotope signatures of flue gases from French urban waste incineration are between 631 +0.07 and +0.19‰ (n = 3, Cloquet et al., 2006). These values match the estimated Zn 632 isotope compositions for flue gases (between -0.06 and +0.13‰) obtained from incinerating 633 634 material having an isotope signature similar to that of "common zinc" (between +0.15 and +0.22%, n = 15, IQR) under the conditions set out previously ($\alpha_{solid-vapor} = 1.0003 - 1.0007$, a 635 loss of 50%) (Fig. S4). 636

In conclusion, the zinc emitted by coal-fired power plants and waste incineration plants hasan isotope signature that is highly dependent on the combustible material. Given that the

coal has very variable $\delta^{66/64}$ Zn values (-0.10 and +1.35‰, n = 14, IQR), Zn isotope 639 compositions emitted when coal is combusted will also be very variable (estimated values 640 between -0.31 and +1.26‰) with values that include the BSE (+0.28 \pm 0.05‰, 2 σ) and 641 sulfide ore (between +0.05 and + 0.26‰, n=294, IQR) ranges. For waste incineration, if we 642 consider that the starting materials have a signature similar to "common zinc" (between 643 +0.15 and +0.22‰, n = 15, IQR), the variation in Zn isotope compositions in the particles 644 emitted will be narrower (value estimated between -0.06 and +0.13‰) with lower values than 645 ores (between +0.05 and +0.26‰, n = 294, IQR). 646

647 Other industries. As zinc metal is widespread in hardware, chemical components and organic materials, liquid effluents discharged into surface water by industries that do not work 648 Zn metal as core processes (e.g. the chemical and agro-food industries), also contain high 649 quantities of dissolved zinc (up to 500 µg/L, Table S1). Effluents coming from various 650 651 industries (hospitals, chemicals, agro-food and surface treatment industries) are presented in supplementary Fig. S4 (this study). Industrial effluents have values for $\delta^{66/64}$ Zn generally 652 between +0.10 and +0.15‰ (n=7, IQR, Fig. S3), lower than the BSE value (+0.28 ± 0.05‰, 653 2σ) and close to that of "common zinc" (between +0.15 and +0.22%, n = 15, IQR). 654

655 5.2 Emission from urban activities

Rivers can be strongly impacted by urban pressure (urban WWTP, zinc roofing, road traffic). 656 Urban WWTP discharge metal-rich effluents directly into surface water. For example, in 657 France, according to the IREP, 69 metric tons of zinc are emitted each year directly into 658 surface **WWTP** (2010-2017 average; 659 water by urban 660 http://www.irep.ecologie.gouv.fr/IREP/index.php). Galvanized zinc is widely used to cover roofs and weathering caused by rainwater carries large quantities of zinc into rivers. Gouzy 661 and Brignon (2014) estimated that 6 metric tons of zinc are discharged each year into 662 surface water in France due to zinc roofing. Road traffic is also a substantial zinc emitter, 663 through engines (gasoline), vehicle wear and tear (brakes, tires) and roadway equipment 664 665 (safety barriers). As an example, CITEPA (Centre Interprofessionnel Technique d'Etudes de la Pollution Atmosphérique) estimates that about 300 metric tons of zinc is emitted into the
atmosphere each year in France due to road traffic (Data: https://www.citepa.org/fr/air-etclimat/polluants/metaux-lourds/zinc).

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- 670

5.2.1 Urban wastewater treatment plants (WWTP)

Urban WWTP effluents can contain high quantities of dissolved zinc (up to 200 µg/L, Table 671 S1). The Zn concentrations and $\delta^{66/64}$ Zn values for raw wastewater and effluents coming from 672 medium WWTP (10,000 to 100,000 Population Equivalent (PE)) and large WWTP (> 100,000 673 PE) are presented in Fig. S5 (Chen et al., 2008, this study). Treated wastewater coming from 674 various WWTP have values for $\delta^{66/64}$ Zn generally between +0.06 and +0.08‰ (n=5, IQR, Fig. 675 S3), close to industrial effluents (+0.10 and +0.15‰, n=7, IQR) and lower than the δ $^{66/64}Zn$ 676 values for raw wastewater (+0.28 \pm 0.02‰, n = 1) and the BSE value (+0.28 \pm 0.05‰, 2 σ). 677 Previous study showed that dissolved Zn in WWTP effluent is mainly organically complexed 678 to organic ligands (Chaminda et al., 2013). However, the $\delta^{66/64}$ Zn for WWTP effluents 679 depleted in heavy isotopes compared to wastewater is not consistent with a change in 680 speciation, which tends to enrich in heavy isotopes organic complexed Zn compared to free 681 682 Zn^{2+} (see section 3).

In WWTP, wastewaters undergoes various treatment stages (primary settling, secondary 683 activated sludge and tertiary flocculation by FeCl₃) to decrease particulate metal 684 concentrations (Buzier et al., 2006). However, several studies have shown that the dissolved 685 686 metal content increases along with the wastewater treatment steps in WWTP (Buzier et al., 2006; Gourlay-Francé et al., 2011). According to Gourlay-Francé et al. (2011), various 687 assumptions may explain this increasing dissolved Zn concentration during the wastewater 688 689 treatment steps: (1) metal desorption from particles and organic matter, (2) dissolution of iron 690 salts added during the dephosphorization treatment, e.g. FeCl₃ containing high trace metal 691 concentrations. Previous studies have reported that the heavier isotopes are preferentially 692 adsorbed onto organic matter, clays and oxides (Fig. 1), so zinc desorption from particles

and organic matter should enrich the solution in heavy Zn isotopes. Therefore, treated 693 wastewater's depletion in heavy isotopes compared to untreated wastewater cannot be due 694 695 to a simple desorption process. Zinc-rich chemical components dissolving during wastewater treatment, depleted in heavy isotopes compared to untreated wastewater, may explain this 696 result. For example, the $\delta^{66/64}$ Zn signature of ferric chloride may be depleted in heavy 697 isotopes due to isotope fractionation during its industrial production process (see section 698 699 5.1.2), or to the initial Fe ore used in this process, which may be, like Zn ores, lower (+0.16%, n = 294) than the BSE value (0.28 \pm 0.05%, 2 σ). Determine the $\delta^{66/64}$ Zn signature 700 701 of ferric chloride would be necessary to verify that it is the addition of zinc-rich chemical components with low $\delta^{66/64}$ Zn value, which explains the lower $\delta^{66/64}$ Zn values for the effluents 702 produced by WWTP (+0.06 and +0.08‰, n=5, IQR) relative to the BSE value (0.28 \pm 0.05‰, 703 704 2σ).

705

706 **5.2.2 Zinc roofing**

In their study of the Seine watershed, Chen et al. (2008) analyzed roof runoff samples collected in the Paris conurbation, known for its zinc roofs. They analyzed also leached samples of zinc roof coverings. These samples contain high Zn contents (up to 2 mg/L for roof runoffs and 92 mg/L for leached sample) and their Zn isotope compositions ($\delta^{66/64}$ Zn) are generally low (between -0.10 and -0.02‰, n = 5, IRQ, Chen et al., 2008, Fig.S3) compared to that of "common zinc" (between +0.15 and +0.22‰, n = 15, IQR).

This difference of $\delta^{66/64}$ Zn values between "common zinc" and roof runoff samples is not consistent with fractionations due to metallic zinc dissolution, which tends to enrich the dissolved Zn²⁺ relative to metal Zn (Fig. S1). These differences can be due to the starting material (electrodeposited zinc?), or to a contribution from particles of industrial origin (see section 5.1.2).

719 **5.2.3 Road traffic**

Zinc emitted by road traffic can be due to non-exhaust emissions (Brake pad liners, tires,roadway equipment) and exhaust emissions (gasoline).

Non-exhaust emissions. Brake pad liners contain a large quantity of zinc (up 2% by mass) 722 mainly in the form of metal (brass), but also zinc oxide and sulfide (ZnO, ZnS, etc.) (Blau, 723 2001; Hjortenkrans et al., 2007; Legret and Pagotto, 1999). Zn isotope compositions for non-724 exhaust emissions are shown in Fig. S5. The mean $\delta^{66/64}$ Zn value for brake pads sold in 725 France and the UK is 0.19 \pm 0.08‰ (2 σ , n=3, Dong et al., 2017; this study). This value is 726 similar to "common zinc" (between +0.15 and +0.22%, n=15, IQR), which matches the fact 727 728 that zinc in the brake pads is mainly present in metal form. During tire production, zinc is added to the rubber in oxide form (ZnO) and also low quantities in the form of organo-zinc 729 compounds to facilitate vulcanization. Tires also generally contain about 1% by mass of zinc 730 (Councell et al., 2004; Legret and Pagotto, 1999). Zn isotope compositions in tires from the 731 USA, Brazil and the UK generally vary between +0.08 and +0.21‰ with a median value of 732 0.13‰ (n = 15, IQR, Dong et al., 2017; Souto-Oliveira et al., 2018; Thapalia et al., 2010, Fig. 733 S3). This slightly lower value than "common zinc" (between +0.15 and +0.22%, n = 15, IQR) 734 is probably related to fractionation during production of tires or raw materials used during 735 vulcanization. Safety barriers at roadsides are coated with zinc by hot galvanization 736 (standard ISO 1461). No analysis of safety barriers is available in the literature, however 737 since they are hot-galvanized, their Zn isotope compositions ought to be similar to that of 738 "common zinc" (between +0.15 and +0.22%, n = 15, IQR). 739

Exhaust emissions. Compared with non-exhaust emissions, gasolines contain zinc, added
as additive, in a lower quantity (up to 150 μg/L of zinc, Barbusse and Plassat, 2005;
Nomngongo and Ngila, 2014). Zn isotope compositions in gasolines between -0.50 and 0.23‰ (n=2, Gioia et al., 2008) are very low compared with values in tires and brakes (Fig.
S5). It is important to note that when fuel combusts in evaporation/condensation reactions it

will also tend to reduce this heavy isotope signature compared to its initial composition (Seesection 5.1.2).

747

748 5.3. Zinc emissions from agricultural activities

749 Agricultural operations like animal and arable farming concentrate high quantities of metals, 750 particularly of zinc, which accumulate in the soil's surface layer. Sprayed inorganic and 751 organic fertilizers, and crop protection treatments, especially for vines, are particular zinc 752 sources (Gouzy and Brignon, 2014). From a study of contamination sources in agricultural 753 land and how those are used, Belon et al. (2007) have estimated that on average 0.514 kg of zinc are applied each year per hectare of Utilized Agricultural Area. For example, in France, 754 14,906 metric tons of zinc is sprayed each year on 29 million hectares of agricultural land. 755 756 The portion of substance emitted on agricultural land that reaches surface water by runoff 757 was estimated between 0.1 and 1% (mean of 0.4%) by Braun et al. (2000). From this estimate, it is possible to calculate that each year about 60 metric tons of zinc is added to 758 surface water in metropolitan France because of agricultural activity. 759

760 **Fertilizers**

Sewage sludge from water treatment plants used as fertilizers generally contains more than 761 500 mg/kg of zinc (Eriksson, 2001; Meeddat, 2009). Organic fertilizers also include animal 762 763 waste from manure and slurry. Effluents from pig farming contain several hundreds of mg/kg 764 of zinc (Eriksson, 2001; Levasseur, 2005; Nicholson et al., 1999). These high contents are due to nutritional supplements with particularly high Zn contents that are given to animals to 765 promote growth, but also supplied from weathering galvanized metal parts present in 766 767 industrial farming (grating, tubes, etc.) (Levasseur, 2005; Levasseur and Texier, 2001; Smith 768 et al., 1962). Manure generally has lower metal concentrations than slurries, because it is diluted by hay provided that contains little metals. Bovine feces contains less zinc (around 769 770 100 mg/kg) than pig feces, but cattle producing almost 10 times as much excrement as pigs

(Brassard et al., 2012; Eriksson, 2001; Nicholson et al., 1999). With Zn contents of the order 771 of a few tens of mg/kg, inorganic fertilizers have lower Zn concentrations than organic 772 773 fertilizers and their concentration varies widely, even in products coming from a single manufacturer (Eriksson, 2001). The isotope compositions for various fertilizers are shown in 774 supplementary Fig. S5. The range of variation for "common zinc" (between +0.15 and 775 +0.22‰, n = 15, IQR) is also shown because of the many galvanized hardware present in 776 777 farms. Since we do not have data on nutritional supplements given to pigs, we used the values for $\delta^{66/64}$ Zn supplements intended for humans. These health products have quite 778 779 variable Zn isotope compositions with $\delta^{66/64}$ Zn values between +0.10 and +0.20‰ (n = 5, IQR, John et al., 2007b, Fig. S3). A study conducted by Balter et al. (2010) on sheep showed 780 781 that Zn isotope signatures in urine and feces of an animal are similar to that of their food. The 782 only manure analyzed (this study) has an isotope signature (+0.31 \pm 0.03%, n = 1) similar to that of BSE ($+0.28 \pm 0.05\%$, 2σ). It is therefore likely from an animal that was fed with feed 783 having a geogenic signature, without any nutritional supplement, which would have a lighter 784 isotope composition (John et al., 2007b) (Fig. S5). The sewage sludge analyzed by Chen et 785 al. (2008) also has a Zn isotope signature (+0.31 \pm 0.02‰, n = 1) similar to that of BSE 786 $(+0.28 \pm 0.05\%, 2\sigma)$. Pig slurries have $\delta^{66/64}$ Zn values between +0.07 and +0.24‰ (n = 3) 787 788 (Fekiacova et al., 2015; this study), which likely reflect both the Zn isotope composition of the 789 animal feed with varying supplements with variable $\delta^{66/64}$ Zn values (between +0.10 and +0.20‰, n = 5, IQR), but also reflect runoff from metal parts on the farm ("common zinc") 790 between +0.15 and +0.22‰, n = 15, IQR). 791

792 $\delta^{66/64}$ Zn values for inorganic fertilizers vary widely (between -0.06 and +0.42‰, n = 4, Chen 793 et al., 2008; Szynkiewicz and Borrok, 2016) (Fig. S5).

794 Crop protection treatments

795 Vineyards are treated by either copper-based fungicides, such as Bordeaux mixture 796 [(CuSO₄·5H₂O + Ca(OH)₂)], or other fungicides containing zinc, such as Mancozeb, a

797 dithiocarbamate (C₈H₁₂MnN₄S₈Zn) (da Rosa Couto et al., 2015). Until now, no Zn isotope analysis has been carried out on these products. The Bordeaux mixture has been widely 798 used in European vineyards since the end of the 19th century. Copper sulfate used in 799 preparing the Bordeaux mixture may contain significant amounts of zinc (Duplay et al., 800 2014). Copper sulfate is produced industrially by treating copper metal with hot concentrated 801 sulfuric acid or its oxides with dilute sulfuric acid. Chalcopyrite has $\delta^{66/64}$ Zn values generally 802 between -0.09 and +0.19‰ (n=11, IQR, Fig. S2), however given that fractionation can occur 803 804 during the extraction of copper or the production of copper oxides and sulfates, we cannot 805 use these values as a representative of the Bordeaux mixture.

806

807 6 Application of zinc isotopes to trace sources and fate of zinc in rivers

Fig. 4 summarizes Zn isotope compositions for various anthropogenic contributions compared to the BSE signature (+0.28 \pm 0.05‰, 2 σ) and to non-impacted rivers (GBSW, between +0.24 and 0.41‰, n = 127, IQR). In Fig. 4, contributions are represented by a boxplot when they are composed of more than four pieces of data. The distribution of data for the various anthropogenic contributions is in Fig. S3. The capacity of Zn isotopes to track anthropogenic contributions (mines, metallurgy, urbanization, agriculture) in surface water was applied and investigated by various studies described below.

815

816 6.1 Rivers impacted by mining activity

Rivers and groundwater in mining zones can have very high dissolved Zn concentrations (up to 70 mg/L) and $\delta^{66/64}$ Zn values generally between +0.01 and +0.29‰ (n = 99, IQR, Aranda et al., 2012; Balistrieri et al., 2008; Borrok et al., 2009; Szynkiewicz and Borrok, 2016; Wanty et al., 2013; this study) (Fig. 5). This range of $\delta^{66/64}$ Zn values is very close to that of sulfide mineralizations (between +0.05 and +0.26‰, n = 294, IQR) and solid waste and effluents present in mining areas (between +0.18 and +0.28‰, n=34, IQR). These similar isotope

signatures are due to the fact that zinc in solution in rivers and groundwater results from the 823 dissolution of zinc-rich minerals contained in ores and tailings, so this process only slightly 824 enriches the solution (Fig. 1). However, $\delta^{66/64}$ Zn values have lower heavy isotope levels for 825 samples from Sardinia (-0.10 \pm 0.24‰, 2 σ , n = 10) compared with other water courses 826 impacted by mining activity (0.16 \pm 0.42‰, 2 σ , n = 89) (Fig. 5). Wanty et al. (2013) state that 827 these signatures are due to the biologically-mediated production of hydrozincite 828 (Zn₅(CO₃)₂(OH)₆), which concentrates heavy isotopes. These results are consistent with 829 laboratory experiments and theoretical data, which showed that hydrozincite precipitation 830 tends to reduce the $\delta^{66/64}$ Zn_{dissolved} value relative to precipitate (see section 3). In conclusion, 831 832 Zn isotope signatures for rivers impacted by mining activity are close to those of natural water. This precludes the use of Zn isotopes to track mining pollution in rivers. However, Zn 833 isotope compositions are a valuable tool for highlighting secondary processes (dissolution, 834 835 precipitation, etc.) between particulate and dissolved phases (Aranda et al., 2012; 836 Skierszkan et al., 2016; Veeramani et al., 2015; Wanty et al., 2013), which control the 837 attenuation and release of zinc in surface water.

838

839

6.2 Rivers impacted by industrial activity

In their studies in the Sepetiba Bay (Brazil), Araújo et al. (2018, 2017a, 2017b) used Zn 840 841 isotope compositions for core samples of stream sediments and SPM to reconstitute a 842 timeline for changes in zinc contamination related to industrial metallurgy. From studying core samples of stream sediment, Sivry et al. (2008) and Petit et al. (2015) have also shown 843 how zinc ore-smelter activity affects the river Lot's watershed (France). In Fig. 6, the data 844 845 from these studies are mixtures between a natural GBSW contribution and an anthropogenic 846 contribution seen in the slags that is related to metallurgic activity. To date no dedicated study has been published on how industrial metallurgy activity impacts the Zn isotope 847 signature in solution in surface water. However, a recent laboratory study on lixiviation of 848 849 slags showed great diversity in Zn isotope signatures in the lixiviates (See section 5.1.2, Yin et al., 2018). The use of Zn isotope compositions to trace the impact of metallurgic activity in surface water must therefore be considered with precaution.

The contribution of atmospheric particles from metallurgical industries can be evaluated in urban aerosols because of their very low signature (between -0.38 and +0.05‰, n = 17, IQR) compared to the GBSW (between +0.24 and +0.41‰, n=127, IQR) (Dong et al., 2017; Souto-Oliveira et al., 2019, 2018). However, it is more difficult to establish the contribution of these atmospheric particles in surface water because of the physical and chemical processes (adsorption, precipitation, etc.) that take place in water (see section 3) modifying their Zn isotope signature.

Regarding the effluents discharged by different types of industries, their depleted signatures (between +0.10 and +0.15‰, n=7, IQR) compared to the GBSW (between +0.24 and 0.41‰, n = 127, IQR) ought to allow them to be traced in surface water (see section 5.1.2 concerning industrial effluents).

863

6.3 Rivers impacted by urbanization

Urbanization impacts surface water for several known reasons. One is point-source 865 discharges in the form of effluents from large WWTP; another is release by runoff and/or 866 erosion of zinc contained in emissions related to road traffic and runoff on zinc-coated roofs. 867 868 In their study on the Seine basin, Chen et al. (2008) showed how urbanization has impacted Zn isotope compositions in the river's dissolved phase (Fig. 7). For zinc in solution present in 869 the Loire, even though the contents are low (+1.3 \pm 0.8 μ g/L, 2 σ , n=10, this study) (Table 870 S2), we see slight decreases in $\delta^{66/64}$ Zn from upstream to downstream (Fig. 7). The same 871 applies for sediments and SPM taken from urban rivers and lakes (Araújo et al., 2019; Chen 872 et al., 2009b; Petit et al., 2015, 2008; Thapalia et al., 2015, 2010; this study), where 873 increased Zn content is accompanied by a lower $\delta^{66/64}$ Zn value (Fig. 7). Fig. 7 shows that 874 875 though the contribution of roof runoff may be excluded in these samples, they correspond to

876 mixtures of a natural GBSW contribution and an anthropogenic contribution due to WWTP 877 effluents and/or non-exhaust road traffic emissions.

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6.4 Rivers impacted by agricultural activity

As previously stated, little data exists on Zn isotope compositions in agricultural 880 contamination sources (fertilizer and crop protection treatment). For French watersheds that 881 882 mainly hold arable and animal farming land we see that sediments and SPM may contain high Zn contents (up to 417 mg/kg) (Table S3), but their isotope composition is similar (0.27 883 \pm 0.06‰, 2 σ , n = 6, this study) to the GBSW (between +0.24 and 0.41‰, n=127, IQR) (Fig. 884 8). This result matches Zn isotope compositions in organic fertilizers, which show similar 885 $\delta^{66/64}$ Zn values (between +0.21 and +0.31‰, n = 5, IQR) to GBSW (between +0.24 and 886 +0.41‰, n = 127, IQR) (Fig. S5). 887

888

889 6.5 Towards a multi-isotopic approach

890 Many studies have successful used a multi-isotope approach, i.e. Zn isotopes combined with other metals (Pb, Cu, etc.) to track the origin of pollution in soils and in atmospheric particles 891 (e.g. Gelly et al., 2019; Souto-Oliveira et al., 2018). In rivers and lakes, due to the same 892 chemical separation protocol, analyses of Zn isotopes are associated with Cu isotopes in 893 several studies (Araújo et al., 2019; Balistrieri et al., 2008; Guinoiseau et al., 2018, 2017; 894 Petit et al., 2008; Thapalia et al., 2010; Vance et al., 2016). Combining measurements of 895 stable Cu and Zn isotopes may be helpful for identifying the exchange processes between 896 the particulate and dissolved fractions in river. Aebischer et al. (2015) used a multi-isotopic 897 approach (Zn, Fe, and Pb) in lake sediments impacted by multiple pollution sources (mining, 898 urban, industrial, gasoline). This study highlighted the potential of a multi-isotope approach to 899 identify metal sources and pathways. However, even though it is a powerful tool, especially 900 901 in soils and atmospheric particles, the multi-isotopic approach should be used with caution in an aquatic environment. The elements used must have a common source and have close
chemical properties to be transported in similar ways in aqueous media. Another important
factor to consider is post-depositional processes, which can induce substantial isotopic
variability according to the element and can hide the initial source signatures.

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- 908

7 Summary and future directions

909 Though zinc is essential for life, in excess it may be toxic to organisms. In addition to natural zinc sources, many human activities mobilize and spread large quantities of zinc in the 910 911 environment (i.e. industry, agriculture, road traffic and treated domestic effluents). 912 Discriminating the various natural and anthropogenic zinc sources in the environment, as 913 well as understanding zinc's fate at a catchment scale in both dissolved and solid phases, is 914 a key challenge in order to take the appropriate measures to prevent degradation of the aquatic environment. Isotope approaches, especially for lead, have proven their efficiency in 915 916 tracing sources in the environment for decades. Compared to these "traditional" isotopes, the 917 worth of tracing with Zn isotopes, more recently developed (2000s), has still to be proven. 918 This review compiles the major findings of previous studies in order to evaluate the ability of Zn isotope compositions to trace metal sources at a catchment scale. 919

920 First of all, we presented the isotope fractionations due to the interactions between minerals 921 or live organisms and aqueous solutions that control how zinc is distributed between the dissolved and particulate phases in surface water and can modify the $\delta^{66/64}$ Zn initial 922 signatures of anthropogenic zinc sources. Though dissolution processes seem to slightly 923 fractionate Zn isotope signatures (-0.2 - 0.0%), the adsorption of zinc on mineral particulate 924 phases as well as its complexation onto organic compounds decreases $\delta^{66/64}$ Zn in the 925 remaining solution (~ +0.30%). Precipitation could increase or decrease $\delta^{66/64}$ Zn in the 926 remaining solution depending on the nature of the newly formed zinc-bearing minerals. 927

928 Uptake by plants and microorganisms generally increases the $\delta^{66/64}$ Zn_{dissolved} when the 929 concentration of free ions in the nutrient solution is high (>~10 µg/L).

Secondly, we summarized available data for the main natural sources of zinc, to define (1) 930 the bulk silicate earth signature (BSE, $\delta^{66/64}Zn = +0.28 \pm 0.05\%$ (2 σ)); (2) the zinc-sulfide ore 931 deposit signature $\delta^{66/64}$ Zn = +0.05 to +0.26‰, with a mean (or median) value of +0.16‰; (3) 932 coal signatures that are highly variable $\delta^{66/64}Zn = -0.10$ to +1.35% depending on the 933 diagenetic processes involved. Rivers draining natural environments generally have low 934 935 dissolved Zn concentrations (<2 μ g/L) and about 200 mg/kg in the particulate phases 936 (sediments and SPM). Zn isotope compositions in natural water, SPM and sediments vary slightly and are used to define the "geological background for surface water" (GBSW, $\delta^{66/64}$ Zn 937 = +0.24 to +0.41% with a median value of +0.30%) that is close to the BSE value. 938

939 Thirdly, the main zinc anthropogenic inputs, with their respective Zn isotope signatures as 940 well as the main processes leading to these specific isotope characteristics, can be 941 summarized as follows: (1) Solid wastes and effluents produced during mining activities have $\delta^{66/64}$ Zn values between +0.18 and +0.28‰, close to GBSW and zinc sulfide ore values; (2) 942 Slags and water leaching the slag tailings have $\delta^{66/64}$ Zn values between +0.51 and +1.20‰, 943 higher than the GBSW values due to condensation and evaporation processes during 944 945 smelting processes. Conversely, particles emitted by smelters into the atmosphere are strongly depleted in heavy isotopes, $\delta^{66/64}$ Zn = -0.38 to +0.05‰ compared to GBSW values; 946 (3) Industrial effluents (chemical industry, agro-food industry) have $\delta^{66/64}$ Zn between +0.10 947 and +0.15‰, lower than the GBSW values; (4) Electroplated zinc has an isotope signature of 948 $\delta^{66/64}$ Zn = -0.56 to -0.20‰, depleted in heavy isotopes relative to GBSW values because of 949 isotope fractionation during the process, while zinc plated by hot-dip galvanization should 950 have $\delta^{66/64}$ Zn values close to "common zinc" (+0.15 to +0.22%), slightly depleted in heavy 951 952 isotopes compared to GBSW values; (5) Particles released into the atmosphere from combustion in power plants should present wide $\delta^{66/64} Zn$ variation because of the isotope 953 variability of the burned material. For instance, the $\delta^{66/64}$ Zn of coal varies between -0.10 and 954

+1.35‰, and covers the range of GBSW values; (6) Treated wastewater effluents have 955 $\delta^{66/64}$ Zn between +0.06 and +0.08‰, lower than the GBSW values, possibly due to zinc-rich 956 957 chemicals added during water treatment processes; (7) The $\delta^{66/64}$ Zn for zinc roof runoff is lower (-0.10 to -0.02‰) compared to GBSW values; (8) Non-exhaust emissions resulting 958 from road traffic have $\delta^{66/64}Zn = +0.11$ to +0.21‰, slightly depleted in heavy isotopes 959 compared with GBSW values. Note that non-exhaust emissions and zinc-plated by hot-dip 960 galvanization have close $\delta^{66/64}$ Zn values because they are both derived from "common Zn". 961 The little data available for gasoline show that $\delta^{66/64}$ Zn are strongly depleted in heavy 962 isotopes (between -0.50 and -0.23‰) compared to GBSW values; finally; (9) Organic 963 fertilizers have $\delta^{66/64}$ Zn values = +0.21 to +0.31% close to the GBSW values. Mineral 964 fertilizers have wide variations (-0.06 to +0.42‰) that cover the range of GBSW values. Note 965 966 that no data are available for crop protection treatments, which can have high Zn contents.

967 Finally, among the environmental studies based on Zn isotopes that track zinc sources in968 rivers:

969 (1) Rivers impacted by acid-mine drainage present, in addition to potentially high Zn 970 concentrations, similar $\delta^{66/64}$ Zn levels to sulfide mineralization because dissolution causes 971 very little fractionation. However, secondary processes (e.g. precipitation and adsorption) 972 can produce Zn isotope shifts.

(2) The impact of the metallurgical industry on river basins has been studied through solid 973 materials (sedimentary cores, stream sediments and SPM) demonstrating that $\delta^{66/64}$ Zn in 974 these particulate phases results from mixing between the natural background and an 975 anthropogenic end-member represented by slags. These studies showed that Zn isotope 976 composition is a powerful tool for tracking the anthropogenic source of slags in particulate 977 978 phases of rivers. No studies report data on the dissolved phase in rivers impacted by metallurgical activities; however, since the weathering of slags leads to a wide range of Zn 979 isotope compositions, it seems that tracking their contribution in surface water would be 980 981 impractical.

(3) The impact of urbanization includes several types of zinc sources (WWTP effluents, road-982 traffic emissions, and zinc-covered roof runoff). WWTP effluents and non-exhaust traffic 983 emissions with their close $\delta^{66/64}$ Zn signatures will be difficult to discriminate. The Zn isotope 984 985 compositions for dissolved loads, sediments and SPM sampled in urban rivers and lakes are 986 a mix between the natural background and an anthropogenic end-member represented by WWTP effluents, and/or non-exhaust road traffic emissions. Though not allowing a clear 987 distinction between all types of urban zinc sources, $\delta^{66/64}$ Zn signatures are an efficient tool for 988 tracking a global urban contribution in rivers. 989

(4) The impact of agriculture is poorly documented to date. Though the scarce data available
do not reveal significant isotope shifts compared to the GBSW, this needs to be further
investigated as agriculture is a major source of diffuse zinc at a catchment scale.

993 On this basis, we highlight research needs and propose future work to make Zn isotopes a 994 relevant tracer of zinc and associated trace metals sources and fate at a catchment scale:

(1) As has been done for lead isotopes, the Zn isotope characterization of anthropogenic
sources needs to be further investigated. In particular, it will be necessary to increase
the number of samples analyzed to create an exhaustive reference database. Zn
emissions from agricultural activities, which are a major source of zinc at a catchment
scale, have to be widely studied.

(2) Zn isotope fractionations linked to processes (biologically mediated or not) that control the distribution of metals between the dissolved and particulate phases in surface water need to be better understood. A multi-technique approach coupling Zn isotope signatures in natural and experimental samples with theoretical studies using *ab initio* calculations to predict isotope fractionation and X-ray absorption spectroscopy to establish zinc speciation will be necessary for understanding the dominant processes that play a role in zinc mobility.

(3) Anthropogenic metal releases into the environment often combine zinc with other metals
 (e.g. Cu in WWTP effluents and Pb in gasoline). In rivers impacted by multiple sources

of pollution, it is necessary to combine Zn isotopes with other metal isotopes to clearly evaluate the impact of various anthropogenic contributions. Moreover, coupling zinc and a combination of carefully selected metal isotopes would take us further in understanding the fate of metals in the different compartments of a river basin by constraining various physical and chemical processes governing the metal distributions between particulate and dissolved phases.

(4) Using new sampling techniques should be considered, for example passive DGT
samplers (Diffusive gradients in thin films) to determine Zn isotope composition in
surface water. DGT can pre-concentrate metals in situ and provide an isotope
composition of water integrated over time. Moreover, DGT-measurable metal fractions
are also considered as a proxy for the dissolved bioavailable metal fraction, which is a
key factor when considering how metals impact the environment.

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1583 Figures



1585 Fig. 1. Summary of the main physical and chemical processes altering the isotope compositions of zinc in the 1586 environment: adsorption onto mineral particles and biological surfaces, organic complexation, mineral phase 1587 precipitation/dissolution, zinc medium uptake by microorganisms and plants (Archer et al., 2004; Arnold et al., 1588 1589 2015, 2010b; Aucour et al., 2015, 2011; Balistrieri et al., 2008; Ban et al., 2002; Bryan et al., 2015; Caldelas et al., 2011; Couder et al., 2015; Coutaud et al., 2014; Dong and Wasylenki, 2016; Fernandez and Borrok, 2009; 1590 Gélabert et al., 2006; Gou et al., 2018; Guinoiseau et al., 2016; Houben et al., 2014; Jamieson-Hanes et al., 1591 2017; John et al., 2007a; John and Conway, 2014; Jouvin et al., 2012, 2009; Juillot et al., 2008; Kafantaris and 1592 Borrok, 2014; Nelson et al., 2017; Pokrovsky et al., 2005; Samanta et al., 2018; Smolders et al., 2013; Tang et al., 1593 2016; Veeramani et al., 2015; Viers et al., 2007; Wanty et al., 2013; Weiss et al., 2005).



Fig. 2. Zinc isotope compositions for sulfide ores (n=294) and non-sulfide ores (n=23) (Aranda et al., 2012; Araújo et al., 2017a; Chapman et al., 2006; Deng et al., 2017; Duan et al., 2016; Gagnevin et al., 2012; John et al., 2008; Kelley et al., 2009; Maréchal et al., 1999; Mason et al., 2005; Mattielli et al., 2009; Mondillo et al., 2018; Novak et al., 2016; Pašava et al., 2014; Shiel et al., 2010; Sivry et al., 2008; Skierszkan et al., 2016; Sonke et al., 2008; Voldrichova et al., 2014; Wanty et al., 2013; Weiss et al., 2007; Wilkinson et al., 2005; Zhou et al., 2014). The mean value for each sample type is represented by a black cross. Box-plots are drawn for sulfide ore data in blue and for non-sulfide ore data in red. The vertical gray line labeled "BSE" is the mean of bulk silicate earth: 0.28 ± 0.05‰ (2o) (Chen et al., 2013).



Fig. 3. $\delta^{66/64}$ Zn value versus zinc content for dissolved zinc (n=63) and solid zinc (suspended particulate matter and sediment) (n= 129) in non-impacted rivers and lakes ([Zn]_{dissolved} $\leq 2 \mu g/L$, [Zn]_{particulate} $\leq 2 \mu g/L$) (Araújo et al., 2019, 2018, 2017a, 2017b; Chen et al., 2014, 2009b, 2008; Guinoiseau et al., 2018, 2017; Little et al., 2014; Petit et al., 2015, 2008; Sivry et al., 2008; Thapalia et al., 2015, 2010; this study). Error bars represent the 2 σ associated with $\delta^{66/64}$ Zn values. Data are also represented with blue box-plots for dissolved zinc in non-impacted rivers without estuary samples (n=46) and solid zinc in non-impacted rivers without Amazon samples (n=81).The horizontal gray line labeled "BSE" is the mean of Bulk Silicate Earth: 0.28 ± 0.05‰ (2 σ) (Chen et al., 2013).





1617 Fig. 4. Zinc isotope compositions for the various anthropogenic contributions: mining contribution (n=34), slags 1618 and slag effluents (n=16), particles zinc smelters (n=17), "common zinc" (n=15), particles in power plants (n=6), 1619 industrial effluents (n=7), WWTP effluents (=5), zinc roof runoff (n=5), non-exhaust road traffic emission (n=18) 1620 and organic fertilizer (n=5) are represented with box-plots (Aranda et al., 2012; Bigalke et al., 2010; Chen et al., 1621 2008; Cloquet et al., 2006; Couder et al., 2008; Dong et al., 2017; Fekiacova et al., 2015; Gelly et al., 2019; John 1622 et al., 2007b; Juillot et al., 2011; Mattielli et al., 2009; Ochoa Gonzalez and Weiss, 2015; Shiel et al., 2010; Sivry 1623 et al., 2008; Skierszkan et al., 2016; Souto-Oliveira et al., 2018; Thapalia et al., 2010; Yin et al., 2018; this study). 1624 "Hot dip" galvanized materials (n=3), zinc electroplated hardware (n=3), exhaust road traffic emission (n=2) and mineral fertilizer (n=4) are represented by dot symbols (Chen et al., 2008; Gioia et al., 2008; Szynkiewicz and 1625 Borrok, 2016). The estimated values for slags and particles coming from zinc smelter, for electrogalvanized 1626 hardware and for particles issued from coal combustion and waste incineration are also represented with 1627 1628 horizontal lines. Dissolved zinc in non-impacted rivers (n=46), solid zinc in non-impacted rivers (n=81) and 1629 "geological background for surface water" (GBSW) (n= 127) are represented by box-plots. The BSE value (+0.28 1630 \pm 0.05‰, 2 σ) and the non-impacted river domain are represented by vertical lines (Chen et al., 2013).



1633 Fig. 5. $\delta^{66/64}$ Zn value versus zinc content for dissolved zinc in rivers and groundwater in mining area (n=107) (Aranda et al., 2012; Balistrieri et al., 2008; Borrok et al., 2009; Szynkiewicz and Borrok, 2016; Wanty et al., 2013; 1634 this study). Error bars represent the 2σ associated with $\delta^{66/64}$ Zn values. The mean value for each type of samples 1635 (USA & France, and Sardinia) is represented by a black cross. Data are represented with light blue box-plot for 1636 1637 "geological background for surface water" (GBSW) (n= 127), pink box-plot for rivers and groundwater in mining area (n=107), with green box-plot for mining solid wastes and effluents (n=34) and with blue box-plot for sulfide 1638 1639 ores (n=294). The gray line labeled "BSE" is the mean of bulk silicate earth: $0.28 \pm 0.05\%$ (2 σ) (Chen et al., 1640 2013).



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Fig. 6. $\delta^{66/64}$ Zn value versus zinc content for sediments and suspended particulate matter in river and bay impacted by metallurgical industries (n=100)(Araújo et al., 2018, 2017a, 2017b; Petit et al., 2015; Sivry et al., 2008). Error bars represent the 2 σ associated with $\delta^{66/64}$ Zn values. Data are represented with light blue box-plot for "geological background for surface water" (GBSW) (n= 127) and pink box-plot for slag (n=11). The estimated values for slags are also represented with a pink line. The gray line labeled "BSE" is the mean of bulk silicate earth: 0.28 \pm 0.05‰ (2 σ) (Chen et al., 2013). The black dashed lines represent theoretical mixing lines between the range of values for "GBSW contribution" and for the "anthropogenic component" due to metallurgical activities (i.e. slags).

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1655 **Fig. 7.** $\delta^{66/64}$ Zn value versus zinc content for urbanized rivers and lakes (a) dissolved load (n=46), (b) sediments 1656 and suspended particulate matter (n=96) (Araújo et al., 2019; Chen et al., 2009b, 2008; Petit et al., 2015, 2008; Thapalia et al., 2015, 2010; this study). Error bars represent the 2σ associated with $\delta^{66/64}$ Zn values. Data are 1657 1658 represented with light blue box-plot for "geological background for surface water" (GBSW) (n= 127), pink box-plot 1659 for WWTP effluents (n=5), brown box-plot for roof runoff (n=5), and red box-plot for non-exhaust road traffic 1660 emissions (n=18). The gray line labeled "BSE" is the mean of bulk silicate earth: $0.28 \pm 0.05\%$ (2 σ) (Chen et al., 1661 2013). The dashed lines represent theoretical mixing lines between the range of values for "GBSW contribution" 1662 and the "anthropogenic components" due to effluents, roof runoff and road traffic contributions.



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Fig. 8. $\delta^{66/64}$ Zn value versus zinc content for sediments and suspended particulate matter in rivers impacted by agriculture activities (n=6) (this study). Error bars represent the 2σ associated with $\delta^{66/64}$ Zn values. Data are represented with light blue box-plot for "geological background for surface water" (GBSW) (n= 127), and orange box-plot for organic fertilizer (n=5). The gray line labeled "BSE" is the mean of bulk silicate earth: 0.28 ± 0.05‰ (2 σ) (Chen et al., 2013).

