# Assessment of the metal contamination evolution in the Loire estuary using Cu and Zn stable isotopes and geochemical data in sediments

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#### Abstract :

In this work, a multi-elemental approach combining Cu and Zn stable isotopes is used to assess the metal contamination evolution in the Loire estuary bulk sediments. Elemental geochemical data indicate an increase of metal concentrations from the beginning of the industrial period peaking in the 1990s, followed by an attenuation of metal contamination inputs to the estuary. Zinc isotope compositions suggest a binary mixing process between Zn derived from terrigenous material and multi-urban anthropogenic sources. Copper isotope systematics indicate a single natural dominant source represented by weathered silicate particles from soils and rocks. This work demonstrates the applicability of Zn isotopes to identify anthropogenic Zn sources in coastal systems, even under a low to moderate degree of contamination. Further studies are required to constrain Cu sources and to elucidate possible effects of grain-size and mineralogy in the Cu isotope composition of sediment in the Loire estuary.

#### Highlights

► Geochemical data and Cu and Zn isotopes were investigated in the Loire estuary. ► Cu and Zn isotope compositions of sediments vary in spatial and temporal scales. ► Zinc isotopes suggest a mixing process between terrigenous and urban sources. ► Cu isotopes indicate a natural dominant source represented by weathered material.

**Keywords** : Coastal pollution, Coastal biogeochemistry, Geochemical tracers, Metal isotopes, Trace metal, Anthropogenic contamination

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#### 1. Introduction

Estuarine ecosystems are of great importance to human development and human wellbeing. However the increasing population and intense exchange of material and energy in the coastal zones make them sensitive and vulnerable to the chemical contamination and environmental degradation (Bianchi, 2007; Agardy and Alder, 2008; Machado *et al.*, 2016; Lu *et al.*, 2018).

Particularly, the anthropogenic contamination of trace metals such as copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), silver (Ag) and mercury (Hg) is of great concern in conjunction with their concentrations and speciation, which could confer them toxicity and impose major risks for human and biota health (Adriano, 2001; Hardy and Reilly, 1999; Long *et al.*, 1995). Trace metals are released by anthropogenic activities (e.g. agriculture, industry, mining, metallurgy, energy production and transport) and dispersed among the different natural compartments such as the soil (Babcsányi *et al.*, 2016; Bigalke *et al.*, 2010; Fekiacova *et al.*, 2015a; Juillot *et al.*, 2011), the water (Araújo *et al.*, 2017a; Borrok *et al.*, 2008; Chen *et al.*, 2008; Skierszkan *et al.*, 2016; Thapalia *et al.*, 2015) and the atmosphere (Dong *et al.*, 2017; Gonzalez *et al.*, 2016; Novak *et al.*, 2016; Souto-Oliveira *et al.*, 2018). To develop correct environmental management strategies, either for remediation actions appropriately targeted as well as to maintain emissions at sustainable levels, it is imperative to identify their sources, to understand their transport and fates in the environment and to examine at what extent the anthropogenic activities affect their biogeochemical cycling.

To this end, the studies of Cu and Zn isotope biogeochemistry have been promising (Weiss *et al.*, 2007). In surface environments, the relative abundance of these isotopes can change during several biogeochemical processes including weathering and pedogenesis (Bigalke *et al.*, 2011; Fernandez and Borrok, 2009; Suhr *et al.*, 2018; Vance *et al.*, 2016), mineral precipitation/dissolution (Veeramani *et al.*, 2015; Wall *et al.*, 2011), adsorption on solid surfaces (Bryan *et al.*, 2015; Dong and Wasylenki, 2016; Guinoiseau *et al.*, 2016), ion-exchange (Maréchal and Albarède, 2002), cellular homeostasis (Caldelas *et al.*, 2011; Wanty *et al.*, 2017), redox reactions and ore refining (smelting and electroplating, (Kavner *et al.*, 2008; Sivry *et al.*, 2008a; Sonke *et al.*, 2002; Yin *et al.*, 2018, 2015). The different mechanisms of Cu and Zn isotope fractionation, *e.g.*, via kinetic or thermodynamic equilibrium, and the significant isotopic signature variability observed among different natural compartments and materials, enable these isotopes to be potential environmental indicators useful to detect trends of pollution over time periods, identifying sources of contamination and elucidate contaminant transport mechanisms (Babcsányi *et al.*, 2016; El Azzi *et al.*, 2013; Petit *et al.*, 2015; Sivry *et al.*, 2008; Thapalia *et al.*, 2015).

Sediments are the main reservoir of trace metal contaminants in aquatic environments, and thus, frequently used to diagnostic the degree of anthropogenic inputs. In coastal areas, Cu and Zn isotope compositions of sediments are mainly controlled by mixing source processes of detrital-continental, marine-autochthonous and anthropogenic materials (Araújo *et al.*, 2017b; Zhang *et al.*, 2018). In Sepetiba bay (Brazil), a site historically contaminated by electroplating wastes, Zn isotope signatures of sediment samples fit well in a ternary mixing model involving detrital terrigenous, anthropogenic and marine authigenic sources (Araújo *et al.*, 2017a,b). In the Gironde fluvial-estuarine system (France), Cu isotope compositions of suspended particulate matter were consistent with a binary mixing processes involving geogenic and anthropogenic inputs, this last one possibly related to the use of Cu sulfate fungicides in the vineyards surrounding the fluvial–estuarine system (Petit *et al.*, 2013).

In this work, we investigate spatial and temporal variations on Cu and Zn isotope compositions and trace metal concentrations of bulk sediments in the Loire estuary (France). This estuarine system has been a receptacle of chronic metal and nutrients inputs of multiple diffuse sources hosted in its fluvial-estuarine watershed (Moatar and Dupont, 2016). Consequently, increases in metal concentration and eutrophication processes have been well documented (Briant *et al.*, 2017; Dhivert *et al.*, 2016; Minaudo *et al.*, 2015). Despite a tendency of attenuation of anthropogenic inputs in the Loire river watershed in the last years (Dhivert *et al.*, 2016), metal source identification and apportionment remain unknown or incipient for most part of metal contaminants. This is in part due to the complexity of discriminating multiple sources that emerged in the past, as it is the case for Cu and Zn (Grosbois *et al.*, 2012), and also due to the difficulty to differentiate between natural and anthropogenically-influenced elements at concentrations close to geochemical baselines.

To overcome such limitations and drawbacks, we propose a combination of Cu and Zn isotope information and a multi-elemental "fingerprinting" approach of trace elements (Pb, Cd, Hg, Ag, Cu and Zn) to assess the trace metal contamination levels and evolution in the Loire estuary. We expect that spatial and temporal patterns of trace metal concentrations coupled to Cu and Zn isotope ratios on sediments can be useful to deconvolve past and current anthropogenic inputs to the estuarine system. Copper is redox sensitive and widely used as a component of agricultural fungicides (Babcsányi *et al.*, 2016, 2014; El Azzi *et al.*, 2013), while Zn is redox-insensitive and a contaminant frequently associated to urban and industrial contamination (Chen *et al.*, 2009; Souto-Oliveira *et al.*, 2018).

## 2. Methods

#### 2.1 Study area

Located in the North Bay of Biscay continental shelf, the Loire estuary (~106 km long) is the outlet the Loire River (1012 Km, surface area of 117,054 km<sup>2</sup>, mean annual water discharge of 846 m<sup>3</sup>/s), one of the largest river systems in Western Europe flowing into the Atlantic ocean (Grobois *et al.*, 2012; Coynel *et al.*, 2016). It drains crystalline and volcanic bedrocks of the southern central and western Armorican massifs, and the sedimentary bedrocks of the central Paris Basin Unit. The Loire basin has integrated along its secular history several economical activities. Firstly, based on textile, leather and fur tanning in the 16<sup>th</sup> century, and then based on exploitation of geological resources (mining and metallurgy), raw materials and energy production from the industrial revolution in the 19<sup>th</sup> century until present.

The Loire Estuary is a macrotidal system with a maximum tidal amplitude of ~6 m at the river mouth (Saint Nazaire; Fig. 1) and a water residence time estimated between 3 and 30 days during flood and low water discharge periods, respectively (Coynel *et al.*, 2016; Gallenne, 1974). The Loire Estuary basin is highly industrialized and urbanized comprising (i) the metropole region of Nantes and Saint-Nazaire cities with its more than 800,000 inhabitants, (ii) the 4<sup>th</sup> French seaport (Nantes-Saint-Nazaire harbour), (iii) one of the biggest French refinery of crude oil (Donges with a capacity of 11.5 million tons/year), (iii) the largest coal-fired thermal electricity production in France (Cordemais), and (iv) various industrial activities such as gas storage, aircraft industry, shipyards, etc. (Coynel *et al.*, 2016; Dhivert *et al.*, 2016). In addition, along the Loire river and its tributaries (Sèvre river), extend one of the main wine producers regions of France ("Loire Valley"). This overall growing economic activity has been driving a continuous industrial, agricultural and urban expansion and, consequently, imposing major risks to the coastal ecosystem (Moatar and Dupont, 2016).

## 2.2 Sampling and sample preparation

Seventeen surface sediments sites along the Loire estuary were considered for this study (Fig. 1). The corresponding surface sediments were acquired from the sample bank of the french monitoring framework ROCCH "Réseau d'Observation de la Contamination Chimique" (see ROCCH-RNO website) handled by the Institut Français de Recherche pour l'Exploitation de la Mer (Ifremer). The surface (1-2cm) sediment samples were collected using an Ekman grab in 2014. After collection, surface sediment samples were stored in plastic bags, deep-frozen, lyophilized, homogenized and sieved at 2 mm.

A sediment core labeled "PV1" (300 cm length) was sampled on the intertidal mudflat "Les Brillantes" located in the inner Loire estuary, on the bank opposite to Donges refinery plant (Fig.1), during the Paleovase mission in Mars 2015. The vibracore was collected using aluminum tubes (6 m long, 74 mm inside diameter and 1 mm thick) driven into the sediment from a barge resting on the sediment at low tide. Core PV1 was subsampled into 2 cm-thick sediment slices every 5 cm in the upper meter and every 10 cm for the rest of the sediment core. A sedimentation rate of approximately 0.7 cm/year was estimated using the <sup>210</sup>Pb technique in the upper 35 cm of the sediment core following the method of (Schmidt *et al.*, 2014). <sup>14</sup>C dating was discarded because it has been proven to give unreliable ages (inversions and inaccuracies), due to multiple factors linked mostly to estuarine hydrodynamics (e.g. erosion, remobilization of sediments, contamination by younger carbon, transport of vegetal material) (Durand *et al.*, 2016). Despite assuming a constant sedimentation rate through the entire core is very approximate, considering the inherent complications in dating estuarine systems, we are at least sure that we record the pre-industrial era. After collection, sub-samples of core PV1 followed the same sample preparation procedure as for surface sediments.

All reagents, labware acid cleaning and solution dilutions used in sample preparation and elemental and isotope analysis were performed using high purity water (18.2 M $\Omega$ .cm H<sub>2</sub>O, Nanop System®) and ultra-pure acids (PlasmaPure *Plus* grade, SCP science®). For sediment digestion, about 200 mg aliquots of dry sediments were weighted in Teflon® bombs and heated on a coated graphite block using multiple-step acid concentrated procedure with HF, HCl and HNO<sub>3</sub>. Firstly, 250 µl of HNO<sub>3</sub>, 750 µl of HCl and 6 ml of HF were added and heated at 130 °C for 4 hours. Then, samples were evaporated to dryness at the same temperature. A second acid-step with 4 ml of HNO<sub>3</sub> and 20 ml of high purity water was added and heated at 130 °C for 6 hours. Then, acid extracts were transferred to Falcon® tubes and diluted to a final volume of 50 ml with high purity water.

Aliquots of the final extract solution were split for subsequent elemental and isotope analysis. Three procedural blanks and three international certified reference materials (MESS-3 and PACS-2 from NRC – CNRC) were processed with each batch of sediment samples (n= 15 samples) and followed the complete procedure (digestion, elemental analysis, ion chromatography and isotope determination).

#### 2.3 Analytical methods

Elemental determination of Cu, Zn, Pb, Cd, Hg, Ag and Al were conducted by inductively coupled plasma mass spectrometry for the core (Q ICP-MS, iCAP Qc, KED mode, using He gas; Thermo Fisher Scientific) and surface sediments samples (Q ICP-MS, X-Series; Thermo Fisher Scientific), externally calibrated, and using internal standards (Rh and In). The accuracy

and average bias were always within 10% of the certified values of both reference materials for considered elements.

Prior to the isotope analysis, Zn and Cu were separated from matrix elements by ionexchange chromatography employing a home-made Teflon® columns filled with 2.0 ml of the anion exchange resin AG-MP1 (100-200 mesh) and a modified protocol of Maréchal *et al.*(1999), Chapman *et al.* (2006) and Borrok *et al.* (2007). The entire chromatography procedure was performed in an overpressured air-filtered cleanroom (Class 100) at the Laboratoire de Biogéochimie des Contaminants Métalliques (LBCM, Ifremer, Nantes). Recovery yielding measured by ICP-MS of chromatographic protocol was  $100 \pm 5\%$  and the total procedural blanks were below 1% of Zn and Cu mass content of the samples. For subsequent mass bias corrections, the Zn ETH standard (Archer *et al.*, 2017) was added to the Cu purified samples after the ion exchange procedure and concentration matched with the ratio 1:1, at concentrations between 100 and 300 µg ml<sup>-1</sup>. Similarly, Cu NIST-976 standard was added to the Zn purified samples.

Copper and Zinc isotopes were measured at the Pôle Spectrométrie Océan (PSO, Ifremer, Brest, France) by MC-ICP-MS (Neptune, Thermo Scientific). Samples were dissolved in 2% (v/v) HNO<sub>3</sub> and introduced into MC-ICP-MS with a stable introduction system (SIS: cyclonic spray chamber) coupled with a low flow PFA nebulizer (50  $\mu$ L min<sup>-1</sup>). The MC-ICPMS was equipped with X skimmer cone and jet sample cone and run in low resolution mode. Copper and Zinc isotope ratios were corrected for instrumental mass bias using the sample standard bracketing method combined to an exponential law. The final isotope compositions are expressed as  $\delta^{65/63}$ Cu and  $\delta^{66/64}$ Zn values reported to NIST SRM 976 and to the "JMC-Lyon" (Johnson Matthey Company, lot 3-0749-L), respectively, as follow below:

$$\delta^{66/64} Zn_{JMC} (\%_0) = \left( \frac{R \left( \frac{^{66}Zn}{^{64}Zn} \right)_{sample}}{R \left( \frac{^{66}Zn}{^{64}Zn} \right)_{ETH}} - 1 \right) x \ 10000 + \ 0.28\%_0 \quad (eq.1)$$

$$\delta^{65/63} C u_{NIST 976} (\%_0) = \left( \frac{R \left( \frac{65}{63} C u \right)_{sample}}{R \left( \frac{65}{63} C u \right)_{NIST 976}} - 1 \right) x \ 1000 \ (eq.2)$$

The Zn ETH standard data are converted to the JMC Lyon values by adding a factor of 0.28‰, as recommended by Archer *et al.* (2017). The use of data reported against JMC standard is advantageous because it allows to compare to most of Zn isotope published data (Araújo *et al.*, 2017c). The error introduced by this conversion is smaller than analytical uncertainty.

For analytical quality control, replicate of digested and purified reference materials were measured two or three times along each analytical session. The  $\delta^{65}$ Cu<sub>NIST</sub> and  $\delta^{66}$ Zn<sub>JMC</sub> average values obtained for marine sediments (MESS-3 and PACS-2) are listed in the Table 1. External precision (2s) average obtained from two to three measurements of reference materials and unknown samples was ±0.05‰ and ±0.04‰ for  $\delta^{65}$ Cu<sub>NIST</sub> and  $\delta^{66}$ Zn<sub>JMC</sub>, respectively. Uncertainty bars reported in the figures correspond to the external precision.

# 2.4 Enrichment Factor

The Enrichment Factor (EF) of trace metals is an index used to estimate anthropogenic inputs discounting dilution effects related to grain size and mineralogical heterogeneities by the normalization of a metal concentration in the sample to the concentration of a reference element (Chen *et al.*, 2009). A reference element should be associated with finer particles (related to grain size) and its concentration without significant anthropogenic influence (Barbieri, 2016). Aluminum is widely used to normalize the metal concentrations in coastal sediments since it represents the alumina-silicates (clay minerals), important bearing phase of trace elements in these systems (Chen *et al.*, 2007). In this work, EF values were calculated as follows:

$$EF = \left(\frac{(M/Al)_{Sample}}{(M/Al)_{UCC}}\right) (eq.3)$$

where "M" is the concentration of the metal of interest and "Al" is the reference element concentration, whereas (M/Al<sub>sample</sub>) represents the concentration ratio in the sample and (M/Al)<sub>UCC</sub> refers to the concentration ratio reported for the Upper Continental Crust (Rudnick and Gao, 2013, Table 1). Enrichment factor values were interpreted as suggested by Chen *et al.*, 2007: EF < 1 indicates no enrichment; EF < 3 is minor enrichment; EF = 3-5 is moderate enrichment; EF = 5-10 is moderately severe enrichment; EF = 10-25 is severe enrichment; EF = 25-50 is very severe enrichment; and EF > 50 is extremely severe enrichment.

## 2.5 Statistics

All descriptive and exploratory statistics were performed using the SPSS® software v.18.0 (IBM®, Armonk, NY, USA). The normality distribution of data was verified using Kolmogorov Smirnov and Shapiro-Wilk tests. A multivariate approach (Principal Component Analysis [PCA]) was used to examine and identify the main interrelations among the isotope and elemental variables. A correlation matrix with varimax rotation was used to calculate the factor loads (Araújo *et al.*, 2017d; Mar da Costa *et al.*, 2016). The principal components (PCs) that had eigenvalues higher than one were selected for discussion (Mulholland *et al.*, 2012). The commonality values of all variables equal or higher than 0.5 were used as criterions for PCA results acceptance.

#### 3. Results

## 3.1 Isotope and geochemical data of sediments

All elemental and isotope data of sediment samples are presented in Table 1. Calculated enrichment factor are provided in the Table 2. All measured trace metal concentration depth profiles of core PV1 display a similar pattern with proximity to the sediment-water interface. There is a trend of general increase from the ~96 cm deep horizon, followed by a peak at ~14 cm and then a sharp decline from 14 cm deep to the top of the core (Fig.2a). In the case of Hg, it is also observed a marked increase from 296 to 163 cm and occurrence of maxima at 69 and 163 cm deep. Considering a mean sedimentation rate of 0.7 cm/year along the sediment core, the 96 cm deep horizon corresponds approximately, in years, to the end of the XIX<sup>th</sup> century (~1880), and hence marks the beginning of the pre-industrial period. In turn, 14 cm deep corresponds to the mid-1990's. Enrichment factor profiles of trace metals present similar patterns as bulk concentrations data (Fig.2b). Among all studied trace metals in the sedimentary archive and surface sediments, the highest enrichment factors were observed for Ag (from 5 to 21), while lower EFs were obtained for Cd (from 1 to 10), Pb (from 3 to 9), Hg (from 0 to 9), Zn (from 1 to 4) and Cu (from 0 to 2). All trace metal concentrations are correlated with each other (Pearson correlation coefficient  $r = \sim 0.85$ , in average, n = 31) considering the whole sediment dataset.

PCA analysis were performed separately in the PV1 core and surface sediments samples to verify interrelations of the dataset in temporal and spatial scales (Fig.3a and 3b, respectively). In the PV1 core, the two extracted main components explained 88% of the variance dataset: the first component (66% of variance) encompasses the Zn, Cu, Ag, Pb, Al variables, while the second component (22% of variance) grouped Hg, Cd and  $\delta^{65}$ Cu values. In the surface sediments dataset, PCA analysis provided two main components accounting for almost 83% of the variance: the first component (69% of variance) associated Zn, Cu, Ag, Pb, Hg, Cd and Al. The second component (14% of variance) included Cd and  $\delta^{65}$ Cu variables. In similar way, the PCA analysis of PV1 core and surface sediment no appointed any correlation between the variable  $\delta^{66}$ Zn value and the other elements.

The average of Cu and Zn isotope compositions ( $\delta^{65}$ Cu and  $\delta^{66}$ Zn) of sediments are - 0.04 ±0.18 (2s, *n*= 31) and +0.24 ±0.11 (2s, *n*= 26), respectively. In core PV1 profile, the  $\delta^{65}$ Cu<sub>NIST</sub> values vary between -0.02 and +0.08‰ (average of +0.04 ±0.07‰, 2s, *n*=12, Fig. 2c), while the  $\delta^{66}$ Zn<sub>JMC</sub> values are ranged between +0.20 to +0.32‰ (average of +0.26 ±0.07‰, 2s, *n*=11, Fig. 2d). Despite these narrow ranges of isotope values, they correspond to more than two and threefold the external precision (2s), indicating detectable but subtle isotope changes in the profile core. In the surface sediments,  $\delta^{65}$ Cu<sub>NIST</sub> values are centered on -0.08 ±0.17‰ (2s, *n*= 17), while  $\delta^{66}$ Zn<sub>JMC</sub> values are around +0.24 ±0.13‰ (2s, *n*= 15).

Zinc and copper isotopes present different spatial and temporal behaviors in relation to their enrichment factors. For Zn, low and moderate correlations between Zn EF and  $\delta^{66}$ Zn values are observed in the PV1 core profile (R<sup>2</sup>= 0.43, *n* = 11, p < 0.05, Fig.4). In surface sediments were weakly correlated but not statistically significant (R<sup>2</sup>= 0.28, *n*= 14, p > 0.05, Fig. 3). For Cu, surface sediments showed a weak correlation between Cu EF and  $\delta^{65}$ Cu (R<sup>2</sup>= 0.27, *n*= 17, p < 0.05, Fig.4). In the PV1 core profile, these variables were uncorrelated (R<sup>2</sup>= 0.14, *n*= 12, p > 0.05). Despite this, it is noticed that before the pre-industrial period (from the base core to 95 cm), sub-samples of PV1 core present an average  $\delta^{65}$ Cu<sub>NIST</sub> of -0.05 ±0.02‰ (2s, *n*=3), whereas sub-samples corresponding to industrial period (96 cm deep upward), show an average of -0.11 ±0.01‰ (2s, n= 9). These  $\delta^{65}$ Cu<sub>NIST</sub> averages are statistically different (test *t*, p < 0.05).

## 4. Discussion

#### 4.1 Assessing temporal and spatial contamination of trace metals

The noticeable increase of trace metal concentrations above 96 cm deep horizon probably reflects the strong industrial development occurring during the 1880-1980 period in the Loire river watershed, while the decreasing trend from 14 cm deep upward shows the attenuation of metal contamination inputs in the 1990's (Fig.2a,b). Previous studies revealed different polymetallic contaminations along the time in the Loire river watershed (Dhivert *et al.*, 2016; Grosbois *et al.*, 2012): (i) the 1900-1950 period, marked by a severe contamination of Hg, Au

and Ag associated to mining activities; (ii) the 1950-1980 period, characterized by a pronounced increase in concentrations of Hg, Bi, Cd, Ag, Zn, Cu, Pb, Sb attributed to several sources including smelting, industrial and urban sources; and lastly, and (iii) the period 1980currently, with a noticeable trend of decreasing in metal contaminants. This decrease results of de-industrialization and industry closure in the Loire watershed (Dhivert *et al.*, 2016), increasing of the rate of recycling and/or treatment of metals within the anthroposphere (Meybeck *et al.*, 2007) and implementation of environmental regulation (e.g., the 2000 European water framework directive) on solid waste management and wastewater treatment in the local municipalities (Grosbois *et al.*, 2012). Important coal mining and burning districts in the Furan sub-basin (St. Etienne coal mining basin) and in the Bourbince–Arroux sub-basins (Blanzy–Montceau coal-basin) stopped their operations in the late 1990's (Dhivert *et al.*, 2016). In the Loire estuary, decreasing of anthropogenic Pb can also be associated to the closing of the Pb refinery (Tréfimétaux) in 1988 near Nantes, and the closing of the lead tetraethyl manufacturing plant (Kuhlmann-Octel) in mid-1990's in Paimboeuf, immediately near the location of PV1.

In the core PV1, Cu, Zn, Cd, Pb, Ag and Hg concentrations upward of 96 cm display similar temporal trends to the sedimentary geochemical records obtained upstream along the Loire River (Dhivert *et al.*, 2016; Grosbois *et al.*, 2012), although with relatively lower concentrations. Since a high proportion of sediment particles of the Loire estuary is of fluvial origin (Negrel, 1997), it is likely that part of anthropogenic metals reach the estuary via fluvial transport associated to particulate material. It is also likely that they reach the estuary after a certain time from their emission, resulting in similar but time-shifted sedimentary geochemical profiles between estuarine and fluvial systems. Human induced erosion and remobilization of deeper horizons may have mixed between layers corresponding to before the industrial period with initial coal mining activities in the Loire watershed. This possible perturbation to the progressive layering of sediment along the length of the core is likely due to dredging linked to a small boat harbor nearby. In the case of Hg and Ag, the high single point maxima at 69 and 163 cm deep may be related to such sediment reworking.

In a spatial analysis, considering the sum of all trace metal enrichment factors for each sample (Table 2, Fig.5a), it is identified an overall enrichment of trace metal in the upper estuary (downstream and upstream of Nantes (samples 1 and 2) and in one sample at the mouth of the estuary (close St Nazaire city, sample 4). This spatial pattern of enrichment is similar for Ag (Fig.5b), the most enriched trace element of the Loire estuary. The metal trace enrichment in these zones have attributed to urban inputs, including effluents from the highly urbanized sub-

watersheds and to domestic and industrial effluents from waste water treatment plants (Coynel *et al.*, 2016). The mixing of trace metal contaminated particles coming from different watershed sources along the course of the Loire river towards the estuary suggest a common mechanism of transport and dispersion in the estuarine system, which explain the fact of all trace metals are correlated among them. The PCA analysis of surface sediments (Fig.4b) also confirm a grouping of all trace elements, including Hg. In the inner estuary, fine-grained ( $<4\mu$ m) particles and metal concentrations are highly correlated in the Loire estuary (Coynel *et al.*, 2016), indicating that grain-size distribution and hydrodynamic features constitute the main controlling factors in the spatial distribution of these elements. The long-distance transport of fine-grain particles coming from the Loire estuary mouth to open ocean and posteriorly to Bourgneuf bay can explain the enrichment in metals in the samples 11, 14 and 18 (Fig. 5a). No major river drains this bay, but it is surrounded by large marshes, drained by dozens of creeks. A second source of metals could be associated to potential local anthropogenic inputs involving shipyard activity and the use of antifouling paints.

As discussed here, trace metal source identification in the Loire estuary is complex due to the presence of multi-anthropogenic activities of which the relative contributions seem to change in spatial and temporal scales (Grosbois *et al.*, 2012). In addition, both intra-estuarine and watershed-derived anthropogenic source inputs are mixed in the inner-estuary, limiting the discrimination of mixing components by elemental concentration data. Alternatives approaches using geochemical ratios (eg., Ag/Pb; Cd/Zn) have been useful to highlight the main mixing end-members in the upper Loire river, and to evidence dominance of urban sources over mining sources for some elements, such as Ag and Zn, during the period 1950-1980 (Dhivert *et al.*, 2016; Grosbois *et al.*, 2012).

## 4.2 Identifying anthropogenic and natural sources using Cu and Zn isotopes

Here we discuss Cu and Zn isotope compositions to infer possible source mixing processes of these elements in the Loire estuary. Surface sediments presented minor enrichment for Cu and Zn (EF< 3). It was observed a major Zn enrichment in the estuary mouth (samples 4, 5, 7, 8), Bourgneuf bay (samples 12, 17 and 18) and in the sample 11, while for Cu the most enriched samples were restricted to the samples 4 (estuary mouth) and samples 12 and 14 (Bourgneuf bay). It was not identified a clear relationship between  $\delta^{66}$ Zn values and  $\delta^{65}$ Cu values, enrichment factor and sample localizations for surface sediments. A study of spatial distribution of metals performed by Coynel *et al.* (2016) in surface sediments showed only high enrichment factor values (5 < EF < 10) for Zn, Pb, Cu in several sites near Nantes city, especially close to

waste water treatment plants. Instead, Negrel *et al.* (1997) verified a gradual enrichment of Zn (~33%) and Pb (~40%) in surface sediments from river outlet toward to marine environment, possibly due to contaminant emissions of inner-anthropogenic sources.

In turn, the PV1 core profile indicated minor enrichment for Cu and moderate enrichment for Zn (Fig. 2ab, Table 2) and a well-marked anthropogenic fingerprint characterized by a multi-metallic enrichment (including Cu and Zn) above 96 cm with a peak maximum of enrichment at ~14 cm (Fig. 2a, 2b, Table 2). Taking into account the EF values of Cu and Zn, the anthropogenic inputs of these metals are more evident in a temporal scale. A moderate correlation between Zn EF and  $\delta^{66}$ Zn values were observed in the core PV1 (R<sup>2</sup> = 0.43, n = 11, p < 0.05), with an overall trend toward lighter Zn isotope compositions with enrichment factor increasing (Fig.4). This trend can be interpreted as a binary mixing process between Zn derived from terrigenous material and multiple anthropogenic Zn sources. Since sediment particle transport from rivers to oceans does not alter significantly Zn isotope compositions of the particulate phase (Araújo *et al.*, 2018; Guinoiseau *et al.*, 2018), isotope ratios in the suspended sediments behave conservatively, reflecting the relative Zn contributions of natural and anthropogenic sources.

In the Loire estuary, sediments are dominantly composed of detrital minerals derived mainly from silicate rocks of the basin. Mineralogical characterization of SPM and bed sediments in the Loire estuary show an assembly of clay minerals dominated by smectites (30%), illites (33%), kaolinites (27%) and chlorites (10%) with feldspars, calcite, biotites, zircons and other accessory minerals originated from the weathering processes of intrusive rocks in the upper Loire watershed (Roger, 1988). Zinc isotope composition of the Upper Continental Crust ranges between +0.2 and +0.3‰ (Moynier *et al.*, 2017), with an estimated average value of +0.28 ±0.05‰ (2s, Chen *et al.*, 2013). The heaviest  $\delta^{66}$ Zn<sub>JMC</sub> values closer to +0.3‰ of low Zn enriched- sediments reflect the natural end-member represented by silicate rocks of the Loire watershed. This value is also very similar to unpolluted fluvial and estuarine sedimentary material (local natural background) reported in many environmental studies: (+0.28 ±0.05‰, 2s, Chen *et al.* 2013;  $\delta^{66}$ Zn =+0.31 ±0.04‰, 2s, Sivry *et al.*, 2008;  $\delta^{66}$ Zn =+0.31 ±0.09, 2s, Sonke *et al.*, 2008).

Common urban anthropogenic Zn present lighter  $\delta^{66}$ Zn<sub>JMC</sub> values than Upper Continental Crust, such as tire wear (from +0.00 to +0.20‰, Souto-Oliveira *et al.*, 2018; Thapalia *et al.*, 2015), vehicle emissions (-0.87 to +0.07‰, Gioia *et al.*, 2008), urban runoff (from +0.13 to +0.15‰, Chen *et al.*, 2009), wastewaters and sludge (~0.1‰; Chen *et al.*, 2009) and atmospheric industrial emissions (< -0.6‰, Souto-Oliveira *et al.*, 2018; from -0.52 to

+0.02‰, Mattielli *et al.*, 2009; from -0.27 to +0.15‰, Ochoa *et al.*, 2016). The large variability of isotope compositions of urban sources is due to different isotope fractionation mechanisms in the anthropogenic Zn cycling involving the ore refining, where high-temperature processes employed during roasting and smelting of ores tend to fractionate zinc isotopes in the gas phase, with an enrichment of the lightest isotopes in air emissions and heavier isotopes in slags and effluents (Yin *et al.*, 2015). The final metallic Zn product (Zn<sup>0</sup>) remain with signatures similar to the average of original concentrated ores (Sivry *et al.*, 2008b; Sonke *et al.*, 2008; Yin *et al.*, 2015). Other studies show that electroplating solid wastes are also enriched in the heaviest isotopes (Araújo *et al.*, 2017a,b).

In the urban environment, runoff on streets, commercial areas and roofs, atmospheric leaching by rainwaters and inputs from domestic and industrial wastewaters are connected to urban sewage network (Grosbois *et al.*, 2012). The mixing of multi-diffuse sources of Zn in the sewage effluents can lead to a homogenous "Zn urban fingerprint", which would explain the identification of a single anthropogenic end-member in the Loire estuary, in both temporal and spatial scales. Analogous Zn binary source mixing setting was observed in the Seine river (France, Chen *et al.*, 2009) involving natural silicate particles transported by river (~0.3‰), and anthropogenic particles derived from wastewater treatment plants or combined sewer overflows (~0.1‰). Likewise for urban lakes of United States of America, Zn source mixing processes comprise a natural end-member (+0.35‰) and other anthropogenic (+0.10‰), related to vehicle sources (tire wear and emissions, Thapalia *et al.*, 2015).

Considering the punctual anomalous enrichment factor of Zn close to waste water treatment plants (Coynel *et al.*, 2016) and the evidence for a homogenous "Zn urban fingerprint", we propose a representative signature of +0.1% to be the main urban anthropogenic source in the Loire estuary. The value of +0.1% as suggested for the anthropogenic end-member in the Loire estuary and Seine River are in line with the ranges from +0.1% to +0.2% attributed to "common" anthropogenic Zn proposed by John *et al.* (2007), based on measurement of a wide variety of materials (electrochemically purified Zn, galvanized steel, electroplated materials, vitamins, laboratorial standards, health products, etc.).

Because natural and anthropogenic ranges of Zn signatures in the Loire estuary are relatively small,  $\delta^{66}$ Zn<sub>JMC</sub> values of some samples overlap partially with both sources, taking into account analytical uncertainties. This partial overlap can lead to a decreasing of resolution for source discrimination and thereby, compromising a precise quantification of source contributions. A theoretical mass balance with different anthropogenic sources reported in the literature illustrate how source discrimination resolution can vary depending of Zn contamination context (Fig.6). This theoretical model estimates that natural terrigenous and urban anthropogenic end-members of Zn overlap for an anthropogenic contribution lesser than 70% of Zn (total mass) in the sample. Therefore, the identification, discrimination and quantification of anthropogenic Zn is difficult due the low degree of Zn enrichment in the investigated samples. This is the case of surface sediments, which were collected in 2014 year, in a period of attenuated Zn contamination. The weak and not significant correlation between  $\delta^{66}$ Zn<sub>JMC</sub> values and Zn EF values (R<sup>2</sup>= 0.28, *n*= 14, p > 0.05, Fig.4) exemplify the difficulty of determining the anthropogenic or natural origin of Zn in these samples. Anyway, a light isotope composition in the sample 1, located in the upper estuary (Fig.5d) is consistent with the urban Zn isotope signature of proposed binary source model.

Copper concentrations were low and variations of Cu isotope compositions on spatial and temporal scale were weakly or no-correlated with Cu EF values. Then, identification of source mixing processes using the Cu isotope dataset is not evident. This may be result of: (i) a possible overlap between anthropogenic *vs.* natural isotope signatures or, (ii) the predominance of natural Cu origin over anthropogenic one, as supported by Cu EF values. The overall  $\delta^{65}$ Cu<sub>NIST</sub> values of the studied sediment samples (-0.04 ±0.18, 2s, *n*= 31) are close to the average of the Upper Continental Crust (+0.07± 0.10‰, Liu *et al.*, 2015; Savage *et al.*, 2015) and fell in the range reported for sedimentary materials from estuaries and river worldwide (Guinoiseau *et al.*, 2018; Vance *et al.*, 2016, 2008). An overall tendency of enrichment in the light isotope of sediments in relation to the UCC have been attributed to an isotope partitioning between dissolved and particulate phase during weathering processes, involving the formation of aqueous organic complexes enriched in the heavy isotope and residual particulate phases (Fe-Mn oxyhydroxides, clay minerals) enriched in the light isotopes (Guinoiseau *et al.*, 2018; Vance *et al.*, 2008).

The main potential anthropogenic Cu sources in the Loire river watershed include urban sources, run-off from vineyard soils and anti-fouling paints employed into embarkations. Souto-Olveira *et al.* (2018) reported several values for urban sources with positive  $\delta^{65}$ Cu<sub>NIST</sub> values: cement ( $\delta^{65}$ Cu<sub>NIST</sub>=+0.30 to +0.61‰); road dust ( $\delta^{65}$ Cu<sub>NIST</sub>=+0.08 to +0.25‰), and vehicular traffic ( $\delta^{65}$ Cu<sub>NIST</sub>=+0.46 to +0.59‰); similar enrichment in the heavy isotope have been reported in antifouling paint (+0.54 ±0.03) and contaminated sediments in the Port Camargue (French mediterranean sea, Briant *et al.*, 2013). Commercial Cu-based fungicides applied in vineyards and remaining in their soils range from -0.35 to +0.91‰ (Babcsányi *et al.*, 2016; El Azzi *et al.*, 2013). The widely applied fungicide Bordeaux mixture (CuSO<sub>4</sub>+Ca(OH)<sub>2</sub>) has light isotope values ( $\delta^{65}$ Cu<sub>NIST</sub>=-0.35‰, El Azzi *et al.*, 2013;  $\delta^{65}$ Cu<sub>NIST</sub>=-0.06‰, Babcsányi *et al.*, *et al.*, 2013;  $\delta^{65}$ Cu<sub>NIST</sub>=-0.06‰, Babcsányi *et al.*, 2013;  $\delta^{65}$ Cu<sub>NIST</sub>=-0.06‰, Cu<sub>NIST</sub>=-0.06‰, Babcsányi *et al.*, 2013;  $\delta^{65}$ Cu<sub>NIST</sub>=-0.06‰, Babcsányi *et al.*, 2013;  $\delta^{65}$ Cu<sub>NIST</sub>=-0.06‰, Cu<sub>NIST</sub>=-0

2016) close to the vineyard soils around Bordeaux city, France ( $\delta^{65}$ Cu<sub>NIST</sub>=-0.37‰ and -0.28‰, Petit *et al.*, 2013). Considering this small dataset available in the literature, and in analogy with the previous Zn discussion, positive  $\delta^{65}$ Cu<sub>NIST</sub> values of urban sources and use of antifouling paints could explain the positive trend between Cu isotope compositions and Cu EF (Fig.3). In turn, run-off of contaminated vineyard soils in the Loire catchment could explain the small shift toward lighter isotope compositions above 96 cm depth in the PV1 core. However, the range of  $\delta^{65}$ Cu<sub>NIST</sub> values of fungicides is wide enough to overlap with those reported for unpolluted soils and sediments, making source discrimination using Cu isotopes uneasy (Fekiacova *et al.*, 2015). Similar drawbacks were verified in soils contaminated by Cu-fungicide, where anthropogenic, pedogenic and geogenic isotope signatures overlapped partially among them (Babcsányi *et al.*, 2016; El Azzi *et al.*, 2013).

Considering the exclusive natural Cu origin, the subtle spatial and temporal changes on Cu isotope ratios could be associated to relative variations on distribution of sediment components such as clay minerals, amorphous solids and organic matter. Determination of isotope compositions in specific phases of sediment using traditional sequential extractions protocols have demonstrated the isotope heterogeneity of different geochemical components in vineyard soils (El Azzi *et al.*, 2013): copper in silicate residual fractions was close to local bedrock ( $\delta^{65}$ Cu<sub>NIST</sub> +0.07‰), while in water soluble fraction of SPM was similar to dissolved river Cu ( $\delta^{65}$ Cu<sub>NIST</sub> = +0.26‰). Copper from fungicide treatment ( $\delta^{65}$ Cu = -0.35‰) was bound to organic matter ( $\delta^{65}$ Cu<sub>NIST</sub> = -0.20‰) without or with slight isotopic fractioning, while Cu adsorbed onto iron oxides were enriched in the heavy isotope ( $\delta^{65}$ Cu = +0.5‰).

Other controlling factors could be associated with hydrological sorting of particle-size along the estuary. Analysis of silt and fine clays fractions of soils showed distinct Cu isotope compositions ( $\pm 0.23 \pm 0.07\%$  and  $\pm 0.37 \pm 0.10\%$ , respectively, Babcsányi *et al.*, 2016). In the Loire estuary, particle sorting and grain-size compositions of surface sediments are highly variable with the proportion of mud (silt+clay) and sand ranging from 0% to 89% and from 3% to 100%, respectively (Coynel *et al.*, 2016). In the inner-estuary, there is a general trend to increasing grain sizes from upstream to downstream, despite coarse can occur in areas affected by buildings of channels navigation close to urban zones (Coynel *et al.*, 2016). Thus, an open question remains whether anthropogenic actions (i.e. dredging of navigation channel and urban development, landscape use changes) modify particles-size and mineralogy distribution, and hence induce changes on Cu isotope composition of sediments. Further investigations probably could elucidate the apparently contrasted isotope signatures obtained for samples 1 and 18.

Considering the low Cu EF values, the hypothesis of a predominant natural origin of Cu over anthropogenic one seems more plausible. As proposed by Coynel *et al.* (2016), anthropogenic influence on the Cu and Zn concentrations in the Loire estuary is restricted to punctual sites. Further studies that increase sampling sites are required to better constrain anthropogenic sources inputs in the estuary and test these models. Here we suggest that the Cu isotope compositions of sediments in Loire estuary, at least at the studied stations reflect mostly the signature of weathered silicate particles. They are derived from soils and rocks of fluvial-estuarine watershed, with their isotope ratios close to those reported for Upper Continental Crust, but with a slight overall tendency of enrichment in the light isotope.

## 4. Conclusions

Metal trace concentrations and Cu and Zn isotopes were used to identify past and current anthropogenic inputs in the Loire estuary. The order of metal enrichment in the sedimentary archive and surface sediments follow Ag > Pb > Cd > Hg > Zn > Cu. In a temporal scale, it recorded an increase of metal concentrations from the beginning of the industrial period and an ongoing attenuation of metal contamination inputs in the Loire estuary in the 1990's. In the inner-estuary, grain-size distribution and hydrodynamic features constitute the main controlling factors in the spatial distribution of these elements.

Zinc isotopes can be used to identify a binary mixing process between Zn derived from terrigenous material, and Zn issued from multi-urban anthropogenic sources. However, because natural and anthropogenic ranges of Zn signatures in the Loire estuary are relatively narrow, a precise quantification of anthropogenic contribution in the samples is difficult, if samples present a very low degree of Zn enrichment. In turn, Cu isotope compositions of sediments in the Loire estuary are controlled by natural sources, reflecting the signature of weathered silicate particles derived from soils and rocks of the Loire river watershed.

In conclusion, this work demonstrates the applicability of Zn isotopes to detect anthropogenic sources in coastal systems, even under a relatively low degree of contamination. Increasing the details of sampling and additional characterization parameters (e.g., sequential leaching, mineralogy, granulometry, fine solid speciation, etc...) in the Loire estuary may help to detect possible diffuse anthropogenic sources of Cu, as well as to better understand the role of grain-size and adsorption processes on mineral surfaces in the isotope fractionation along the estuary.

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Fig.1 The Loire estuary location and sampling sites of surface sediments (star) and a sediment core (PV1 core, pentagon).



**Fig 2.** Profiles of trace element concentrations and Cu and Zn isotope compositions in the PV1 core. The Cu and Zn isotope composition ranges of Upper Continental Crust for Cu and Zn are compiled in Table 1. Zinc urban anthropogenic source refers to values reported by John *et al.*(2008) and Chen *et al.*(2009). The value of the pesticide namely "Bordeaux mixture" is reported by (El Azzi *et al.*, 2013,  $\delta^{65}$ Cu<sub>NIST</sub> = -0.34‰)



Fig.3 Principal Component Analysis (PCA) performed in the (a) PV1 core and (b) surface sediments datasets.



Fig.4 Dispersion plots of enrichment factors and  $\delta^{65}Cu_{NIST}$  and  $\delta^{66}Zn_{JMC}$  values of surface sediments and PV1 core subsamples.



**Fig.5** Spatial data distribution of surface sediments: (a) plot of the sum of trace metal EF values ( $\Sigma$ EF) in the samples; (b) plot of Ag EF values. The EF values and delta values of Cu and Zn are presented in (c) and (d), respectively.



Anthropogenic source contribution

**Fig.6** Theoretical binary mixing source processes between natural ( $\delta^{66}$ Zn<sub>JMC</sub> = +0.25‰, starting point) and anthropogenic end-members: electroplating wastes ( $\delta^{66}$ Zn<sub>JMC</sub> = +0.86‰, electroplating wastes); urban sources ( $\delta^{66}$ Zn<sub>JMC</sub> = +0.1‰, Chen *et al.*, 2009; Thapalia *et al.*, 2015); atmospheric industrial emissions ( $\delta^{66}$ Zn<sub>JMC</sub> = -1.5‰, Souto-oliveira *et al.*, 2018). Hypothetical samples with less 70% of urban source contribution fell in the in the same range of Upper Continental Crust (+0.28 ±0.05‰, 2s, Chen *et al.* 2013).

Sample/sampling site	Code	δ <sup>65</sup> Cunist (‰)	2s	δ <sup>66</sup> Zn <sub>JMC</sub> (‰)	2s	[Cu] (mg.kg <sup>-1</sup> )	[Zn] (mg.kg <sup>-1</sup> )	[Cd] (mg.kg <sup>-1</sup> )	[Pb] (mg.kg <sup>-1</sup> )	[Hg] (mg.kg <sup>-1</sup> )	[Ag] (mg.kg <sup>-1</sup> )	[Al] (%)
surface sediment												
Sainte Luce	1	0.08	0.04	0.16	0.05	26.2	126	0.24	64.3	0.09	0.45	6.2
Indre	2	-0.06	0.04	0.27	0.02	26.2	126	0.24	64.3	0.09	0.45	6.2
Pont de Saint-Nazaire	3	-0.24	0.06	0.31	0.01	11.7	63	0.14	45.1	0.06	0.34	4.9
Face pointe de Mindin	4	-0.10	0.05	-	-	35.8	179	0.21	65.7	0.14	0.54	6.8
St Brévin Mindin	5	-0.15	0.02	0.15	0.05	30.9	168	0.16	63.4	0.09	0.48	7.4
Villes - Martin	6	-0.16	0.03	0.33	0.00	6.2	40	0.03	38.0	0.02	0.15	4.6
Face St Brévin	7	-0.15	0.01	0.29	0.19	23.1	127	0.17	53.9	0.07	0.42	6.2
Est Petit Gavi	8	-	-	0.18	0.02	25.4	142	0.15	53.8	0.10	0.44	6.3
Grand Traict 2	9	-0.13	0.08	-	-	6.5	53	0.09	27.4	0.01	0.21	3.5
Ouest Lancastria	10	-0.12	0.07	0.25	0.02	12.1	82	0.13	40.3	0.04	0.26	5.2
Sud phare de la Banche	11	-0.03	0.05	0.19	0.09	28.1	158	0.2	57.9	0.11	0.43	6.4
Mariolle	12	-0.10	0.00	0.25	0.10	36	164	0.24	63.6	0.12	0.61	6.8
Noirmoutier	13	-0.15	0.06	0.13	0.15	7.3	52	0.12	23.9	0.02	0.15	3.0
Embarcadère	14	0.07	0.08	-	-	14	32	0.18	15.8	0.02	0.11	2.0
Coupelasse Nord	15	-0.11	0.04	0.30	0.00	12.9	95	0.1	34.3	0.04	0.22	4.7
Banc de Bourgneuf	16	-0.09	0.04	-	-	17.5	125	0.1	48.2	0.06	0.38	5.5
Loire 26	17	-0.06	0.03	0.18	0.01	21.1	147	0.09	55.5	0.08	0.34	6.8
Sennetière	18	0.05	0.15	0.25	0.10	9.6	71	0.17	30.6	0.04	0.22	3.4
Paleovase sediment Core PV1 (depth)												
1 cm	PV_1	0.00	0.06	0.27	0.02	32	178	0.40	88	0.15	0.67	7.3
6 cm	PV_6	0.02	0.00	0.29	0.05	33	183	0.60	91	0.19	0.64	7.0
9 cm	PV_9	0.02	0.02	0.25	0.01	35	200	0.59	103	0.20	0.73	7.1
14 cm	PV 14	0.02	0.01	0.25	0.04	41	225	0.67	134	0.23	0.92	7.6

Table 1. Geochemical data and Cu and Zn isotope compositions of sediments in the Loire estuary.

21 cm	PV_21	0.01	0.04	0.20	0.01	45	237	0.70	132	0.22	1.00	7.7
35 cm	PV_35	-0.02	0.21	0.25	0.05	40	212	0.69	124	0.21	1.02	7.4
42 cm	PV_42	0.06	0.01	0.27	0.00	42	219	0.73	106	0.21	0.93	7.4
69 cm	PV_69	0.06	0.04	0.21	0.05	44	233	0.79	116	0.24	0.95	7.4
96 cm	PV_96	0.02	0.04	0.32	0.02	27	159	0.55	76	0.19	0.52	6.4
163 cm	PV_163	0.08	0.03	0.28	0.01	31	188	0.73	83	0.24	0.60	6.8
210 cm	PV_210	0.06	0.02	0.24	0.09	28	162	0.50	75	0.22	0.44	6.6
296 cm	PV_296	0.09	0.02	-	-	19	130	0.31	58	0.19	0.29	6.1
Certified reference materials	3*											
MESS-3		0.00	0.10	+0.27	0.02							
PACS-2		+0.05	0.06									
Upper Continental Crust**		+0.07	0.1	+0.28	0.05	28	67	0.09	17	0.05	0.06	8.2

\* Copper isotope determination were performed in several replicates for MESS-3 (n = 6) and PACS-2 (n = 2), while zinc isotope compositions were determined exclusively in replicates of MESS-3 (n = 4). For certified reference materials, each replicate was prepared separately with different digestions and chromatographic separation for isotope determinations.

\*\*Elemental concentrations reported by Rudnick and Gao (2013). Copper and zinc isotope compositions reported by Savage *et al.*(2015) and Chen *et al.* (2013), respectively.

Sampling site	Code	EF(Cu)	EF(Zn)	EF(Cd)	EF(Pb)	EF(Hg)	EF(Ag)	∑EF
Sainte Luce	1	1.2	2.5	3.5	5.0	2.2	11.2	25.7
Indre	2	1.2	2.5	3.5	5.0	2.2	11.2	25.7
Pont de Saint-Nazaire	3	0.7	1.6	2.6	4.4	1.9	10.7	21.8
Face pointe de Mindin	4	1.5	3.2	2.8	4.6	3.3	12.2	27.7
St Brévin Mindin	5	1.2	2.8	2.0	4.1	2.0	10.0	22.0
Villes - Martin	6	0.4	1.1	0.6	4.0	0.6	5.0	11.7
Face St Brévin	7	1.1	2.5	2.5	4.2	1.9	10.5	22.7
Est Petit Gavi	8	1.2	2.8	2.2	4.1	2.5	10.9	23.5
Grand Traict 2	9	0.5	1.8	2.3	3.8	0.6	9.2	18.3
Ouest Lancastria	10	0.7	1.9	2.3	3.7	1.2	7.7	17.4
Sud phare de la Banche	11	1.3	3.0	2.8	4.3	2.7	10.3	24.4
Mariolle	12	1.5	2.9	3.2	4.5	2.9	13.7	28.8
Noirmoutier	13	0.7	2.1	3.6	3.8	1.3	7.7	19.2
Embarcadère	14	2.0	1.9	8.1	3.8	1.6	8.5	25.9
Coupelasse Nord	15	0.8	2.5	1.9	3.5	1.2	7.2	17.1
Banc de Bourgneuf	16	0.9	2.7	1.6	4.2	1.9	10.6	21.9
Loire 26	17	0.9	2.6	1.2	3.9	1.8	7.7	18.2
Sennetière	18	0.8	2.6	4.6	4.4	1.9	10.1	24.3
Paleovase sediment Core PV1 (depth)								
1 cm	PV_1	1.3	3.0	5.0	5.8	3.4	14.1	32.6
6 cm	PV_6	1.4	3.2	7.8	6.2	4.4	14.1	37.1
9 cm	PV_9	1.4	3.4	7.4	6.9	4.6	15.6	39.4
14 cm	PV_14	1.6	3.6	8.1	8.5	4.9	18.8	45.5
21 cm	PV_21	1.7	3.7	8.3	8.2	4.5	19.9	46.4
35 cm	PV_35	1.6	3.5	8.5	8.0	4.6	21.3	47.5
42 cm	PV_42	1.6	3.6	9.0	6.9	4.7	19.4	45.2
69 cm	PV_69	1.7	3.8	9.7	7.5	5.3	19.7	47.8

**Table 2.** Enrichment factors of sediments in the Loire estuary.

96 cm	PV_96	1.2	3.0	7.8	5.7	4.7	12.5	35.0
163 cm	PV_163	1.3	3.4	9.7	5.9	5.7	13.6	39.7
210 cm	PV_210	1.2	3.0	6.8	5.5	5.3	10.2	32.0
296 cm	PV_296	0.9	2.6	4.6	4.6	5.1	7.5	25.4