Spatiotemporal and multi-isotope assessment of metal sedimentation in the Great Lakes

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A B S T R A C T

This study investigates spatiotemporal dynamics in metal sedimentation in the North American Great Lakes and their underlying biogeochemical controls. Bulk geochemical and isotope analyses of n = 72 surface and core sediment samples show that metal (Cu, Zn, Pb) concentrations and their isotopic compositions vary spatially across oligotrophic to mesotrophic settings, with intra-lake heterogeneity being similar or higher than inter-lake (basin-scale) variability. Concentrations of Cu, Zn, and Pb in sediments from Lake Huron and Lake Erie vary from 5 to 73 mg/kg, 18–580 mg/kg, and 5–168 mg/kg, respectively, but metal enrichment factors were small (<2) across the surface- and core sediments. The isotopic signatures of surface sediment Cu ($\delta^{65}Cu$ between $-1.19‰$ and $+0.96‰$), Zn ($\delta^{66}Zn$ between $-0.09‰$ and $+0.41‰$) and Pb ($^{206/207}Pb$ from 1.200 to 1.263) indicate predominantly lithogenic metal sourcing. In addition, temporal trends in sediment cores from Lake Huron and Lake Erie show uniform metal concentrations, minor enrichment, and Zn and Pb isotopic signatures suggestive of negligible in-lake biogeochemical fractionation. In contrast, Cu isotopic signatures and correlation to chlorophyll and macronutrient levels suggest more differentiation from source variability and/or redox-dependent fractionation, likely related to biological scavenging. Our results are used to derive baseline metal sedimentation fluxes and will help optimize water quality management and strategies for reducing metal loads and enrichment in the Great Lakes and beyond.

1. Introduction

Sediments form a major global sink for metals in aquatic environments, including in marine, lacustrine, and riverine systems (Heard et al., 2014; Boyd et al., 2017). Consequently, sediment records are extensively used for the paleo-reconstruction of metal inputs, their spatiotemporal occurrence patterns, and biogeochemical mobility on annual-to-millennial timescales (Juillot et al., 2023; Kurek et al., 2013; Fang et al., 2023). The accumulation of metals in sediments is controlled by the complex interplay of water column hydrochemistry and redox conditions, dilution versus concentration dynamics imposed by sedimentation rates and properties (i.e., grain size, mineralogy, and organic matter content), biological activity and metal scavenging, as well as lateral diffusion and bioturbation in the benthic zone (Boyd et al., 2017; Algül and Beyhan, 2020; Zhou et al., 2020). Understanding the importance of these factors across different depositional environments is crucial for assessing the global biogeochemical cycling of metals and the risks associated with metal accumulation at locally (anthropogenically) enriched sites (Hsu et al., 2016; Nriagu et al., 1998).

Trace metals like copper (Cu), zinc (Zn), and lead (Pb) are major historic and current industrial 'heavy metal' pollutants that continue to threaten water quality worldwide. Sediments enriched in Cu, Zn, or Pb constitute archives of historic inputs that can help assess the effectiveness of remediation efforts but also form repositories for continued latent sourcing to overlying waters (Nriagu et al., 1998; Araújo et al., 2019; Thapalia et al., 2010). Complementary to traditional monitoring of total (bulk) metal concentrations, stable isotopes of Cu, Zn, and Pb (e.g., $\delta^{65}Cu$, $\delta^{66}Zn$, $^{206/207}Pb$) are increasingly used to determine the sources, mobilities, and fates of these metals in aquatic environments (Wiederhold, 2015; Weiss et al., 2007). Because Pb isotopes do not fractionate in low-temperature environments, they are a useful indicator of Pb sources, including anthropogenic (Peng et al., 2022a). In contrast,

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Cu and Zn may fractionate by biogeochemical processes, and can, therefore, be applied as tracers of biological scavenging or adsorption onto mineral phases, amongst others (Wiederhold, 2015). In order to track sources and processes, isotopic patterns of Cu, Zn, and Pb in sediments have been deployed to investigate the controls of biological activity (Navarrete et al., 2011; Peel et al., 2009), mineral dissolution/precipitation (Veeramani et al., 2015), adsorption (Bryan et al., 2015), redox reactions (Bigalke et al., 2011; Vance et al., 2016), and anthropogenic inputs (Souto-Oliveira et al., 2019; Heard et al., 2014; Thapalia et al., 2010; Peel et al., 2009; Aebischer et al., 2015). Previous studies in aquatic systems have demonstrated the value of isotopic systems analysis for assessing heavy metal sources (Pb, Peng et al., 2022b; Desaulty and Petelet-Giraud, 2020; Cu, Junqueira et al., 2023). Unfortunately, the application of Cu, Zn, and Pb isotopes in lacustrine sediments remains mostly limited to enriched (contaminated) sites and small scales (Thapalia et al., 2010; Jeong and Ra, 2021): a comprehensive understanding of metal cycling at baseline levels is lacking for most larger lakes, and inferred processes cannot be readily extrapolated across the widely variable morphometric properties of freshwater lakes (Wiederhold, 2015). Determining the isotopic compositions of multiple metals may be a powerful method for identifying different sources or governing biogeochemical processes. However, many sediment studies have focused on a single metal of concern, not leveraging the variable physicochemical fractionation of multiple metals that could be assessed in combination, e.g., Zn, Fe, and Pb (Aebischer et al., 2015), Cu and Pb (Jeong and Ra, 2021), or Cu and Zn (Araújo et al., 2019). Isotope analyses of Cu, Zn and Pb have been applied in combination to discriminate among individual metal sources in urban aerosols (Souto-Oliveira et al., 2019) and in coastal sediments (Araújo et al., 2019). Yet, the application of multi-isotope data to quantify metal sourcing or biogeochemical controls on metal cycling remains particularly scarce in large freshwater lakes.

The North American Great Lakes constitute a globally unique and important freshwater reserve. Comprising five interconnected major lakes, they receive water from thousands of tributaries from across the United States and Canada and together form one of the largest drainage basins on the continent (Sterner et al., 2017). The individual Great Lakes have distinct physicochemical and hydrodynamic characteristics. For instance, their catchment geology is variable from Precambrian bedrock surrounding Lake Superior and north of Lake Huron, to Phanerozoic rock around Lakes Michigan, Erie and south of Lake Huron; Larson and Schaetzl, 2001). Compared to the downstream Lakes Erie and Ontario, Lake Huron is deeper, colder and has a significant residence time (>20 years), whereas Lake Erie is shallower, warmer and has an order-of-magnitude shorter residence time (~2 years; Quinn, 1992; Trumpickas et al., 2015). Furthermore, population and agricultural density and associated P loads in the Lake Erie basin make the lake much more susceptible to seasonal algal blooms than Lake Huron (Dove and Chapra, 2015). The Great Lakes also have a long history of metal contamination, particularly in the so-called areas-of-concern (Aliff et al., 2019; Corcoran et al., 2018; Bellinger et al., 2016), and Cu, Zn, and Pb are no exception (Bentley et al., 2022; Nelson and Steinman, 2013; Gewurtz et al., 2008; Aliff et al., 2020). Metal dynamics in Great Lakes' sediments have received attention in polluted locations, e.g., Hamilton Harbour, Spanish Harbour, and the Bay of Quinte (Dixit et al., 1998; Poulton, 1992). However, the baseline levels of metals in other parts of the Great Lakes are not well-characterized, and their exact sourcing mechanisms remain poorly quantified (Aliff et al., 2019). Recent metal mass-balance calculations by Bentley et al. (2022) have indicated that sedimentation likely constitutes a major sink for these metals in the Great Lakes (e.g., between 300 and 4000 tonnes per year [TPY] for Cu or between 1000 and 10,000 TPY for Zn; Bentley et al., 2022). However, uncertainties in metal flux estimates remain significant across these interconnected lakes, confirmed by widely contrasting metal concentrations measured in a limited number of sediment cores from across the Great Lakes basin (Corcoran et al., 2018; Aliff et al., 2020; Reavie et al.,

2017). Such variability is particularly large for transition metals such as Ni, Cu, and Zn, which have been less studied than known Great Lakes contaminants in sediments, such as mercury (Hg; Marvin et al., 2004; Wiener et al., 2012). In addition, the biogeochemical processes responsible for Cu, Zn, and Pb cycling at background levels and their fates once introduced to the lakes remain unclear and constitute an urgent knowledge gap for large-scale and long-term water quality management, as well as for the assessment of ongoing remediation in other parts of the Great Lakes (Bentley et al., 2022).

To this end, we investigated spatiotemporal variations in Cu, Zn, and Pb concentrations and isotopic compositions in surface sediments collected across nearshore-to-offshore gradients, as well as in sediment cores from contrasting limnological conditions dating back >50 years. We quantified Cu, Zn, and Pb export to the sediment record and applied isotope geochemistry to constrain the biogeochemical controls underlying the sedimentary fluxes of these metals, for the first time in this complex lake system.

2. Materials and methods

2.1. Sediment coring, extrusion, and subsampling

Sediments from Lake Huron and Lake Erie were collected as part of the Great Lakes sediment monitoring program of Environment and Climate Change Canada (ECCC). The samples were collected in 2014 and 2017 using an Ocean Instrument model 750 box-corer (dimensions 40 cm × 40 cm) onboard the Canadian Coast Guard ship *Limnos*, following the methodology of Marvin et al. (2004). The time interval between the sampled years in Lake Huron and Lake Erie corresponds to the closest consecutive sampling times allowed for by the rotational Great Lakes sediment surveillance program conducted by Environment and Climate Change Canada (ECCC). The box coring equipment was thoroughly rinsed at least 3 times with site water before and after sampling. Surficial sediments were grab-sampled from a 6.5 cm internal diameter and 3 cm length cylindrical sub-core from the box core using disposable high-density polypropylene (PP) spatula, homogenized, and stored in pre-cleaned Nalgene PP jars that were frozen at −20 °C. Sediment cores were also subsampled from the box core using deeper, 10 cm diameter, 40–50 cm length cylindrical cores. These cores were extruded on-board, sliced in 1 cm intervals for the top 15 cm and 2 cm intervals for the remainder of the core. The slices were stored in pre-cleaned Nalgene PP jars, and frozen at −20 °C for transport to the laboratory. For this work, a selection of 15 surface sediments and 4 sediment cores (with a total of n = 57 subsamples) from Lakes Huron and Erie were analyzed for metal isotope composition. Sampling co-ordinates, dates and subsample aliquots of these samples are provided in Table S1. Sediment cores were dated as detailed in **Methods S1**.

2.2. Sample processing and geochemical analyses

Surface sediments and core intervals were freeze-dried in pre-cleaned beakers at −50 °C for 48h to constant dry weight (LabConco Freezone) and homogenized and powdered using an agate mortar and pestle. Approximately 100 mg aliquots of the dried sediments were acid-digested in a microwave (AntonPaar Multiwave 3000) for analysis of total elemental composition, as well as Cu, Zn, and Pb isotope ratios. For acid-digestion, sample aliquots were weighed into pre-cleaned Teflon-PFA vessels inside an over-pressurized air-filtered Class 1000 clean room at the Queen's Facility for Isotope Research (QFIR, Queen's University, Canada). Subsequently, 3 mL nitric acid (HNO$_3$), 9 mL hydrochloric acid (HCl), 2 mL hydrogen peroxide (H$_2$O$_2$), and 3 mL hydrofluoric acid (HF) were added to each vessel and heated at 240 °C for 4h. All acids and peroxides used for digestion were of ultra-pure grade: 47–51% hydrofluoric acid (OmniTrace), 67–70% ultrapure nitric acid (Anachemia), 30–32% ultrapure hydrogen peroxide (VWR Avantor), and 36–38% high-purity hydrochloric acid (Sigma-Aldrich); 18.2 MΩ cm^{-1} de-

ionized (DI) water (Milli-Q) was used for dilution. Three procedural blanks and solid certified reference materials (NRC-MESS-4, VHG-SSD1-A and VHG-SL1) were processed in each batch of n = 15 samples; the recovery of certified concentrations was within ±10% (Table S2). To minimize (cross-)contamination, all consumables were pre-cleaned with 50% ultrapure HNO$_3$ and DI water rinses; microwave vessels were additionally cleaned by sub-boiling with 50% HNO$_3$–HCl at 80 °C for 12h between runs.

Total elemental concentrations in the acid-digestates were measured by inductively coupled plasma-mass spectrometry (ICP-MS) and optical emission spectroscopy (ICP-OES) at QFIR. Aqueous certified reference materials (AQUA-1, NIST1643f, SLRS-6) were measured every n = 10 samples; the recovery of certified elemental concentrations was 94 ± 5%, averaged across elements and reference solutions (Table S3). Elemental concentrations measured in the digestates were additionally reconciled with bulk elemental compositions determined by x-ray fluorescence spectroscopy (XRF; handheld Bruker Titan Tracer5) on dry sediment samples (data not shown). Sediment composition and mineralogy were characterized using x-ray diffraction (XRD) and Fourier Transformed Infrared spectroscopy as described in **Methods S2**.

Finally, total nitrogen, phosphorus, and organic carbon contents in a selection of dried sediment aliquots were determined by ECCC according to standard methods (ECCC, 2020). In brief, total phosphorus (TP) was determined by heated digestion with sodium persulfate following spectrometric analysis of orthophosphate, and total organic carbon (TOC) and total nitrogen (TN) were analyzed by combustion on a CEC 240-XA Elemental Analyzer or LECO CS844 Combustion Analyzer. Sediment chlorophyll *a* (including its isomers and main diagenetic products) was determined using spectral absorbance as described in **Methods S3. 2.3 Isotope analyses**.

Lead isotope ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb) of digested sediments were measured by triple quadrupole (TQ)-ICP-MS (iCAP Qc, Thermo Fisher) at the CCEM at IFREMER (Brest, France). Mass bias and instrumental drift were corrected with a standard bracketing method using the NIST SRM-981 reference material. The internal relative standard deviations on ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb were 0.23 ± 0.04% and 0.36 ± 0.12% (1σ, n = 38), respectively, for unknown samples and the certified reference material MESS-4 (Table S4).

For Zn and Cu isotope analysis of sediment digestates, these elements were first isolated from matrix elements using ion-exchange chromatography column packed with AG-MP1 resin eluted in different HCl solution molarities (Junqueira et al., 2023). The procedure was performed in an over-pressurized air-filtered Class-1000 cleanroom. Total procedural blanks contained <1% of the average Zn and Cu mass content of samples. Copper and Zn isotopes were measured using a multi-collector ICP-MS (Neptune, ThermoScientific) at IFREMER. After digestion, samples were evaporated, re-dissolved in 2% HNO$_3$, refluxed on a hotplate for 12h, and introduced at concentrations between 100 and 500 ng g^{-1} with a cyclonic spray chamber and a low-flow PFA nebulizer (50 μL min^{-1}). The measured isotope compositions are expressed as δ^{65}Cu and δ^{66}Zn values relative to NIST SRM-976 and "JMC-Lyon" (Johnson Matthey Company 3-0749-L), respectively, as follows:

$$\delta^{65}Cu(‰) = \left[\frac{\left(\frac{Cu^{65}}{Cu^{63}}\right)_{sample}}{\left(\frac{Cu^{65}}{Cu^{63}}\right)_{NIST\ SRM\ 976}} \right] \times 1000 \qquad \text{Equation 1}$$

$$\delta^{66}Zn(‰) = \left[\frac{\left(\frac{Zn^{66}}{Zn^{64}}\right)_{sample}}{\left(\frac{Zn^{66}}{Zn^{64}}\right)_{JMC-Lyon}} \right] \times 1000 \qquad \text{Equation 2}$$

Certified commercial and in-house solid and aqueous reference materials (NRC-MESS-4 (marine sediment; δ^{66}Zn = 0.22 ± 0.07‰; δ^{64}Cu =

−0.09 ± 0.07‰; Jeong et al., 2021; Araújo et al., 2017) and VHG-SSD-1-A (sludge-amended soil; δ^{64}Cu = 0.20 ± 0.08‰; Junqueira et al., 2023) were used to validate the chromatography protocol and isotope measurements and presented recoveries of 98 ± 10% on the isotope ratios (Table S4). Average external precision (2σ) obtained from measurements of unknown samples and certified sediment standards was ±0.03‰ and ±0.06‰ for δ^{65}Cu$_{NIST}$ and δ^{66}Zn$_{JMC}$, respectively.

2.3. Calculation of mass accumulation rates and enrichment factors

Sediment mass accumulation rates (MAR; Table S5) were calculated by multiplication of interval age, total vertical sedimentation rates (**Methods S1**), and dry sediment weight that was assumed vertically constant within each slice, the latter justified by the reasonably consistent relative abundances of sand, silt, and clay particle fractions in the cores (Table S6). Obtained MAR for each core quantitatively aligned with previously determined MAR for Great Lakes sediment cores (Aliff et al., 2019; Corcoran et al., 2018). Enrichment factors (EF) for Cu, Zn, and Pb in the sediment samples were calculated as described in **Methods S4**. Finally, Cu, Zn, and Pb concentrations in surface sediments from Lakes Erie and Huron were interpolated in ArcGIS Pro (ESRI) using second-order ($p = 2$) variable-radius inverse distance weighting at a search neighborhood equal to the maximum distance between two sampling locations. Lake-wide metal sedimentation fluxes were subsequently estimated by integration of spatially interpolated sediment concentrations and MAR, as described in **Methods S4**. Multivariate Principal Component Analysis (PCA) was employed to analyze and discern primary relationships among the dataset variables (i.e., isotopic signatures and elemental variables). Parameters selected for PCA were centered and scaled (min-max normalized) to ensure all variances were treated equally, and the analysis was conducted using the JMP software (SAS).

3. Results and discussion

3.1. Metal levels and isotope signatures vary significantly spatially

Concentrations of Cu, Zn, and Pb in surface sediments from Lake Huron and Lake Erie vary from 5 to 73 mg/kg, 18–580 mg/kg, and 5–168 mg/kg, respectively (Fig. 1; Table S6). The average concentrations of these metals were 39, 151, and 53 mg/kg, respectively, higher than their average crustal abundances (25, 71, and 17, respectively for Cu, Zn and Pb; Taylor and McLennan, 1995), possibly due to enrichment in select areas of the Lakes. Lake Erie surface sediments generally exhibit higher Zn and Pb concentrations than Lake Huron, but average Cu concentrations are slightly higher in Lake Huron. The abundances of these metals and other major elements are normally distributed (skewness<|1|) in Lake Huron surface sediments, whereas variability in Lake Erie is generally higher: intra-lake variability is on the same level or higher than inter-lake variability (p < 0.03). Surface sediment levels of Cu, Zn, and Pb appear spatially correlated to each other across both lakes (Fig. 1): higher concentrations of all metals are observed near historically contaminated sites (e.g., Hamilton Harbor or Georgian Bay; Nriagu et al., 1998; Dixit et al., 1998; Gemza, 1995) and urban areas (e. g., Cleveland or Toledo; Aliff et al., 2019; Munawar and Thomas, 1989), but not exclusively. Namely, offshore samples in central Lake Huron present higher metal concentrations than nearshore samples, whereas samples from areas known to be impacted by (historic) pollution (e.g., Saginaw Bay; Bazzi et al., 2002) or large urban areas (e.g., Western Lake Erie downstream of Detroit) do not reveal particularly elevated concentrations. Despite significant spatial variability, metal concentration ranges measured here agree with previous data from Great Lakes surface sediments (Gewurtz et al., 2008; Painter et al., 2001; Marvin et al., 2004), albeit not with concentration gradients as abrupt as previously found (e.g., up to one order-of-magnitude across ~10 km spatial separation; Corcoran et al., 2018; Aliff et al., 2020). Further, spatial metal
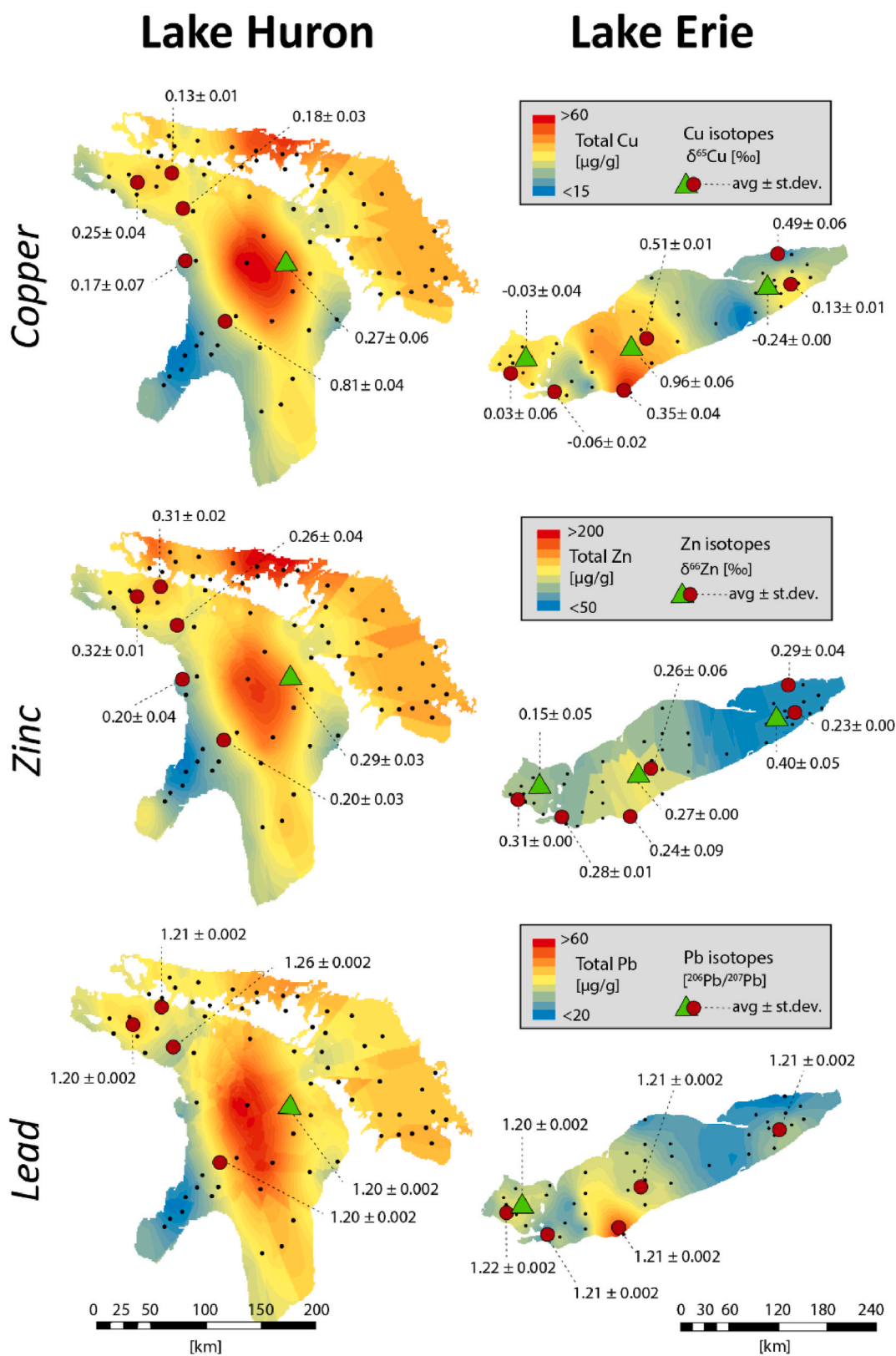
Fig. 1. Interpolated bulk total concentrations of Cu (top), Zn (middle) and Pb (bottom) in surface sediments from Lake Huron (left) and Lake Erie (right), with corresponding color scales indicated for each metal. Total concentrations were analyzed in n = 68 samples in Lake Huron and n = 43 samples in Lake Erie. Select locations for which isotope compositions of surface sediments were determined are shown by the green triangles (core top intervals) and red circles (grab samples), with associated isotopic signatures indicated.

concentration variability does not support predominantly atmospheric or riverine sourcing, as would have been evidenced by more uniform distributions or consistent nearshore metal enrichment, respectively, although atmospheric deposition could constitute an important source for anthropogenic Pb and Zn in the Great Lakes (Bentley et al., 2022, 2023).

Metal isotope compositions in Lake Huron and Erie sediments are all slightly positive, but whereas δ^{66}Zn and $^{206/207}$Pb are spatially consistent between +0.20 and +0.32‰ and 1.20 to 1.26, respectively, δ^{65}Cu varies significantly between −0.06 and + 0.96‰ (Fig. 1). Metal isotope ratios are only weakly or not at all correlated to their total concentrations, and thus not suggestive of a dominant single source, including for Pb (Fig. 2). Metal isotope ratios are also unrelated to sample distance from shore, in contrast to what has been observed in other lakes (Thapalia et al., 2010), or for bulk concentrations of metals or rare earth elements in the Great Lakes (Junqueira et al., 2024).

Generally, δ^{65}Cu compositions of Lakes Huron and Erie sediments fall within the broad range of typical anthropogenic sources, including urban aerosols (−0.42 to +0.98‰; Souto-Oliveira et al., 2019), road dusts (+0.12 to +0.94‰; Jeong et al., 2021), mine tailings (+0.95 to +1.10‰; Viers et al., 2019) and pesticides (−0.49 to +0.91‰; Blotevogel et al., 2018), as well as geogenic sources (e.g., δ^{65}Cu +0.07‰; Liu et al., 2015), and previous work on river water from the Lake Huron and

Lake Ontario basins; Junqueira et al., 2023). This overlap across the broad range of geogenic versus anthropogenic Cu isotope signatures complicates an assessment of Cu sourcing in the studied Great Lakes sediments. For Zn, positive δ^{66}Zn values across both Lake Huron and Erie surface sediments suggest that Zn is mostly derived from geogenic contributions, as δ^{66}Zn signatures in anthropogenic emissions are mostly lighter than the average Upper Continental Crust (+0.28‰; Chen et al., 2013), e.g., for wastewater and sludges (~0.1‰; Chen et al., 2009), atmospheric industrial emissions (from −0.52 to +0.15‰; Mattielli et al., 2009), urban runoff (+0.13 to +0.15‰; Chen et al., 2009), and contaminated soils (−0.57 to −0.04 ‰; Wang et al., 2022). For $^{206/207}$Pb, the observed ratios of around 2.05 indicate typically natural Pb sources (Li et al., 2017) and align with signatures of natural materials (e.g., mineral dust; Biscaye et al., 1997). The observed ratios are notably higher than anthropogenic sources, with values ranging from 1.11 to 1.33 (smelting and metallurgical activities; Véron et al., 1999; Komárek et al., 2008) or from 1.05 to 1.28 (gasoline and vehicular emissions; Novák et al., 2003; Farmer et al., 1999). Overall, metal isotope signatures observed in this research align with those found in non-contaminated and pristine marine and lake sediments (Sullivan et al., 2022; Vance et al., 2008; Thapalia et al., 2015).

Sediment mass accumulation rates (MAR) across Lakes Huron and Erie vary considerably, i.e., from 0.007 to 0.237 g cm^{-1} yr^{-1} (Table S5) and subsequent relative metal dilution or concentration could explain at least part of the spatial variability in metal content (Corcoran et al., 2018; Aliff et al., 2020). However, even though metal levels vary between the oligotrophic Lake Huron and mesotrophic Lake Erie basins, the order-of-magnitude variability in sedimentation rates is not reflected in metal concentrations that are different by at most a few factors, nor by their spatially consistent isotope signatures (Fig. 1). The consistency of Zn and Pb isotope compositions in particular implies that their sedimentation results from spatially consistent processes and homogeneous sources. In contrast, the variability of Cu isotope compositions implies that Cu sourcing and/or sedimentation differ more significantly, potentially related to its redox-sensitivity and heterogeneity in water column hydrochemistry (Sullivan et al., 2022) as well as dispersion of distinct Cu inputs through gyre circulation patterns (Bai et al., 2013; Beletsky et al., 1999). The sediment metal contents and isotopic signatures from Lakes Huron and Erie thus suggest geogenic inputs as the main source of Zn and Pb, but the wider range of Cu isotopic compositions complicate assessment of its exact sourcing.

Principal component analysis conducted on the core- and surface sediment samples from Lakes Huron and Erie reveal that the two first components only explained 62% of the dataset variance for Lake Huron and 57% for Lake Erie (Fig. S1). The bivariate plots of both lakes present similar relative variable positioning and contributions, suggesting that similar mechanisms may explain dataset variability in both lakes. The PCA also provided no indications that Cu, Zn and Pb isotopes were related to their bulk concentrations, as observed in previous isotope studies on aquatic environments (Araújo et al., 2019). Furthermore, isotopes of Pb, Zn, and to a lesser extent Cu, did not appear strongly correlated with total organic carbon and chlorophyll *a*, corroborating the poor regressions observed in Fig. 5 (see below), and showing that the mechanisms governing the fractionation of these elements may be more complex.

3.2. Metal sedimentation in recent decades

Concentrations and isotope signatures for Cu, Zn, and Pb in four sediment cores are provided in Fig. 3; additional metal and major element data is provided in Table S6.

In Lake Huron, concentration profiles for Cu, Zn, and Pb vary from 53 to 71 mg/kg, from 168 to 223 mg/kg, and from 63 to 115 mg/kg, respectively. All metal concentrations consistently increased up to the late 1970s and subsequently either decreased (Pb and Zn) or remained constant (Cu). Metal concentrations in cores from the western and
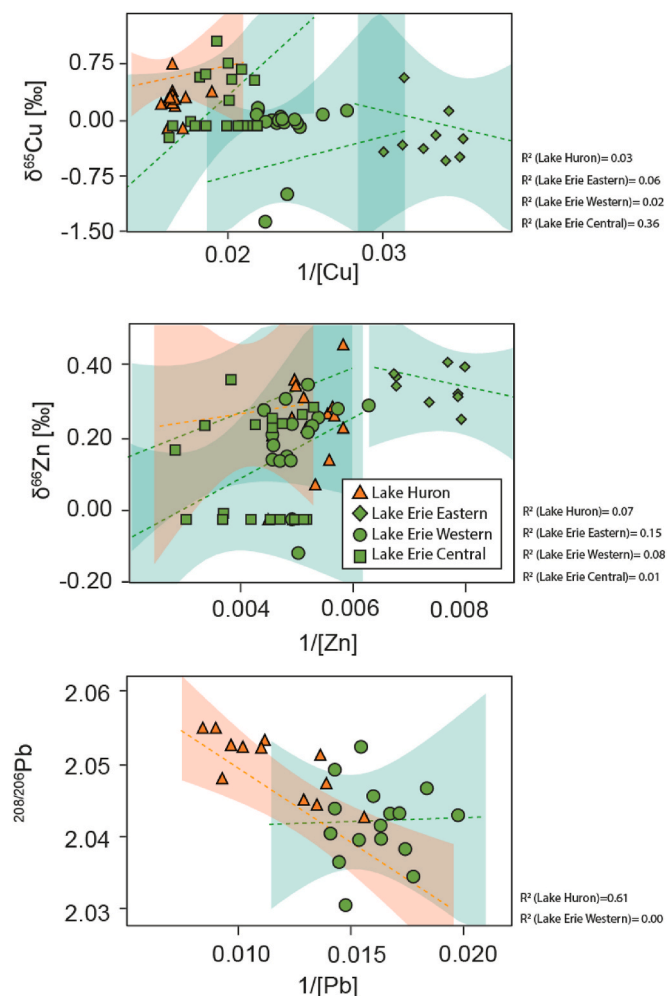

Fig. 2. Sediment metal concentrations versus their isotopic compositions. Metal concentration data (x-axes) are inversed and plotted against isotope signatures (y-axes) for sediment core samples only. Linear trend lines and corresponding prediction envelopes (90% confidence intervals) and R² values are indicated for each core. Legend in the middle frame applies to all frames.
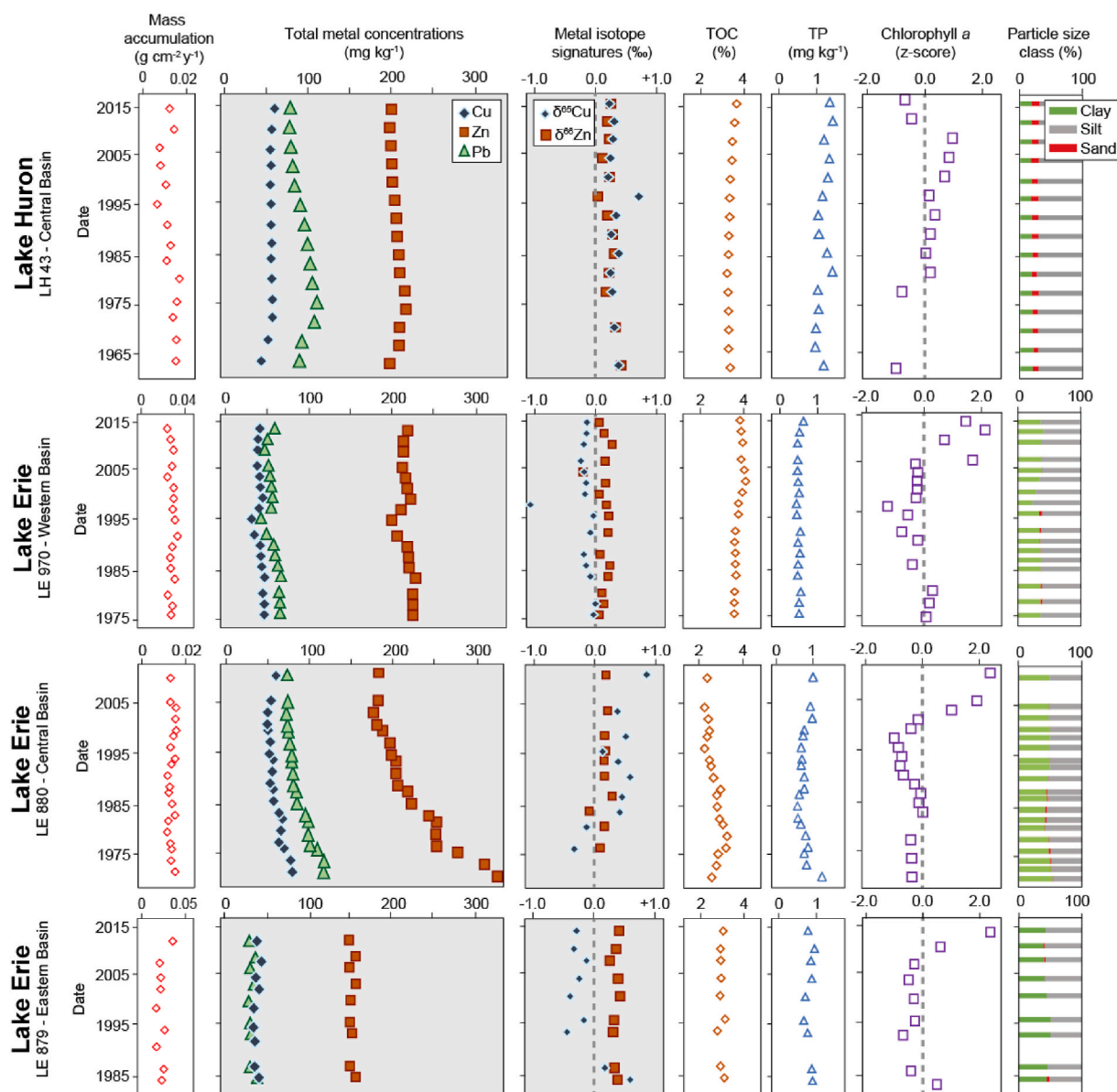
Fig. 3. Sediment composition in cores from Lake Huron (LH43; top) and Lake Erie (LE970 [western], LE880 [central], and LE879 [eastern]). Provided against depth/ age are, from left-to-right: mass accumulation rate, total Cu, Zn, and Pb concentrations, $\delta^{65}Cu$ and $\delta^{66}Zn$ isotope compositions, TOC and TP, chlorophyll *a*, and particle size, all on linear x-axes that are consistent across the cores. The legends at the top apply to all vertically overlying panels; analytical uncertainties were negligible on the provided scale (Table S1).

central Erie basins are comparable to those of Lake Huron and show decreasing trends since the late 1970s, except for subtle increases in metal contents in the western Erie core between 1995 and 2000. The eastern Lake Erie core shows the lowest Cu, Zn, and Pb contents, with averages of 34, 120, and 28 mg/kg, respectively; although this core does not date as far back as the other Lake Erie cores, its metal concentrations do not reveal a major decrease over time. Whereas metal contents are similar between the Lake Huron and central Lake Erie cores in recent times, the Lake Erie cores display consistently different metal concentrations between one another and, when compared to Lake Huron, reflect the spatial variability observed in surface sediments (Fig. 1).

Metal isotope compositions recorded in sediment cores are in the range of values determined for surface sediments (Table S6). In the Lake Huron core, $\delta^{65}Cu$ and $\delta^{66}Zn$ values are consistently positive with depth, varying from +0.27 to +0.73‰, and from +0.09 to +0.46‰, respectively (Fig. 3). A minor excursion occurs around ~1996, with a more depleted $\delta^{66}Zn$ value coinciding with $\delta^{65}Cu$ enrichment. Compared to

Cu and Zn isotope values, $^{206}Pb/^{207}Pb$ ratios in the Lake Huron core are strikingly constant from 1.20 to 1.21 (in Lake Erie, $^{206}Pb/^{207}Pb$ ratios were only analyzed for the western core). In Lake Erie, $\delta^{66}Zn$ values are also reasonably constant with depth: average $\delta^{66}Zn$ signatures range from +0.22‰ in the western to +0.35‰ in the eastern basins, and only one interval (1984 in the central basin; $\delta^{66}Zn$ −0.02‰) was above 3σ (3 × standard deviation) the average of that core. In contrast to reasonably consistent Zn and Pb isotopic compositions, Cu isotope patterns vary more significantly. Namely, the western Erie core exhibits quite negative $\delta^{65}Cu$ values (−1.19 to +0.10‰) compared to more positive $\delta^{65}Cu$ values in the eastern and central cores (−0.38 to +0.56‰, and −0.13 to +0.96‰, respectively). Further, $\delta^{65}Cu$ values in eastern Lake Erie gradually decrease over time, those in central Lake Erie increase, and those in western Lake Erie do neither, but contain a major negative $\delta^{65}Cu$ excursion around 1996 (Fig. 3). Furthermore, temporal trends in $\delta^{65}Cu$ signatures, as well as those in $\delta^{66}Zn$ and $^{206/207}Pb$ ratios, do not coincide with variation in bulk metal and other elemental

concentrations (Figs. 1 and 2 and S2).

Metal isotope signatures observed in these Great Lakes cores are comparable to those found in unpolluted fluvial and estuarine sediments, e.g., shallow riverbed sediments (δ^{66}Zn = +0.31 ± 0.04‰, Sivry et al., 2008; δ^{65}Cu = −0.04 ± 0.18‰, Guinoiseau et al., 2018) or lake sediment cores (δ^{66}Zn = +0.04 ± 0.06‰ to +0.31 ± 0.09‰, Juillot et al., 2023; Mattielli et al., 2009; Sonke et al., 2008). Previous studies have attributed variability in Cu isotope compositions to fractionation during biological uptake, complexation to organic matter, sorption onto bacterial cells, sequestration into sulfide minerals in the anoxic zone, as well as effects of mineralogy, particle size, and redox sensitivity (Sullivan et al., 2022). Complexity in interpreting the observed trends in sediment geochemistry for the Great Lakes arises from the different residence times of the serially connected lakes, temporal variability in connecting channel and riverine metal loads, the wide range of anthropogenic activities in the basin, and complex, seasonally variable lake circulation patterns (Bai et al., 2013; Beletsky et al., 1999). We further examine some of these processes below, but, overall, the spatiotemporally consistent $^{206/207}$Pb and δ^{66}Zn values in and between Lakes Huron and Erie suggest that geogenic sourcing has likely predominated during sedimentation over time, with some negative peaks for δ^{66}Zn being potentially anthropogenic given the typical ^{66}Zn depletion of anthropogenic versus geogenic sources. For Cu, spatial and temporal variability in isotopic signatures between the lakes and within Lake Erie requires the consideration of additional factors, as discussed below.

3.3. Enrichment factors and metal baselines

Metal enrichment factors were calculated by normalization of their bulk concentrations (Table SX) to that of a reference element (Li et al., 2017) as described in Methods S4 (equation S3). In Lake Huron, metal enrichment factors vary from 0.72 to 1.3 for Cu, 0.5 to 1.21 for Zn, and 0.30 to 1.50 for Pb across the surfac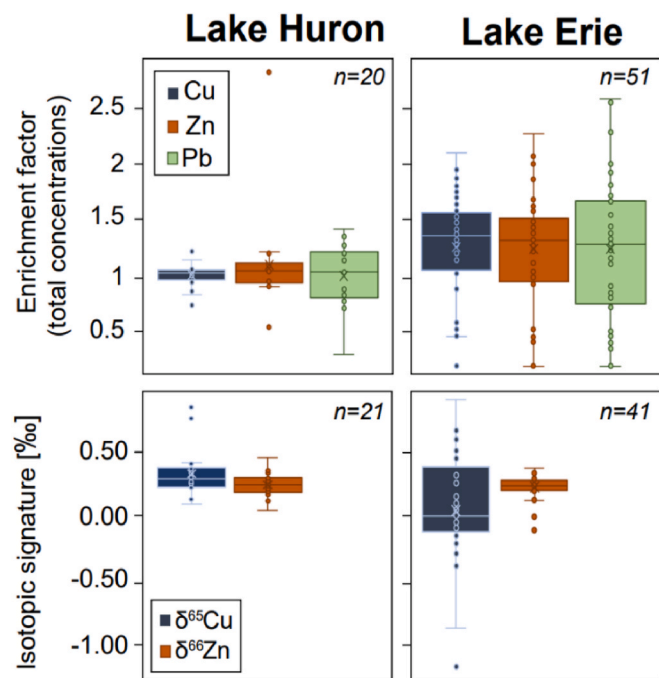e sediments and core samples (Fig. 4; Table S7). The EFs for Pb and Cu in the Lake Huron core gradually increase over time, whereas EFs for Zn are relatively constant. One elevated EF for Zn in 1996 in Lake Huron coincides with an enrichment of ^{65}Cu (δ^{65}Cu +0.73‰) and ^{66}Zn depletion (δ^{66}Zn = +0.09 ‰), but significant correlations between metal EFs and their isotopic compositions across the sample set are not observed (Fig. S3). In Lake Erie, the western core contains the highest EFs for Cu (1.2–1.9), but not Zn (1.0–1.8) and Pb (1.1–1.8). In the western core, metal EFs peaks between 1998 and 2002 and subsequently decreases. The highest EFs in western Lake Erie coincides with more negative δ^{65}Cu (between −0.88 and −0.04‰) and δ^{66}Zn values between +0.15 and +0.27‰. The eastern Lake Erie core has the lowest EFs for all metals, without a prevalent temporal trend, and the central Erie core has gradually decreasing but generally higher, EFs for Pb and Zn than the western core. Whereas lighter Cu isotopic signatures are linked to higher EFs in the central Erie core (Fig. S3), no correlations between EFs and isotopic compositions are observed for the other metals or the other Erie cores.

Compared to contaminated sediments in the Great Lakes basin (e.g., at the Spanish Harbor [EF > 10], Dixit et al., 1998; or Bay of Quinte [EF > 5], Crowder et al., 1989), metal EFs in surface sediment and cores reported here indicate virtually no enrichment. This aligns with the observed isotopic composition ranges that are typical for non-contaminated lacustrine systems, as discussed above, and that are significantly different from those seen in contaminated lakes (Lake Ballinger, USA, Thapalia et al., 2010; 2015) and other aquatic systems (e.g., mine waste effluents, Viers et al., 2018). The apparent lack of significant anthropogenic contamination therefore suggests that the present dataset could be considered as a baseline for metal occurrence in the Great Lakes, as well as representative for larger-scale sedimentary metal fluxes in the basin. Therefore, by extrapolating area-weighted metal concentrations and bulk sediment accumulation rates onto lake-wide sedimentation fluxes (**Methods S4**), rates in the range of 161-1866 tons of Cu/yr for Lake Huron, and 758-4898 tons Cu/yr for Lake Erie can be projected, and for Pb and Zn, lake-wide estimates of sedimentary fluxes are in the same order-of-magnitude (Table S8). These extrapolated fluxes agree quantitatively with estimates derived from independent hydro-geometric mass-balance assessments of riverine metal loads (Nelson and Steinman, 2013). Thus, although considerable uncertainty regarding the spatial variability of these fluxes remains (e. g., nearshore-offshore and in the Georgian Bay), both the alignment between these estimates and the temporal consistency in sediment core EFs and isotope signatures (Fig. 3) instill confidence in these lake-wide flux estimates and confirm the importance of sedimentation in the biogeochemical cycling of metals in the Great Lakes.

3.4. Biological versus mineralogical controls on metal sedimentation

Like metal concentrations, total organic carbon [TOC], total phosphorus [TP], and total nitrogen [TN] contents are spatially variable across the surface sediments, but, except for TP, quite consistent temporally within sediment cores from both Lakes Huron and Erie (Fig. 3; Table S6). Despite higher P inputs and a shorter residence time in Lake Erie (Dove and Chapra, 2015; Quinn, 1992), Lake Huron surface and core sediments have slightly higher macronutrient levels than those from Lake Erie, likely related to lower MAR in Lake Huron overall (Aliff et al., 2020). Total organic carbon is well-correlated with TP and TN across the dataset (not shown), indicating that biological material is common in both Lakes. Indeed, chlorophyll a concentrations (Table S9) are substantial in Lake Erie samples (varying from 0.007 to 0.026 mg/g; z-scores between −1 and + 3), and mostly higher than those in Lake Huron (0.003–0.006 mg/g; z-scores between −1.5 and + 1.5), in line with a higher productivity. The variability of chlorophyll a in cores from Lake Erie (increasing post-2000) and Lake Huron (decreasing recently; Fig. 3) suggests that productivity has changed more significantly and differently than metal levels and their isotope signatures, in both lakes.

Across all sediments and both lakes, metal concentrations are

Fig. 4. Distributions of enrichment factors (top frames) and Cu and Zn isotopic signatures (bottom frames) of sediment cores and surface samples combined in Lakes Huron (left panels) and Erie (right panels). Boxplots show the 25th percentile, median, and 75th percentile, whiskers illustrate the 95th percentiles, and outliers (>3 times ± standard deviation of a subset) are represented separately.

positively but not very strongly ($R^2 < 0.49$) correlated to TOC, TN, and TP, but not to chlorophyll *a* (Figs. S4 and S5). Surface sediments in both Lakes Erie and Huron alone exhibit no correlation between chlorophyll *a* or nutrient levels, metal abundance, or isotopic composition. Correlations between TN and Zn or Pb concentrations and isotope signatures are statistically insignificant for individual cores ($R^2 < 0.2$; p = 0.18) but somewhat stronger for Cu, especially for Lake Erie cores ($R^2 > 0.49$; p = 0.04; Fig. 5). Metal concentrations are more strongly correlated to TP than to TN, particularly for Cu and in eastern Lake Erie ($R^2 > 0.51$). Interestingly, correlations between Zn and TP are directionally opposite in Lake Huron (negative) compared to Lake Erie (generally positive; Fig. 5).

Even though Lake Erie receives higher P loads than Lake Huron, both have offshore waters that are strongly P-limited (Dove and Chapra, 2015) and water column N and P concentrations may be strongly decoupled from those in the sediment altogether (Ginn et al., 2012). The generally poor regressions between chlorophyll *a* against Zn and Pb isotope ratios, as well as the decoupling of these variables in the PCA analyses (Fig. S1), suggest that sedimentation of these metals is not likely to be significantly coupled to biological scavenging. For Cu, somewhat stronger correlations imply that a (limited) control of biological scavenging on Cu sedimentation, at least locally, cannot be excluded from our isotope data.

Surface and core sediment samples from both Lakes Huron and Erie show reasonably similar mineralogy, including quartz, clay minerals,

and carbonate minerals, overprinted by significant fractions of amorphous material (example XRD diffractogram in Fig. S6; modal mineralogy of select samples in Table S10). Quartz is the most abundant phase in sediments from all cores (36–49%), while clay percentages range from 25 to 45 % and those of carbonates from 2 to 20%. Carbonate abundance is notably higher in Lake Erie than in Lake Huron sediment samples due to the differences in geological background. The otherwise relatively constant mineralogy in both spatial and temporal dimension results in poor regression between mineral abundances and metal abundance or isotope signatures (Fig. 5, Fig. S7). This implies that a geologically consistent input of basin weathering material has driven a quite consistent Pb and Zn sedimentary isotopic composition, preserved over variable mass accumulation rates, but is probably not linked to more significant isotopic variations for Cu.

Finally, infrared spectroscopy analyses displayed peaks typical of lake sediments, including a mixture of crystalline silicate minerals (quartz, montmorillonite), amorphous silicates, and carbonate phases (calcite, dolomite and vaterite; example spectra in Fig. S8; data in Table S11). Amorphous opaline silica may be detrital or biogenic (frustules of diatoms; Vogel et al., 2016). Quartz and amorphous opaline silica are present in all samples, whereas strong evidence for carbonates is seen exclusively for eastern Lake Erie samples. In the western Lake Erie samples, carbonate features were present although poorly defined, suggesting lower abundance. Weak spectral features possibly related to organic compounds (e.g., organic C=C or P–OH bonds) are also
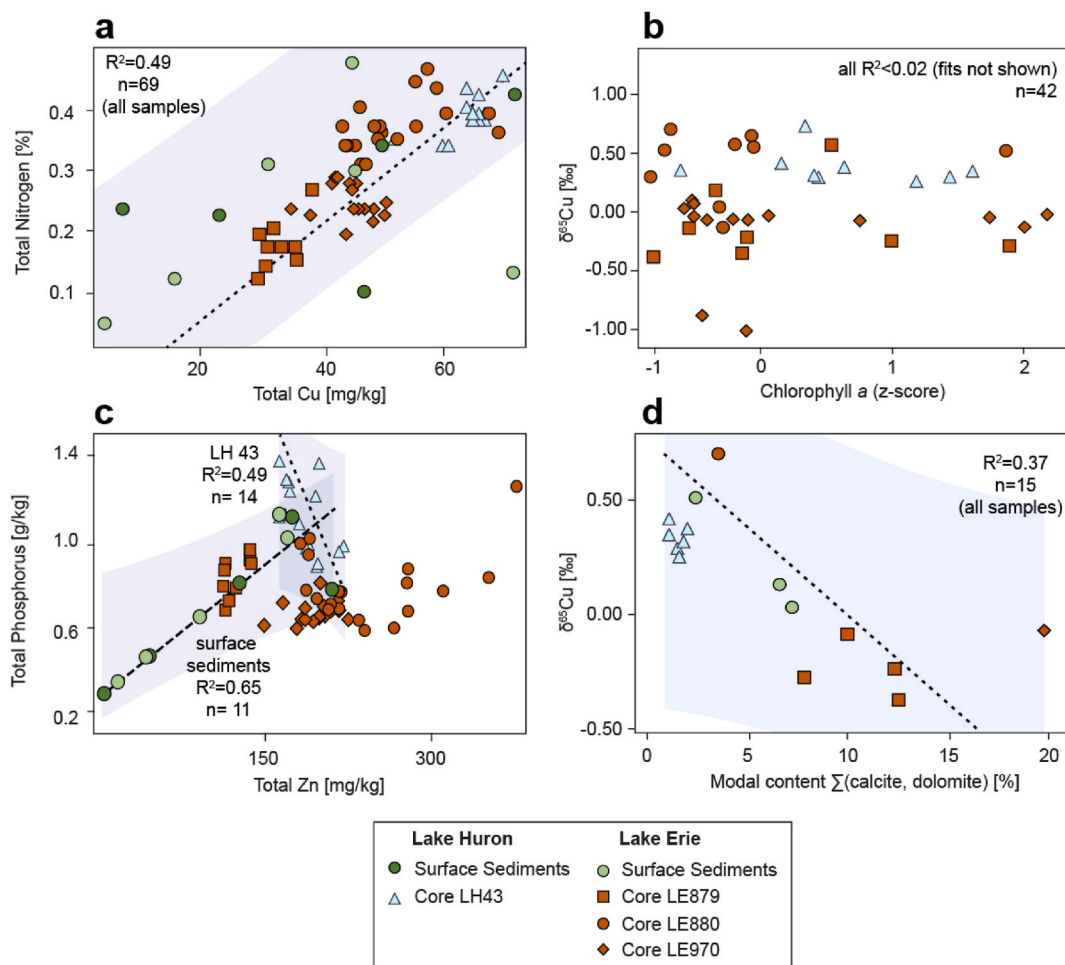
Fig. 5. a, correlations between total N and total Cu concentrations; **b,** correlations between total P and total Zn concentrations; **c,** correlations between δ^{65}Cu signatures and chlorophyll *a*; and **d,** correlations between mineralogical carbonate content, respectively, across the investigated sediment samples. Symbols and colors represent the different cores and surface sediments (grouped by lake; legend at the bottom applies to all frames). Linear regression lines, prediction envelopes (90% confidence interval), and corresponding correlation coefficients are provided in each frame.

detected. Although the qualitative spectra interpreted here could not be significantly correlated with bulk metal content or isotopic signatures, similar the identified patterns confirm the comparatively consistent (XRD-derived) mineralogical composition and provide support for biological activity controlling Cu cycling in some of the Great Lakes' sediments studied here, i.e., with peaks characteristic for biogenic Si and organic matter.

3.5. Sedimentation imposes strong controls on metal distribution patterns

Our data reveals spatiotemporally consistent Pb isotope ratios, suggestive of geogenic sourcing and little fractionation, in line with the conservative nature of Pb isotope ratios in biogeochemical processing under ambient conditions (Komárek et al., 2008; Anbar and Rouxel, 2007). Although subtle differences in concentration spatially (Fig. 1) may be explained by hydrodynamic mixing and sediment accumulation, on a basin-scale, geogenic Pb inputs appear more important than anthropogenic (e.g., atmospheric) sourcing.

Zinc signatures in the studied Great Lakes sediments are more variable than Pb yet relatively homogeneous as well, with an average δ^{66}Zn similar to that of the Bulk Silicate Earth ($+0.28 \pm 0.05$‰; Chen et al., 2013) and natural soils and continental sediments (-0.14‰ to $+0.49$‰, Desaulty and Petelet-Giraud, 2020; Fig. S9). This consistency in Zn isotopes indicates a predominantly geogenic origin and little anthropogenic impact on the basin-scale (Fig. 1): whereas further study may focus on local enrichments, particularly nearshore, any unresolved Zn anomaly will likely be constrained to the immediate vicinity of its riverine input. Zinc is a micronutrient and (controlled laboratory) studies have shown that biological uptake (active Zn-transporter in diatoms and bacteria) may induce small fractionation in δ^{66}Zn (Köbberich and Vance, 2019; Samantha et al., 2018). Additionally, enrichment of ^{66}Zn can be caused by complexation with organic functional groups or adsorption onto bacterial cells and inorganics (Gelabert et al., 2006; Jouvin et al., 2009). However, the δ^{66}Zn isotope values, their consistency (Fig. 3), and the lack of correlation between Zn and macronutrients or mineralogy (Fig. 5), all suggest that Zn does not significantly fractionate by either biological or abiotic processes once introduced to the Great Lakes.

Lastly, low Cu enrichment factors in Great Lakes sediments (Fig. 4) point to a likely geogenic sourcing, as for Zn and Pb, but Cu isotopes are more variable and their signatures less-conclusive because of a multitude of potential endmember contributions and contrasting and overlapping fractionation patterns. Specifically, significant Cu fractionation (up to -4.4‰) can occur as a result of biological processes, i.e., active cellular transport and regulation, due to the reduction of Cu(II) to Cu(I) (Sullivan et al., 2022; Zhu et al., 2002). Redox cycling of Cu also induces significant fractionation abiotically, with reduced versus oxidized Cu mineral precipitation inducing up to ± 4.0‰ fractionation (Fig. S9; Sullivan et al., 2022). The tendency for Cu to fractionate more than Zn or Pb explains the variability in Cu isotopes (Figs. 2 and 3), but the relative effects of kinetic versus equilibrium isotope fractionation remain challenging to quantify. Mineralogical sediment composition is largely similar across the investigated systems, more so than chlorophyll *a* and macronutrient levels, which suggests that biological processes control Cu isotope variations rather than abiotic adsorption. The fact that macronutrient or chlorophyll *a* data does not correlate with Cu concentrations or its isotopic signatures may in turn be explained by different fractionation across aquatic organisms (Sullivan et al., 2022).

With long hydraulic residence times and reasonable equilibrium between lake water and suspended sediment, the Great Lakes-St. Lawrence drainage basin likely exports geogenic Pb ratios and Zn signatures towards the Atlantic Ocean (in line with trends observed previously, Bridgestock et al., 2016; Lemaitre et al., 2020), but the global export of Cu is more challenging to assess: signatures are not consistently positive as in Vance et al. (2008) and are observed to be more variable than Pb and Zn across Great Lakes tributaries (Junqueira et al., 2023).

Additional study of metal fractionation by in-situ Great Lakes microbial communities, the speciation and apportionment of metals in the sediment (e.g., sequential extraction), and of isotope dynamics on shorter timescales (e.g., during high primary production or a bloom event; Juillot et al., 2023; Peel et al., 2009) may help to better define the roles of biological versus geochemical processes in metal fractionation during sedimentation.

4. Conclusions

We investigated in detail Cu, Zn, and Pb abundances and their isotopic signatures in surface sediments and sediment cores from both Lake Huron and Lake Erie, and complimented by analysis of chlorophyll *a*, macronutrients (TOC, TON and TP) and mineralogy. From this comprehensive screening of Great Lakes sediments, we conclude that.

- both Lake Huron and Lake Erie sediments present large variability in metal and major element concentrations, likely related to a combination of transport mechanisms into and between the lakes, dilution, particulate-water interactions, biological uptake and particle size.
- enrichment factors of Cu, Zn, and Pb show minor to no enrichment, aligning with their isotopic compositions that are typical for non-contaminated, pristine lacustrine systems. Further lack of correlation between Zn and Pb abundances, isotopic signatures and biological indicators suggests minor in-lake differentiation and that their dynamics are predominantly controlled by lithological sourcing.
- whereas Zn and Pb isotopes in Great Lakes sediments are spatiotemporally homogeneous, subtle variability in Cu isotopic signatures are attributed to changes in redox state and sedimentation regimes, and imply that Cu isotopes could be useful to identify changes in biogeochemical scavenging, even in large lakes.

Overall, our data shows for the first time that elevated metal levels at sites with historic contamination from anthropogenic and industrial activity remain spatially constrained and do appear not affect the Great Lakes sediments further offshore. Further, we show that sedimentation is a critical sink for metals in the Great Lakes that enforces a major control on metal distribution patterns across the basin. This study also demonstrates that multiple isotopic systems can be successfully applied in complex lake systems to better understand sedimentation, and ultimately lead to optimized water quality management and policy aimed at reducing metal contamination, including in the Great Lakes.

CRediT authorship contribution statement

Tassiane P. Junqueira: Writing – review & editing, Writing – original draft, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Daniel F. Araújo:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Hyeryeong Jeong:** Writing – original draft, Methodology, Data curation, Conceptualization. **Adriana Guatame-Garcia:** Writing – original draft, Investigation, Data curation, Conceptualization. **Tim Pascoe:** Resources, Methodology, Data curation. **Anna L. Harrison:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Matthew I. Leybourne:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **John P. Smol:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Bas Vriens:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Bas Vriens reports financial support was provided by Natural Sciences and Engineering Research Council of Canada. Bas Vriens reports financial support was provided by Canadian Foundation for Innovation. Bas Vriens reports a relationship with Natural Sciences and Engineering Research Council of Canada that includes: funding grants. Bas Vriens reports a relationship with Canadian Foundation for Innovation that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2024.119176.

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