Contrasting sources and mobility of trace metals in recent sediments of western Lake Erie

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ABSTRACT

Concentrations of the major and trace metals varied considerably in the western basin of Lake Erie, ranging from 0.9 to 25.3 mg/g for aluminum, from 2.9 to 36.5 mg/g for iron, from 6.4 to 74.8 mg/g for calcium, from 1.2 to 13.5 μg/g for cobalt, from 2.8 to 61.6 μg/g for copper, from 2.7 to 83.0 μg/g for lead, from 0.1 to 2.9 μg/g for cadmium, and from 7.1 to 127.3 μg/g for strontium. Distinct patterns of sediment metal variability allowed the identification of two major fluvial sources and some active in-lake biogeochemical processes. The inputs of Sr were largely from the Maumee River, the inputs of Cu, Pb, Cd, and Co were dominated by the Detroit River, and the inputs of Fe and Al were roughly evenly from the two rivers. The removal of Sr and Ca from the water column was mainly through coprecipitation with calcite. In contrast, the transfer of Cu, Pb, Cd, and Co was largely attributed to the removal of fine sediment particles from the Detroit River mouth and adjacent nearshore areas and the deposition of the metals scavenged by settling organic materials in the basin's central deeper areas. The mobility of the trace metals was different during the in-lake mass transfer, with Co being the most mobile and Cd being the least mobile. Furthermore, the trace metal mobility differences have decreased significantly during the past half-century due to a substantial increase in organic matter from eutrophication in the basin.

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Introduction

Owing to the presence of elevated toxic metals in Lake Erie, sources and mobility of the metals have been the subject of investigations for several decades (Kelly et al., 1991; Nriagu et al., 1979; Opfer et al., 2011). Early studies of sediment cores taken from across Lake Erie revealed varying degrees of trace metal enrichments caused by increased pollutant inputs from anthropogenic sources (Kemp and Thomas, 1976; Nriagu et al., 1979; Walters et al., 1974). Later, analyses of sediment cores from the western and central basins of Lake Erie showed that concentrations of several trace metals have been considerably reduced since the enactments of stringent regulations in the 1970s; however, Cd, Pb, and Hg were still well above the pre-industrial levels (Azcue et al., 1996; Elsayed, 2002). Recent work on a sediment core from the Sandusky basin of Lake Erie suggested that the moderate reductions of trace metals were attributed to increases in the fluvial metal fluxes from enhanced biogeochemical cycling and transfer in the eutrophic western basin upstream (Yuan, 2017).

Concentration profiles of trace metals in sediment cores from lakes and reservoirs have been widely used to study historic changes in elemental inputs to aquatic ecosystems (Balogh et al., 2009; Yohn et al., 2004). However, uncertainty remains regarding the extent to which the metals are subject to post-depositional migration (Boyle, 2001; Carignan and Nriagu, 1985; Robbins and Callender, 1975). For example, in central Lake Erie, the upward diffusion of metals from sediments to the overlying water column was considered significant as shown by concentration gradients of dissolved trace metals in sediment pore waters (Azcue et al., 1996). Additionally, the metal-bearing sediments that deposited earlier in the lake were subject to resuspension during mixing, strong storms, and high waves (Dusini et al., 2009; Lick et al., 1994; Valipour et al., 2017). The trace metals may be transported and redistributed during the generally west to east movement of water and fine-grained particulate across Lake Erie (Azcue et al., 1996; Kemp et al., 1977; Lum and Gammon, 1985; Yuan et al., 2014). Furthermore, correlations of the trace metals (Cu, Cr, Pb, Ni, and Cd) with the major metals, organic matter and grainsize distribution (Kemp and Thomas, 1976; Opfer et al., 2011; Szalinska et al., 2007; Yuan, 2017) suggested that the transfer and deposition of these trace metals were affected by multiple environmental factors such as the inputs from anthropogenic activities, lake hydrodynamics, and algal productivity in the basin. But

it is unclear how the mobility of the trace metals has changed over the course of eutrophication of the lake.

Here, we present an analysis of sources and mobility of trace metals through analyses of surface sediments and surface sediment cores from western Lake Erie. The objectives of this work are: 1) to provide a geochemical dataset for the trace metals Cu, Cd, Co, Pb, and Sr in recent sediments, 2) to examine and identify patterns of changes in sediment trace metals, and 3) to infer the major sources and the relative mobility of the trace metals in the western basin. This study is not only relevant to addressing the environmental concern on the mobility of the toxic heavy metals but also helps improve our understanding of the lake's biogeochemistry in response to eutrophication and cyanobacterial blooms in Lake Erie.

Materials and methods

The western basin of Lake Erie is relatively shallow (2–10 m) polymictic, and cyanobacterial blooms occur every summer (Stumpf et al., 2016). The basin receives the majority of its waters (and pollutants) from the Detroit and Maumee Rivers and several other smaller tributaries such as Crane Creek in Ohio and the River Raisin in Michigan (Fig. 1a). The Detroit River provides the majority of the basin's water, but the Maumee River has much higher nutrient concentrations and triggers the western basin algal blooms (Kane et al., 2014; Stow et al., 2015; Stumpf et al., 2016).

In spring 2016, a seismic survey was performed in the US half of the western basin with a sub-bottom profiling system to help identify optimal locations for sediment coring. A total of 85 surface sediment samples were collected from the western basin (Fig. 1b), with a standard Ponar stainless steel grab (22.5 cm W × 22.5 cm L), including 6 samples from the lower Maumee River (a 20-km reach from the river mouth). The grab sediments were pulled up slowly with a hand winch and placed gently in a plastic tub. The center top 3-cm sediments were sampled with a clean plastic spatula and stored (capped) in a 500 ml wide mouth plastic bottle. Additionally, three locations (S16, E16, and L16) were chosen to take surface sediment cores using an HTH gravity corer (Renberg and Hansson, 2008). The cores were extruded vertically and sectioned at 1-cm intervals right after core recovery. Cored sediments were transferred into a 50-ml polypropylene conical centrifuge tube. All sediment samples were temporarily stored in a large cooler before transferring to a refrigerator.

The sediment samples were thawed and subsampled with a clean plastic spoon. The subsampled sediments were hand-picked to remove large particles such as mussel shells, oven dried at 60 °C for up to 72 h and described before being ground with a ceramic mortar and pestle. Grainsize was semi-quantitatively analyzed on the surface sediment samples, which were divided into five groups with discrete G-scores: clay (1), silty clay (2), clayey silt (3), silt (4), and fine sand (5). Analysis of total organic carbon (TOC) was performed on dried decarbonated sediments, using a LECO carbon and sulfur analyzer (CS-200) at Zhejiang University, China. Dried sediment powder materials averaging 0.2 g were loaded into Teflon vessels and digested with HNO_3, H_2O_2, and HCl at 95 ± 5 °C, following the EPA method 3050b (USEPA, 1996). After removal of residual particles in the digested solution by centrifugation, the major metals were analyzed, using an ICP-AES at the Nanjing Institute of Geography and Limnology of the Chinese Academy of Science (NIGLAS) with detection limits of 5 μg/g for Fe, 20 μg/g for Al, and 5 μg/g for Ca, and the trace metals were measured, using an ICP-MS at NIGLAS with detection limits of 0.02 μg/g for Cu, 0.01 μg/g for Co, 0.02 μg/g for Pb, 0.01 μg/g for Cd, and 0.1 μg/g for Sr.

For all metal analyses, blanks, replicates, spiked samples, and reference sediment materials GBW07358 (GSD-15) were run along sample batches to monitor the inter-sample contamination of samples and evaluate the quality of analysis (precision and accuracy). All blanks were below or slightly above the method detection limits. The average relative errors for 27 (17%) replicates ranged from 0.5% for Fe to 1.4% for Cd. The average recovery rates of four spiked samples were 130% for Al, 98% for Ca, 99% for Fe, 94% for Co, 99% for Cu, 98% for Sr, 88% for Cd, and 97% for Pb. The relative standard deviations of 12 (7.5%) measurements of reference materials ranged from 0.6% for Fe to 2.6% for Pb, with an average of 1.5%. The average leach recovery rates (measured vs. certified total metal values) of the standard GSD-15 were 39% for Al, 73% for Fe, 66% for Ca, 64% for Co, 91% for Cu, 84% for Pb, and 33% for Sr.

Concentration contour maps were generated by ordinary kriging interpolations, using the R software version 3.2.4 (Venables and Smith, 2017). The kriging predictions, considered as best linear unbiased estimators, are the weighted combinations of the observed values in the searching neighborhood (van Beers and Kleijnen, 2003). The R package gstat was used to determine the optimal variogram models and subsequently make the geostatistical predictions (Pebesma and Wesseling, 1998). The kriging surfaces produced were checked against the raw data to ensure the accuracy of the contouring. In addition, correlation
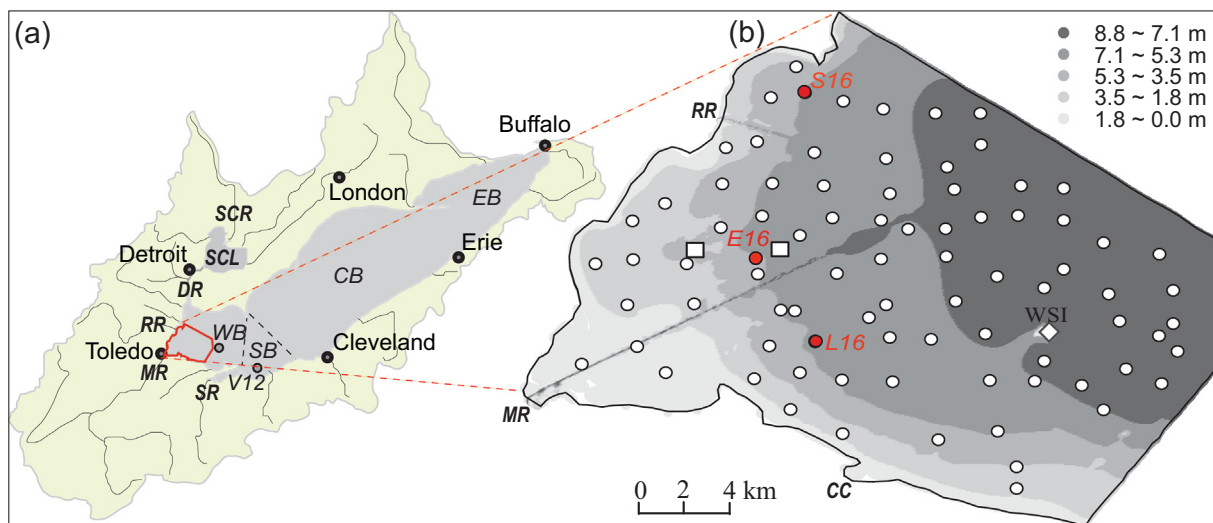

Fig. 1. (a) Map showing the study area in Lake Erie. Open circles denote sites of core WB in the Western Basin (Ritson et al., 1994) and core V12 in the Sandusky Basin (SB; Yuan, 2017). SCR: Saint Clair River; SCL: Saint Clair Lake; RR: River Raisin; MR: Maumee River; CC: Crane Creek; SR: Sandusky River; CB: Central Basin; EB: Eastern Basin. (b) Locations of surface sediment samples (open circles) and coring sites (filled red circles) in the western basin. Open squares denote two disposal sites for dredged materials. Open diamond denotes West Sister Island (WSI). Original bathymetric data are from the National Geophysical Data Center (NOAA, 1999). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)