UC Santa Cruz
UC Santa Cruz Previously Published Works

Title

Using lead isotopes and trace element records from two contrasting LakeTanganyika sediment cores to assess watershed – Lake exchange

Permalink

https://escholarship.org/uc/item/7xz9d1g7

Authors

Odigie, Kingsley O.
Cohen, Andrew S.
Swarzenski, Peter W.
et al.

Publication Date

2014

Peer reviewed

Using lead isotopes and trace element records from two contrasting Lake Tanganyika sediment cores to assess watershed – Lake exchange

Kingsley O. Odigie [a,*], Andrew S. Cohen [b], Peter W. Swarzenski [c], A. Russell Flegal [a]

[a] WIGS Laboratory, Environmental Toxicology, University of California at Santa Cruz, CA 95064, USA
[b] Department of Geosciences, University of Arizona, 1040 E 4th Street, Tucson, AZ 85721, USA
[c] United States Geological Survey, 400 Natural Bridges Drive, Santa Cruz, CA 95060, USA

ARTICLE INFO

ABSTRACT

Lead isotopic and trace element records of two contrasting sediment cores were examined to reconstruct historic, industrial contaminant inputs to Lake Tanganyika, Africa. Observed fluxes of Co, Cu, Mn, Ni, Pb, and Zn in age-dated sediments collected from the lake varied both spatially and temporally over the past two to four centuries. The fluxes of trace elements were lower (up to 10-fold) at a mid-lake site (MC1) than at a nearshore site (LT-98-58), which is directly downstream from the Kahama and Nyasanga River watersheds and adjacent to the relatively pristine Gombe Stream National Park. Trace element fluxes at that nearshore site did not measurably change over the last two centuries (1815–1998), while the distal, mid-lake site exhibited substantial changes in the fluxes of trace elements – likely caused by changes in land use – over that period. For example, the flux of Pb increased by ~300% from 1871 to 1991. That apparent accelerated weathering and detrital mobilization of lithogenic trace elements was further evidenced by (i) positive correlations ($r = 0.77$–0.99, $p < 0.05$) between the fluxes of Co, Cu, Mn, Ni, Pb, and Zn and those of iron (Fe) at both sites, (ii) positive correlations ($r = 0.82$–0.98, $p < 0.01$, $n = 9$) between the fluxes of elements (Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn) and the mass accumulation rates at the offshore site, (iii) the low enrichment factors (EF < 5) of those trace elements, and (iv) the temporal consistencies of the isotopic composition of Pb in the sediment. These measurements indicate that accelerated weathering, rather than industrialization, accounts for most of the increases in trace element fluxes to Lake Tanganyika in spite of the development of mining and smelting operations within the lake's watershed over the past century. The data also indicate that the mid-lake site is a much more sensitive and useful recorder of environmental changes than the nearshore site. Furthermore, the lead isotopic compositions of sediment at the sites differed spatially, indicating that the Pb (and other trace elements by association) originated from different natural sources at the two locations.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. Trace element contamination in Central Africa

It has been well documented that all kinds of human activities have markedly impacted the cycling and fate of many trace elements in the environment (Warren, 1981; Sañudo-Wilhelmy and Flegal, 1994; Nriagu, 1996; Soto-Jimenez et al., 2006). For example, 75% of global atmospheric Pb contamination during the latter half of the 20th century has been attributed to anthropogenic emissions, primarily from the combustion of leaded gasoline (Nriagu

and Pacyna, 1988; Dunlap et al., 2008). These global perturbations have also been documented in Africa (Nriagu, 1992; Ettler et al., 2011), as evidenced in recent studies by Yang et al. (2010) and Conaway et al. (2012) that associated increased Hg fluxes to equatorial African lakes with increased atmospheric emissions of Hg from fossil fuel combustion over the past two centuries. However, such studies are few in number, and more information is still needed to adequately characterize the impacts of anthropogenic activities in Central Africa.

In addition to industrial emissions from fossil fuel combustion, other anthropogenic activities, including mining and smelting operations, have resulted in elevated trace element deposition in some parts of Africa on both local and regional scales (Banza et al., 2009; Nakayama et al., 2011). Unfortunately, these activities are particularly deleterious in developing countries, where environmental regulations are sometimes inadequate and/or poorly

* Corresponding author at: WIGS Laboratory, Environmental Toxicology, University of California at Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, USA. Tel.: +1 (831) 459 5336; fax: +1 (831) 459 3524.

E-mail address: kodigie@ucsc.edu (K.O. Odigie).

enforced. For example, highly elevated concentrations of labile Cu, Pb, and Zn were measured in sediment collected close to the Kabwe Mine in Zambia, which was recently ranked as one of the most polluted sites in the world (Tembo et al., 2006; Blacksmith Institute, 2007). Very high levels of Co (610 mg kg^{-1}), Cu (27,000 mg kg^{-1}), Pb (480 mg kg^{-1}), and Zn (450 mg kg^{-1}) were also measured in the topsoil near the Nkana copper smelter in the Copperbelt Province of Kitwe in Zambia, which were attributed predominantly to contamination from those mining and smelting operations (Ettler et al., 2011). Similarly, elevated levels of trace elements released from mining and smelting activities have been documented in other countries in the region, including the Democratic Republic of the Congo (Banza et al., 2009) and Tanzania (Marwa et al., 2012). Furthermore, environmental degradation has been exacerbated around Lake Tanganyika by the unregulated discharge of untreated industrial waste within its basin (West, 2001).

In addition to these industrial activities, many other anthropogenic perturbations – including widespread deforestation, agricultural development, and rapid urbanization – may contribute to elevated trace element releases into the environment via accelerated weathering and erosion. For example, deforestation (rates of up to 100% have been reported in some parts of the lake's watershed) and land-use conversions, which are a major threat to the lake, have been shown to increase soil erosion rates by up to 100-fold in Burundi (Bizimana and Duchafour, 1991; Cohen et al., 1993, 2005a; Wells et al., 1999; O'Reilly et al., 2005). Elsewhere, studies (e.g., Quinton and Catt, 2007) have shown associations between land-use (e.g., agriculture) linked erosion and accelerated mobilization of trace elements. Moreover, it has been predicted that climate change-induced weathering and erosion rates will increase in much of the world, including Africa, which will exacerbate trace element fluxes (Yang et al., 2003; IPCC, 2013).

Consequently, projected trends in accelerated trace element releases and associated ecological impacts across much of Africa, including countries that border Lake Tanganyika pose substantial risk to human and environmental health (Banza et al., 2009; Marwa et al., 2012). These concerns have already been substantiated by measurements of blood Pb (BPb) levels in children in Kabwe, Zambia (Blacksmith Institute, 2007). On average, their BPb levels were ~10–20 times the current US level of concern (5 µg dL^{-1}) (CDC, 2012). Similarly, elevated levels of trace elements have been measured in cattle (e.g., up to 400 mg kg^{-1} of Cu and 250 mg kg^{-1} of Zn in dry tissue) in Kabwe, Zambia (Yabe et al., 2011).

1.2. Environmental changes in Lake Tanganyika

In addition to the previously noted developmental changes that are occurring in Africa today, air and water temperatures at Lake Tanganyika have been increasing. For example, average annual air temperatures around the lake have increased by 0.5–0.7 °C since the late 1970s (O'Reilly et al., 2003), and the temperature of the lower metalimnion (~110 m-depth water column) of the lake has increased by 0.9 °C between 1913 and 2000 (Tierney et al., 2010). Moreover, it has been predicted that surface temperatures in Central Africa could rise by 1.25–1.5 °C by the end of this century (IPCC, 2013). Wildfires and soil erosion, which mobilize trace elements and enhance their bioavailability, are therefore expected to increase with climate change (Yang et al., 2003; McKenzie et al., 2004; IPCC, 2013). Also, recurring natural and deliberate forest fires (often associated with land-use conversions), which are a major disturbance to the lake's watershed, would further increase soil erosion rates and exacerbate release of sediment-bound trace elements (Eva and Lambin, 2000). As a result, concerns about these threats to the lake led to the creation of the UN-funded

Lake Tanganyika Biodiversity Project (LTBP, http://www.ltbp.org/) and the Lake Tanganyika Authority (LTA, http://lta.iwlearn.org/).

These programs and similar efforts have provided a vehicle for a wide range of sustained scientific data collection on diverse topics, including climate change impacts, water quality, and land-use on the lake (Cohen et al., 1993; Tierney et al., 2010). They have resulted in new data on historic profiles of Cd, Fe, Mo, Re, and U in the lake's sediment (Brucker et al., 2011) and a report on Hg fluxes to the lake (Conaway et al., 2012). However, there are no comparable measurements of temporal changes of industrial trace elements (e.g., Co, Cu, Pb, and Zn) fluxes associated with mining and smelting operations and land-use changes around the lake.

To address those concerns, in addition to measuring the concentrations of trace elements, we included stable lead isotopic composition analyses to determine the sources and fate of Pb contamination in the lake (Ellam, 2010; Flegal et al., 2010). Lead isotopic composition data have been used to identify the combustion of leaded gasoline as the dominant source of Pb contamination in the 20th century, which subsequently led to the phase-out of Pb from gasoline in many countries, including the United States (Nriagu, 1990; Needleman, 2000). Consequently, the objective of this study was to quantify trace element inputs, along with lead isotopic compositions, at two contrasting sites in Lake Tanganyika over the past two to four centuries to better understand the flux of natural and industrial trace elements into Lake Tanganyika.

2. Materials and methods

2.1. Study site and sample collection

Lake Tanganyika is the world's second largest (in volume) and second deepest freshwater lake (Coulter and Spigel, 1991; Tierney et al., 2010). It covers an area of 32,600 km^2; has an average depth of 570 m, with a maximum depth of 1.47 km; and is bordered by Burundi, Tanzania, Zambia, and the Democratic Republic of the Congo (Coulter and Spigel, 1991; Cohen et al., 2005a). The lake is an invaluable source of food and drinking water to millions of people that live around the lake (Molsa et al., 1999; Tierney et al., 2010), and it is surrounded by some of the world's fastest growing human populations, which could further impact the health of the lake (West, 2001; Than, 2011).

Subsamples from two sediment cores, a nearshore core (LT-98-58) and an offshore core (MC1), collected from Lake Tanganyika with a Hedrick-Marrs multi-corer deployed from a ship were used for this study (Fig. 1). The cores were collected with intact sediment–water interface after an extensive mapping survey of the lake bottom as described elsewhere (Cohen et al., 2005a). The nearshore core (4.6883°S, 29.6167°E) was collected in relatively shallow water (76 m) just off the Nyasanga/Kahama delta region which drains a small (~3.8 km^2) sparsely populated (<5 people per km^2) area within the relatively pristine Gombe Stream National Park in northern Tanzania (Cohen et al., 2005a; McKee et al., 2005): a watershed that has been effectively uninhabited since the early 1960s. The offshore core (6.5525°S, 29.9747°E) was collected in deep (309 m) water off the Kalya Platform in the relatively remote south-central part of the lake. The sediment cores were both dated with excess ^{210}Pb (using constant rate of supply (CRS) model for Core LT-98-58 and constant initial concentration (CIC) model for MC1) and ^{14}C using accelerator mass spectrometry. The age models and determination of sedimentation rates for Core LT-98-58 and Core MC1 are described in detail in McKee et al. (2005) and Tierney et al. (2010), respectively. These two sites differ dramatically in their depositional regimes; the nearshore site receives more direct, local inputs from relatively pristine sources whereas the offshore site integrates more dispersed inputs.
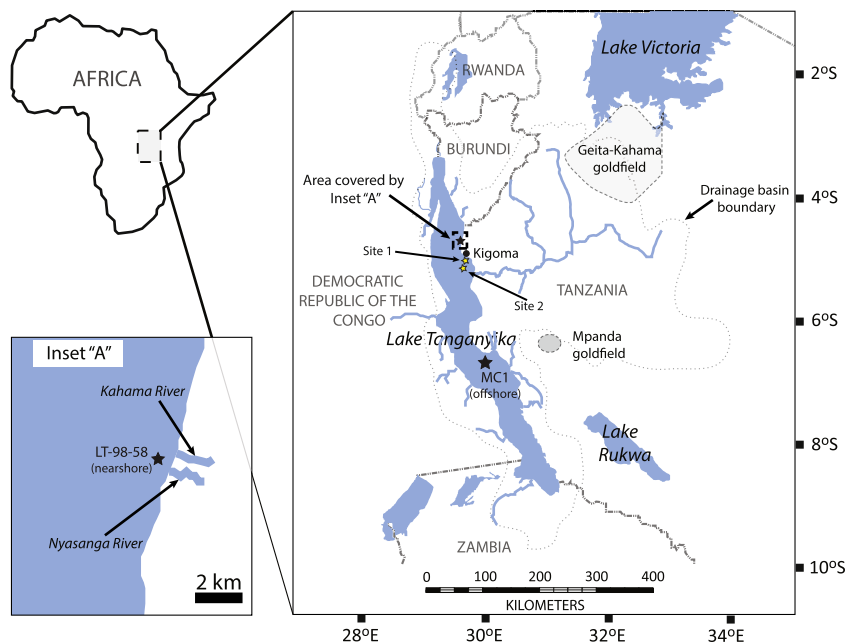
Fig. 1. Map showing sample collection sites from Lake Tanganyika in Africa and the approximate drainage basin of the lake (adapted from Bergonzini et al., 1997; Conaway et al., 2012). Also included on the map are the collection sites, Site 1 (72 m depth) and Site 2 (332 m depth), of sediment cores studied by Brucker et al. (2011).

2.2. Sample processing and analysis

High purity (18.2 MΩ cm) water (Milli-Q) and trace metal grade or ultrapure (2× sub-boiling quartz distilled) grade reagents were used for cleaning labware and processing samples. Thirty-seven (37) samples, including four (4) aliquots in triplicate, along with procedural blanks, National Bureau of Standards (NBS) Standard Reference Material (SRM) 1645, and NBS SRM 2704, were processed concurrently using established methods (Soto-Jimenez et al., 2006). Briefly, 0.3–0.5 g of sediment or SRM was transferred to a trace metal clean Teflon digestion vial, dried overnight at 65 °C, cooled, and weighed. The sediment was then refluxed in 10 mL of hot (~130 °C) concentrated aqua regia (HNO_3 + HCl, 1:3 v/v) in a closed vial overnight, dried, cooled, and re-dissolved in 10 mL of 1 M ultrapure HNO_3 (Odigie and Flegal, 2014). The "near-total concentrations" of Co, Cu, Ni, Pb, and Zn in the digests were then determined with a Finnigan ELEMENT 2 high resolution inductively coupled plasma-mass spectrometer (HR ICP-MS) using established methods (Dunlap et al., 2008). Lead isotopic compositions ($^{207}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, and $^{208}Pb/^{207}Pb$) were measured separately, after optimizing the Pb concentrations of the solutions, with HR ICP-MS, as previously described (Odigie and Flegal, 2011; Zurbrick et al., 2013). Concentrations of Al, Fe, and Mn in the digests were then determined with a PerkinElmer Optima 4300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). Internal standards were used to correct for instrumental drift during analyses, and concurrent measurements of National Institute of Standards and Technology (NIST) SRM 981 (common lead) were used to correct the lead isotopic ratios for instrumental fractionation (Kristensen et al., 2014). Isobaric interference of ^{204}Hg with ^{204}Pb was corrected using established, state of the art methods, i.e., by concurrently measuring ^{200}Hg and ^{202}Hg, calculating ^{204}Hg by assuming natural abundance ($^{204}Hg/^{202}Hg = 0.2298$), and subtracting the ^{204}Hg counts from the total counts at $m/z = 204$ ($^{204}Hg + ^{204}Pb$), as detailed elsewhere (Wu and Boyle, 1997; Gallon et al., 2011; Zurbrick et al., 2013). The detection limit, digestion recovery, and analytical precision for each analyte are presented in Tables S1–S4 (where "S" here and hereafter denotes that the table is in the Supplementary material file). Enrichment factors (EFs) for each element were calculated by normalizing the concentration of the element in a sample to the average concentration of the element in pre-industrial (before 1890) samples from the sediment core (Nriagu et al., 1982; El Bilali et al., 2002). The fluxes of elements ($\mu g\ cm^{-2}\ yr^{-1}$ or $mg\ cm^{-2}\ yr^{-1}$) were calculated by multiplying the mass accumulation rate (MAR, $g\ cm^{-2}\ yr^{-1}$) by each element concentration ($\mu g\ g^{-1}$ or $mg\ g^{-1}$). These elemental concentrations, fluxes, and enrichment factors are considered conservative because the digestion did not include treatment with concentrated HF, which is needed for complete dissolution of refractory elements bound in aluminosilicate minerals. Concentrations of charcoal particles (>100 μm) were previously determined for LT-98-58 using samples collected from a matched parallel core (Palacios-Fest et al., 2005) and for MC1 using subsamples collected from the core (Tierney et al., 2010).

3. Results and discussion

3.1. Overview

The "near total" concentrations of Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn for the two cores are listed in Table S5. Sediment fluxes of these elements, along with the $^{206}Pb/^{207}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{207}Pb$ ratios of the sediment, are listed in Table S6. Temporal profiles for the concentrations of the elements and lead isotopic ratios are presented in the Supplementary material file (Figs. S1–S10). Fluxes of trace elements at the offshore site (MC1) were consistently lower (⩽10-fold) than those at the nearshore site (LT-98-58), which was directly impacted by surface runoff and fluvial discharges from the Kahama and Nyasanga Rivers (Figs. 1 and 2). The latter site's relatively high individual element inputs corresponded with the relatively high mass accumulation rates (MARs) at that site, which were over an order of magnitude greater than those at the offshore site (Fig. 3a). However, trace element concentrations at both sites had comparable levels of enrichment, which were close to 1, except for Zn, which showed recent increased input, although its EFs were still less than 5 and within the range of natural variability.
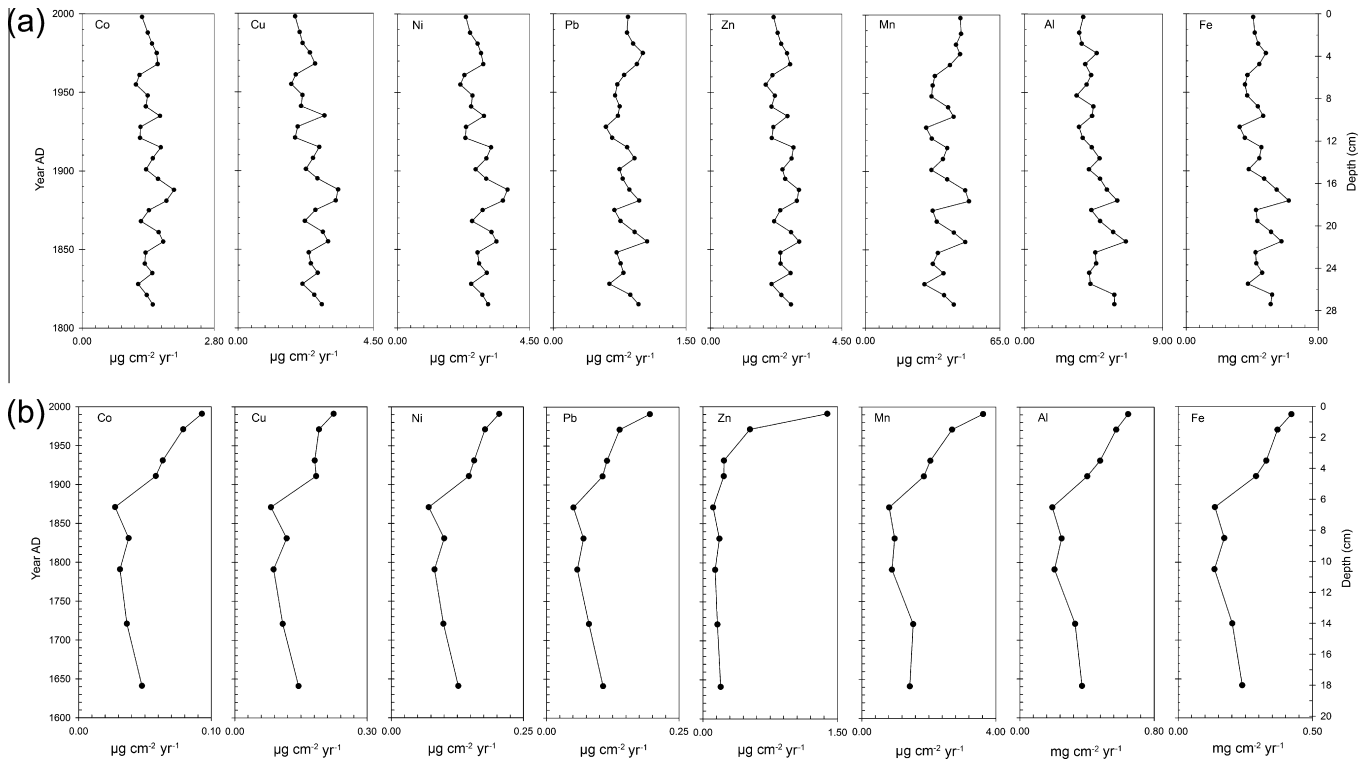
Fig. 2. (a) Down core fluxes of elements (Co, Cu, Ni, Zn, Mn, Al, and Fe) at the nearshore site, LT-98-58, in Lake Tanganyika, (b) down core fluxes of elements (Co, Cu, Ni, Pb, Zn, Mn, Al, and Fe) at the offshore site, MC1, in Lake Tanganyika.
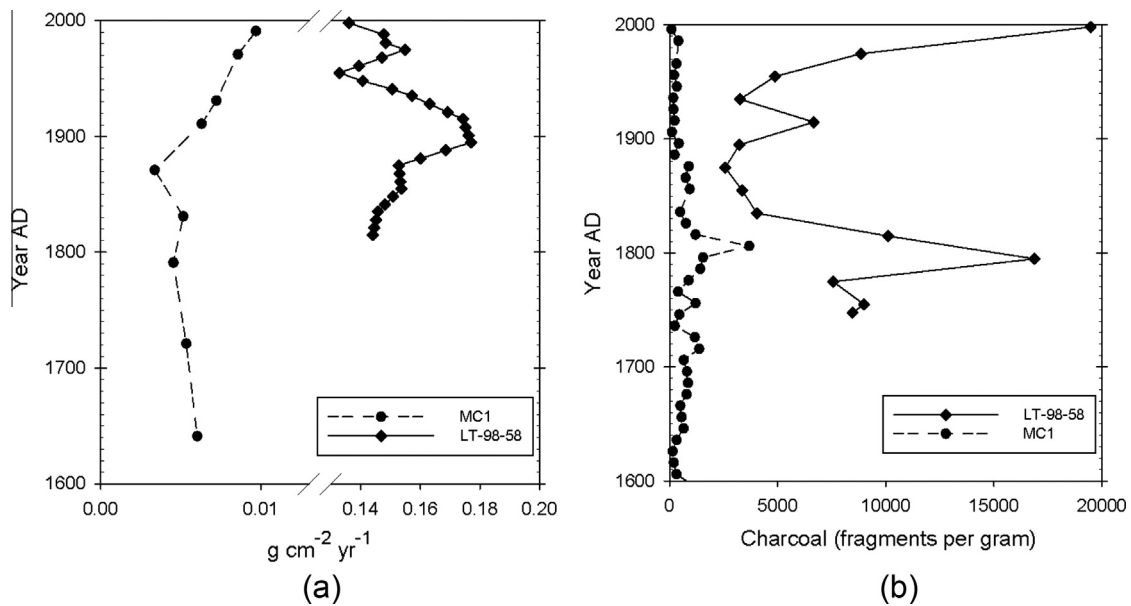

Fig. 3. (a) Mass accumulation rate (MAR, g cm^{-2} yr^{-1}) plots for cores MC1 (offshore) and LT-98-58 (nearshore) (adapted from Conaway et al., 2012, data from Tierney et al., 2010; McKee et al., 2005). (b) Charcoal abundance profiles for MC1 (offshore site) and LT-98-58 (nearshore site) (adapted from Conaway et al., 2012, data from Palacios-Fest et al., 2005; Tierney et al., 2010).

3.2. Nearshore site (Core LT-98-58)

The "near total" concentrations of Cu (16 ± 2 µg g^{-1}, mean ± standard deviation, n = 28) in the nearshore sediment core are comparable with that of Cu (21 µg g^{-1}) measured in nearshore sediment from Lake Tanganyika by Chale in 2002, but the concentrations of Pb (5 ± 1 µg g^{-1}, mean ± standard deviation, n = 28) and Zn (16 ± 2 µg g^{-1}, mean ± standard deviation, n = 28) in our near-

shore core are substantially lower than those of Pb (14 µg g^{-1}) and Zn (28 µg g^{-1}) reported for nearshore sediment in that study (Chale, 2002). In contrast, Mn concentrations (253 ± 44 µg g^{-1}, mean ± standard deviation, n = 28) in our nearshore sediment core were substantially higher than the value (73 µg g^{-1}) reported by Chale (2002), but are comparable to Mn concentrations (235 ± 65 µg g^{-1}, mean ± standard deviation, n = 10) measured in relatively pristine Zambian soil (Mihaljevic et al., 2011). Similarly,

the concentrations of Al (30 ± 6 mg g^{-1}, mean ± standard deviation, $n = 28$) and Fe (33 ± 5 mg g^{-1}, mean ± standard deviation, $n = 28$) in the nearshore core are comparable to those of Al (54 ± 19 mg g^{-1}, mean ± standard deviation, $n = 10$) and Fe (44 ± 15 mg g^{-1}, mean ± standard deviation, $n = 10$) measured by Brucker et al. (2011) in a sediment core collected at a comparable depth (72 m) from the Luiche Platform in Lake Tanganyika. Averages of the measurements by Brucker et al. (2011) are higher than those of the elements (Al and Fe) we measured, presumably due to the different digestion methods (total versus near-total) employed in the two studies.

Fluxes of Co, Cu, Mn, Ni, Pb, and Zn correlated (simple linear regressions) positively with those of Fe ($r = 0.77$–0.88, $p < 0.01$, $n = 28$) at the nearshore site (Table S7). None of the fluxes systematically changed over the last two centuries (1815–1998) (Fig. 2a), and all of their EFs were consistently low (<5). Consequently, the sources of those trace elements (Co, Cu, Mn, Ni, Pb and Zn), as well as those of Al and Fe, at the nearshore site are primarily attributed to the weathering of natural sources, rather than industrial inputs, even during the 20th century.

Those relatively consistent temporal trends of natural element fluxes are comparable to the relatively conservative trends reported for the concentration and accumulation rate of total organic matter (TOC) at the site (Palacios-Fest et al., 2005). Trace elements sorb to organic matter, which could substantially influence their behavior in terrestrial and aquatic systems (Schwab et al., 2008; Hartland et al., 2011).

These conservative temporal trends were expected because the nearshore site: (i) drains a basin with a relatively small human population (<5 people per km^2), (ii) has a relatively low level of disturbance – including deforestation in its watershed, and (iii) has not had major soil erosion pulses within its watershed since the late 19th century (Cohen et al., 2005a, 2005b; O'Reilly et al., 2005).

In contrast to the element fluxes, there were pronounced temporal changes in charcoal fluxes, which increased by ~500% between 1935 and 1998, to sediment at the nearshore site that do not appear to be from local inputs (Palacios-Fest et al., 2005). Specifically, charcoal fluxes were relatively high at the nearshore site (2574–19,473 fragments per gram) compared to those at the offshore site (90–3680 fragments per gram), which were relatively constant throughout the core (Fig. 3b). Since the site abuts the protected Gombe Stream National Park, that increase in charcoal fluxes has been attributed to regional, rather than local, increases in anthropogenic activities around Lake Tanganyika during the 20th century (Palacios-Fest et al., 2005; Conaway et al., 2012). The regional source of charcoal versus the apparently local source of elements in sediment at the nearshore site was also evidenced by the relatively low and statistically insignificant correlations between the fluxes of most of those elements (Al, Co, Cu, Fe, Ni, Pb, and Zn) and that of charcoal ($r = -0.35$–0.49, $n = 10$, $p > 0.1$). Consequently, the naturally high rates of sedimentation at the nearshore site (MAR = 0.13–0.18 g cm^{-2} yr^{-1}) swamp the relatively small increases in sediment fluxes associated with fires and anthropogenic activities over the last century. But those increases are apparent in the offshore site, where sedimentation rates are over an order of magnitude lower (MAR = 3.4–9.7 mg cm^{-2} yr^{-1}), as discussed in Section 3.3.

The isotopic compositions of Pb in sediment at the nearshore site (Figs. 4 and 5), which are assumed to be predominantly characteristic of relatively uncontaminated sediment in the Nyasanga/Kahama drainage basin, are markedly different from those of Pb at the offshore site of the lake. Small temporal changes in the lead isotopic compositions suggest that the site could have received Pb from anthropogenic sources. However, the influence of that deposition on the flux of Pb at the site appears to be minimal. Consequently, the relative consistency of the isotopic ratios of Pb over
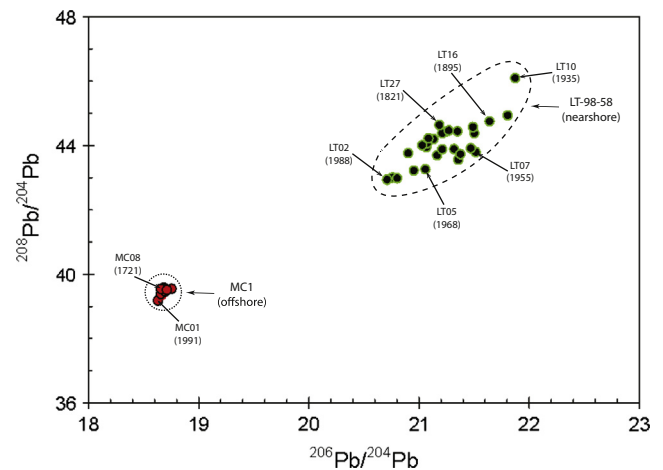

Fig. 4. Lead isotopic composition ($^{206}Pb/^{204}Pb$: $^{208}Pb/^{204}Pb$) of sediment core samples (LT-98-58 and MC1) collected from Lake Tanganyika, Africa. LT02 denotes Core LT-98-58 (nearshore site) and a depth of 1–2 (1.5) cm and so forth. MC denotes Core MC1 (offshore site).
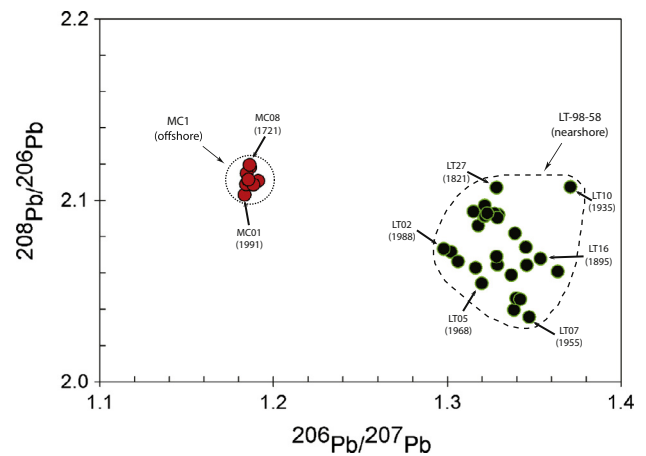

Fig. 5. Lead isotopic composition ($^{206}Pb/^{207}Pb$: $^{208}Pb/^{206}Pb$) of sediment core samples (LT-98-58 and MC1) collected from Lake Tanganyika, Africa. LT02 denotes Core LT-98-58 (nearshore site) and a depth of 1–2 (1.5) cm and so forth. MC denotes Core MC1 (offshore site).

the past two centuries at the nearshore site (Figs. 4 and 5) suggests that the Pb is primarily from local, natural sources. The predominantly local sources of Pb (and other trace elements by association) was corroborated by the statistically significant ($p < 0.05$, t-test) positive correlations between the fluxes of trace elements and those of Fe as previously discussed (Table S7). Unfortunately, lead isotopic composition data on the Lake Tanganyika area are limited; thus, a comprehensive comparison of our data to others was not possible.

3.3. Offshore site (Core MC1)

The "near total" concentrations of Cu (23 ± 3 µg g^{-1}, mean ± standard deviation, $n = 9$), Pb (16 ± 2 µg g^{-1}, mean ± standard deviation, $n = 9$), and Zn (49 ± 37 µg g^{-1}, mean ± standard deviation, $n = 9$) in the offshore sediment core are similar to those of Cu (21 µg g^{-1}), Pb (14 µg g^{-1}), and Zn (28 µg g^{-1}) measured in nearshore sediment from Lake Tanganyika by Chale (2002), but are substantially higher than the concentrations of Cu (3.6 µg g^{-1}), Pb (1.4 µg g^{-1}), and Zn (2.2 µg g^{-1}) he measured in offshore sediment. The Mn concentrations (269 ± 58 µg g^{-1}, mean ± standard

deviation, $n = 9$) in the offshore sediment core from our study are significantly ($p < 0.01$, t-test) higher than the value (75 µg g^{-1}) reported by Chale (2002), but are similar to Mn concentrations (235 ± 65 µg g^{-1}, mean ± standard deviation, $n = 10$) measured in relatively pristine Zambian soil (Mihaljevic et al., 2011). Concentrations of Al (60 ± 8 mg g^{-1}, mean ± standard deviation, $n = 9$) and Fe (40 ± 6 mg g^{-1}, mean ± standard deviation, $n = 9$) in the offshore sediment are within the ranges of those of Al (72 ± 21 mg g^{-1}, mean ± standard deviation, $n = 7$) and Fe (51 ± 16 mg g^{-1}, mean ± standard deviation, $n = 7$) measured by Brucker et al. (2011) in a sediment core collected at a comparable depth (332 m) off the Luiche Platform in Lake Tanganyika. The Al and Fe measured in these studies are considered to be natural since these elements are naturally abundant and relatively difficult to measurably increase through contamination. Thus, the strong positive correlations between the concentrations of the other elements and those of Fe indicate that these elements are predominantly from local, natural sources.

As at the nearshore site, down core fluxes of Co, Cu, Mn, Ni, Pb, and Zn correlated positively with those of Fe ($r = 0.77$–0.99, $p \leqslant 0.02$, $n = 9$) at the offshore site (Table S7). In contrast to the nearshore site, those fluxes systematically varied over the past four centuries (1641–1991) (Fig. 2b). For example, the fluxes of Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn increased by approximately 200%, 200%, 200%, 200%, 300%, 200%, 300%, and 1000%, respectively, from 1871 to 1991. Regardless, the strong positive and statistically significant correlations between the fluxes of Co, Cu, Mn, Ni, and Pb and those of Fe ($r = 0.95$–1.00, $p < 0.02$, $n = 5$) over the past two centuries (1871–1991) as well as the low EFs (<5) of those elements at the offshore site indicate that the mid-lake sediment core is a sensitive and useful recorder of land use changes.

The one, modest, exception is Zn. Correlation between the flux of Zn and that of Fe ($r = 0.75$) was positive, but not statistically significant ($p > 0.1$, $n = 5$) during that period (1871–1991). Still, the recent (1931–1991) steep increase in the flux of Zn suggests that Zn was enriched at this site, possibly by industrial activities.

The MAR at the offshore site also increased during the past two centuries (1871–1991, Fig. 3a), presumably from accelerated erosion rates associated with substantial deforestation (∼40–60%) that occurred in the lake's watersheds mostly in the 20th century (Cohen et al., 1993). Correlations between the fluxes of Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn and MAR ($r = 0.82$–0.98, $n = 9$) were statistically significant ($p < 0.01$, t-test), suggesting that the increase in fluxes of elements is due to local disturbance of sediment in the lake's drainage basin. Therefore, we attribute the pronounced temporal increases in trace element fluxes at the offshore site primarily to increases in erosion rates associated with land-use changes in the lake's drainage basins.

The temporal consistency of lead isotopic compositions (Figs. 4 and 5) of sediment at the offshore site over the past four centuries also indicates that the temporal increases in Pb (and most other trace elements by association) originated predominantly from increases in local, natural fluxes. The apparent local sources of those fluxes were further evidenced by the positive correlations of their fluxes with those of Fe.

4. Conclusions

The concentrations of trace elements (Co, Cu, Mn, Ni, Pb, and Zn), the significant positive correlations of their fluxes with those of Fe, and their low respective enrichment factors (<5) in Lake Tanganyika all suggest that these trace elements were predominantly derived from local sources. The spatial differences between the fluxes of respective trace elements (Fig. 2a and b) at the nearshore (LT-98-58) and offshore (MC1) sites are tentatively attributed to several factors, including: proximity to shore (MC1 is much farther from direct terrestrial sediment sources), water conditions (e.g., DO concentrations at the different water depths: 76 m at LT-98-58 and 309 m at MC1), sediment focusing, and the relative levels of disturbance (e.g., increased erosion rates associated with deforestation) (Conaway et al., 2012).

Spatially different, but predominantly consistent lead isotopic compositions at the two sites over time indicate that the Pb (and other trace elements by association) originated from relatively distinct sources. This spatial difference in Pb isotopic compositions could have resulted from an elevated atmospheric contribution of Pb to the offshore site, compared to the nearshore site. Concentrations of some elements measured in this study are similar to previously published values in terrestrial and lacustrine sediment from and around Lake Tanganyika, including Lake Victoria, another large lake in the same region (Kishe and Machiwa, 2003; Brucker et al., 2011). Therefore, these data are coherent.

Consequently, the impact of human activities, especially those related to land use and development, on the fluxes of trace elements was minimal at the nearshore site, presumably because of the naturally high sediment influx to the site and its relatively pristine drainage area. But that impact was pronounced at the offshore site. The results indicate that the offshore site is a more sensitive and reliable recorder of environmental changes within the lake's basin. Temporal changes in trace element fluxes at the offshore site appear to be primarily due to land use changes that increase erosion – rather than additional inputs of industrial elements. These land use-driven changes in the fluxes of elements contrast with the increase in Hg fluxes at both sites that were attributed predominantly to global industrial emissions (Conaway et al., 2012).

In summary, results from this study indicate that the impacts of industrial waste discharged to the northern reach of the lake and wildfires around the lake on the fluxes of trace elements at both sites are relatively limited. However, the projected global increase in wildfire intensity and frequency in response to climate change, along with increasing population in the lake's drainage basin, could substantially impact the trace element fluxes to the lake over the next century, as recently observed elsewhere (Odigie and Flegal, 2011; Stein et al., 2012; Odigie and Flegal, 2014). Consequently, studies aimed at further characterizing different natural and industrial sources of elements to Lake Tanganyika are needed to improve our understanding of the extent of anthropogenic perturbations in the lake and its basin.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.10.007.

References

Banza, C.L.N., Nawrot, T.S., Haufroid, V., Decree, S., De Putter, T., Smolders, E., Kabyla, B.I., Luboya, O.N., Ilunga, A.N., Mutombo, A.M., Nemery, B., 2009. High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. Environ. Res. 109, 745–752.

Bergonzini, L., Chalié, F., Gasse, F., 1997. Paleoevaporation and paleoprecipitation in the Tanganyika basin at 18,000 years B.P. inferred from hydrologic and vegetation proxies. Quat. Res. 47, 295–305.

Bizimana, M., Duchafour, H., 1991. A drainage basin management study: The case of the Ntihangwa River Basin. In: Cohen, A.S. (Ed.), Report of the First International Conference on Conservation and Biodiversity Support Program, Washington, DC, pp. 43–45.

Blacksmith Institute, 2007. The world's worst polluted places. In: The Top Ten of the Dirty Thirty. <http://www.blacksmithinstitute.org/wwpp2007/finalReport2007.pdf> (retrieved 12.09.12).

Brucker, R.P., McManus, J., Severmann, S., Owens, J., Lyons, T.W., 2011. Trace metal enrichments in Lake Tanganyika sediments: controls on trace metal burial in lacustrine systems. Geochim. Cosmochim. Acta 75, 483–499.

CDC, 2012. Blood Lead Levels in Children, p. 2. <http://www.cdc.gov/nceh/lead/ACCLPP/Lead_Levels_in_Children_Fact_Sheet.pdf> (retrieved 16.10.13).

Chale, F.M.M., 2002. Trace metal concentrations in water, sediments and fish tissue from Lake Tanganyika. Sci. Total Environ. 299, 115–121.

Cohen, A.S., Bills, R., Cocquyt, C.Z., Caljon, A.G., 1993. The impact of sediment pollution on biodiversity in Lake Tanganyika. Conserv. Biol. 7, 667–677.

Cohen, A.S., Palacios-Fest, M.R., McGill, J., Swarzenski, P.W., Verschuren, D., Sinyinza, R., Songori, T., Kakagozo, B., Syampila, M., O'Reilly, C.M., Alin, S.R., 2005a. Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: I. An introduction to the project. J. Paleolimnol. 34, 1–18.

Cohen, A.S., Palacios-Fest, M.R., Msaky, E.S., Alin, S.R., McKee, B., O'Reilly, C.M., Dettman, D.L., Nkotagu, H., Lezzar, K.E., 2005b. Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: IX. Summary of paleorecords of environmental change and catchment deforestation at Lake Tanganyika and impacts on the Lake Tanganyika ecosystem. J. Paleolimnol. 34, 125–145.

Conaway, C.H., Swarzenski, P.W., Cohen, A.S., 2012. Recent paleorecords document rising mercury contamination in Lake Tanganyika. Appl. Geochem. 27, 352–359.

Coulter, G.W., Spigel, R.H., 1991. Hydrodynamics. In: Coulter, G.W. (Ed.), Lake Tanganyika and its Life. Oxford University Press, New York, pp. 49–75, p. 354.

Dunlap, C.E., Alpers, C.N., Bouse, R., Taylor, H.E., Unruh, D.M., Flegal, A.R., 2008. The persistence of lead from past gasoline emissions and mining drainage in a large riparian system: evidence from lead isotopes in the Sacramento River, California. Geochim. Cosmochim. Acta 72, 5935–5948.

El Bilali, L., Rasmussen, P.E., Hall, G.E.M., Fortin, D., 2002. Role of sediment composition in trace metal distribution in lake sediments. Appl. Geochem. 17, 1171–1181.

Ellam, R.M., 2010. The graphical presentation of lead isotope data for environmental source apportionment. Sci. Total Environ. 408, 3490–3492.

Ettler, V., Mihaljevic, M., Kribek, B., Majer, V., Sebek, O., 2011. Tracing the spatial distribution and mobility of metal/metalloid contaminants in Oxisols in the vicinity of the Nkana copper smelter, Copperbelt province, Zambia. Geoderma 164, 73–84.

Eva, H., Lambin, E.F., 2000. Fires and land-cover change in the tropics: a remote sensing analysis at the landscape scale. J. Biogeogr. 27, 765–776.

Flegal, A.R., Gallon, C., Hibdon, S., Kuspa, Z.E., Laporte, L.F., 2010. Declining-but persistent-atmospheric contamination in Central California from the resuspension of historic leaded gasoline emissions as recorded in the lace lichen (*Ramalina menziesii* Taylor) from 1892 to 2006. Environ. Sci. Technol. 44, 5613–5618.

Gallon, C., Ranville, M.A., Conaway, C.H., Landing, W.M., Buck, C.S., Morton, P.L., Flegal, A.R., 2011. Asian industrial lead inputs to the North Pacific evidenced by lead concentrations and isotopic compositions in surface waters and aerosols. Environ. Sci. Technol. 45, 9874–9882.

Hartland, A., Fairchild, I.J., Lead, J.R., Zhang, H., Baalousha, M., 2011. Size, speciation and lability of NOM-metal complexes in hyperalkaline cave dripwater. Geochim. Cosmochim. Acta 75, 7533–7551.

IPCC, 2013. Climate Change 2013: The Physical Science Basis. Cambridge Univ. Press, New York.

Kishe, M.A., Machiwa, J.F., 2003. Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania. Environ. Int. 28, 619–625.

Kristensen, L.J., Taylor, M.P., Odigie, K.O., Hibdon, S.A., Flegal, A.R., 2014. Lead isotopic compositions of ash sourced from Australian bushfires. Environ. Pollut. 190, 159–165.

Marwa, E.M.M., Meharg, A.A., Rice, C.M., 2012. Risk assessment of potentially toxic elements in agricultural soils and maize tissues from selected districts in Tanzania. Sci. Total Environ. 416, 180–186.

McKee, B.A., Cohen, A.S., Dettman, D.L., Palacios-Fest, M.R., Alin, S.R., Ntungumburanye, G., 2005. Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: II. Geochronologies and mass sedimentation rates based on C-14 and Pb-210 data. J. Paleolimnol. 34, 19–29.

McKenzie, D., Gedalof, Z., Peterson, D.L., Mote, P., 2004. Climatic change, wildfire, and conservation. Conserv. Biol. 18, 890–902.

Mihaljevic, M., Ettler, V., Sebek, O., Sracek, O., Kribek, B., Kyncl, T., Majer, V., Veselovsky, F., 2011. Lead isotopic and metallic pollution record in tree rings from the Copperbelt mining-smelting area, Zambia. Water Air Soil Pollut. 216, 657–668.

Molsa, H., Reynolds, J.E., Coenen, E.J., Lindqvist, O.V., 1999. Fisheries research towards resource management on Lake Tanganyika. Hydrobiologia 407, 1–24.

Nakayama, S.M.M., Ikenaka, Y., Hamada, K., Muzandu, K., Choongo, K., Teraoka, H., Mizuno, N., Ishizuka, M., 2011. Metal and metalloid contamination in roadside soil and wild rats around a Pb-Zn mine in Kabwe, Zambia. Environ. Pollut. 159, 175–181.

Needleman, H.L., 2000. The removal of lead from gasoline: historical and personal reflections. Environ. Res. 84, 20–35.

Nriagu, J.O., 1990. The rise and fall of leaded gasoline. Sci. Total Environ. 92, 13–28.

Nriagu, J.O., 1992. Toxic metal pollution in Africa. Sci. Total Environ. 121, 1–37.

Nriagu, J.O., 1996. A history of global metal pollution. Science 272, 223–224.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.

Nriagu, J.O., Wong, H.K.T., Coker, R.D., 1982. Deposition and chemistry of pollutant metals in lakes around the smelters at Sudbury, Ontario. Environ. Sci. Technol. 16, 551–560.

Odigie, K.O., Flegal, A.R., 2011. Pyrogenic remobilization of historic industrial lead depositions. Environ. Sci. Technol. 45, 6290–6295.

Odigie, K.O., Flegal, A.R., 2014. Trace metal inventories and lead isotopic composition chronicle a forest fire's remobilization of industrial contaminants deposited in the Angeles National Forest. PLoS ONE 9 (9), e107835. http://dx.doi.org/10.1371/journal.pone.0107835.

O'Reilly, C.M., Alin, S.R., Plisnier, P.D., Cohen, A.S., McKee, B.A., 2003. Climate change decreases aquatic ecosystem productivity of Lake Tanganyika, Africa. Nature 424, 766–768.

O'Reilly, C.M., Dettman, D.L., Cohen, A.S., 2005. Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: VI. Geochemical indicators. J. Paleolimnol. 34, 85–91.

Palacios-Fest, M.R., Cohen, A.S., Lezzar, K., Nahimana, L., Tanner, B.M., 2005. Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: III. Physical stratigraphy and charcoal analysis. J. Paleolimnol. 34, 31–49.

Quinton, J.N., Catt, J.A., 2007. Enrichment of heavy metals in sediment resulting from soil erosion on agricultural fields. Environ. Sci. Technol. 41, 3495–3500.

Sañudo-Wilhelmy, S.A., Flegal, A.R., 1994. Temporal variations in lead concentrations and isotopic composition in the Southern California Bight. Geochim. Cosmochim. Acta 58, 3315–3320.

Schwab, A.P., Zhu, D.S., Banks, M.K., 2008. Influence of organic acids on the transport of heavy metals in soil. Chemosphere 72, 986–994.

Soto-Jimenez, M.F., Hibdon, S.A., Rankin, C.W., Aggarawl, J., Ruiz-Fernandez, A.C., Paez-Osuna, F., Flegal, A.R., 2006. Chronicling a century of lead pollution in Mexico: stable lead isotopic composition analyses of dated sediment cores. Environ. Sci. Technol. 40, 764–770.

Stein, E.D., Brown, J.S., Hogue, T.S., Burke, M.P., Kinoshita, A., 2012. Stormwater contaminant loading following southern California wildfires. Environ. Toxicol. Chem. 31, 2625–2638.

Tembo, B.D., Sichilongo, K., Cernak, J., 2006. Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia. Chemosphere 63, 497–501.

Than, K., 2011. "Ocean" creatures that evolved in huge lake under threat. National Geographic Daily News. <http://news.nationalgeographic.com/news/2011/12/111201-lake-tanganyika-evolution-lakes-oceans-environment-science/> (retrieved 17.05.14).

Tierney, J.E., Mayes, M.T., Meyer, N., Johnson, C., Swarzenski, P.W., Cohen, A.S., Russell, J.M., 2010. Late-twentieth-century warming in Lake Tanganyika unprecedented since AD 500. Nat. Geosci. 3, 422–425.

Warren, L.J., 1981. Contamination of sediments by lead, zinc and cadmium – a review. Environ. Pollut. B 2, 401–436.

Wells, T.M., Cohen, A.S., Park, L.E., Dettman, D.L., McKee, B.A., 1999. Ostracode stratigraphy and paleoecology from surficial sediments of Lake Tanganyika, Africa. J. Paleolimnol. 22, 259–276.

West, K., 2001. Lake Tanganyika: Results and Experiences of the UNDP/GEF Conservation Initiative (RAF/92/G32) in Burundi, D.R. Congo, Tanzania, and Zambia, p. 138. <http://iwlearn.net/iw-projects/398/reports/> (retrieved 13.09.12).

Wu, J., Boyle, E.A., 1997. Low blank preconcentration technique for the determination of lead, copper, and cadmium in small-volume seawater samples by Isotope Dilution ICPMS. Anal. Chem. 69, 2464–2470.

Yabe, J., Nakayama, S.M.M., Ikenaka, Y., Muzandu, K., Ishizuka, M., Umemura, T., 2011. Uptake of lead, cadmium, and other metals in the liver and kidneys of cattle near a lead-zinc mine in Kabwe, Zambia. Environ. Toxicol. Chem. 30, 1892–1897.

Yang, D.W., Kanae, S., Oki, T., Koike, T., Musiake, K., 2003. Global potential soil erosion with reference to land use and climate changes. Hydrol. Process. 17, 2913–2928.

Yang, H.D., Engstrom, D.R., Rose, N.L., 2010. Recent changes in atmospheric mercury deposition recorded in the sediments of remote equatorial lakes in the Rwenzori Mountains, Uganda. Environ. Sci. Technol. 44, 6570–6575.

Zurbrick, C.M., Gallon, C., Flegal, A.R., 2013. A new method for stable lead isotope extraction from seawater. Anal. Chim. Acta 800, 29–35.