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Pyrogenic Remobilization And Transport Of Toxic Metals

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PYROGENIC REMOBILIZATION AND TRANSPORT OF TOXIC METALS

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ENVIRONMENTAL TOXICOLOGY

by

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ABSTRACT

Pyrogenic Remobilization and Transport of Toxic Metals

Kingsley O. Odigie

The effects of wildfires and deforestation on the remobilization of persistent inorganic contaminants are not completely understood. In forests, trace metal contaminants (e.g., lead) are sequestered in terrestrial sediment, soil organic matter, and vegetation, where they are relatively immobile. However, the combustion of soil organic matter and vegetation releases these contaminants in more labile forms. The associated deforestation and accelerated weathering increase the mobilization of trace metals from forests by simply increasing rates of erosion. These remobilized contaminants are transported to water bodies, increasing the loads of contaminants in these aquatic systems.

This project used analyses of trace metal inventories and lead isotopic compositions to study the remobilization and transport of toxic metals with respect to forest fires and deforestation associated with land-use. Chapters 2 and 3 present the results of investigation of the pyrogenic remobilization of trace metals at two contrasting sites in California: the relatively pristine Santa Barbara and the more populated and industrialized Los Angeles Metropolitan Area. The results indicate that wildfires are increasing the remobilization and transport of persistent contaminants (e.g., lead) in both study areas. Chapter 4 presents the results of a similar study conducted in Chile, in which geochronology and lead isotopic

compositions were used to investigate the impact of historic (about a century ago) slash and burn practices on the deposition of trace metals in Lake Thompson, Patagonia. The results show a positive relationship between fire size and the flux of metals to the lake. These findings are significant because the frequency and intensity of wildfires are expected to increase with global climate change. Chapter 5 presents the results of a study in which contaminant remobilization was linked to land-use practices by characterizing temporal changes in the flux of trace metals to Lake Tanganyika, Africa. The results indicate that deforestation is the predominant factor accelerating trace metals transport to the lake. This land-use associated remobilization of contaminants is projected to increase with population growth and industrialization in Africa.

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~dedicated to the memory of my dad, Mr. Joseph E. Odigie~

Co-Author Contributions

Chapter 4: Odigie, K.O., Khanis, E., Hibdon, S.A., Jana, P., Araneda, A., Urrutia, R., and Flegal, A.R. *Sediment Records of Trace Elements and Lead Isotopic Composition Chronicle Historic Pyrogenic Remobilization of Contaminants in Patagonia, Chile.* In preparation.

Jana, P., Araneda, A., and Urrutia, R. collected samples, dated the sediment core, and determined the charcoal abundance in the samples.

Odigie, K.O. processed the samples and analyzed the digests for trace elements, major elements, and lead isotopic compositions.

Khanis, E. and Hibdon, S.A. determined the concentrations of arsenic in the digests.

All co-authors provided comments and revisions on the final draft of the manuscript.

Chapter 5: Odigie, K.O., Cohen, A.S., Swarzenski, P.W., and Flegal, A.R. 2014. *Using Lead Isotopes and Trace Element Records from Two Contrasting Lake Tanganyika Sediment Cores to Assess Watershed – Lake Exchange*. In revision.

Cohen, A.S. and Swarzenski, P.W. collected samples, dated the sediment cores, and determined the mass accumulation rates for the sediments.

Odigie, K.O. processed the samples and analyzed the digests for trace elements, major elements, and lead isotopic compositions.

All co-authors provided comments and revisions on the final draft of the manuscript.

Prof. A. Russell Flegal directed and supervised the research in all the chapters of this dissertation.

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CHAPTER 1: INTRODUCTION

Historic Emissions of Trace Elements

Anthropogenic emissions of trace element contaminants can be traced back to ancient times, perhaps as far back as the domestication of fire and have continued through the development of mining technology to present day (Hong et al., 1994, 1996; Nriagu, 1996). These emissions contaminated air, terrestrial sediments, and aquatic ecosystems, thus effectively altering the biogeochemical cycles of many trace elements in the biosphere (Ng and Patterson, 1982; Veron et al., 1993). One of the most pervasive environmental contaminants known since ancient times is lead (Pb) (Hong et al., 1994). Lead was widely used among the elites in the Roman Empire, leading many researchers to argue that Pb poisoning is, at least partly, responsible for the fall of the Roman Empire (Hong et al., 1994; Nriagu, 1996). Still, the rate of increase in the amount of anthropogenic Pb emitted to the biosphere since the industrial revolution, especially after the introduction of leaded gasoline, has been alarming (e.g., Fig. 1) (Nriagu, 1990, 1996). The impacts of these emissions on environmental and human health have been extensive (Huseman et al., 1992; Nriagu et al., 1996; Dunlap et al., 2008).

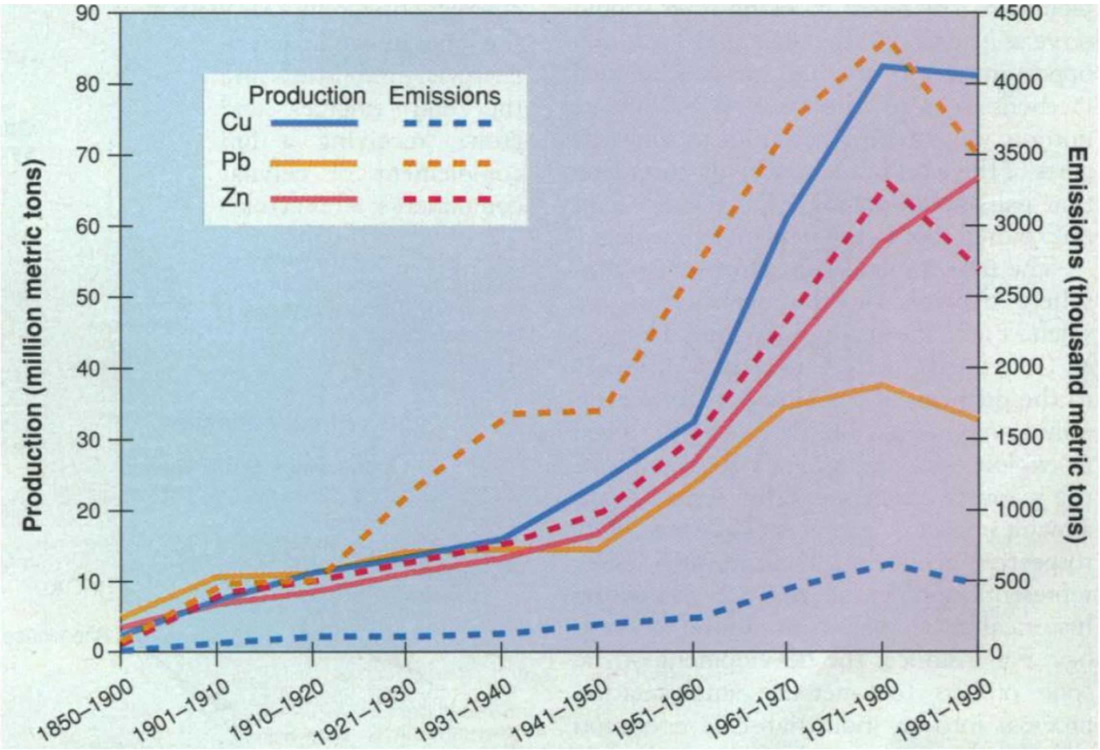

Figure 1. Global production and emissions of selected trace elements from 1850 to 1990 (Figure from Nriagu, 1996). Reprinted with permission from AAAS.

Approximately 75% of total global Pb aerosols during the second half of the last century was attributed to anthropogenic emissions, predominantly from the combustion of leaded gasoline (Dunlap et al., 2008). Air Pb concentrations in Philadelphia, USA were between 1.3 and 1.6 µg/m^3 in 1977, compared to the estimated baseline level of Pb (0.0006 µg/m^3) in a relatively pristine atmosphere (Chow et al., 1972; Needleman, 2000). In San Pedro Basin, which drains parts of the Los Angeles Metropolitan Area in California, the influx of Pb increased by ~7-fold following the introduction of leaded gasoline (Chow et al., 1973). From the 1750s to the mid-1960s, the concentrations of Pb in Greenland snow increased by approximately 20-fold and this was attributed primarily to the combustion of leaded gasoline (Boutron et al., 1995).

The impacts of those emissions on human health were indicated by elevated blood Pb (PbB) levels in children (Pirkle et al., 1994; Jones et al., 2009). The average PbB level of US children (ages 1 – 5 years) was as high as 15 µg/dL in 1976 – 1980, but decreased to 3.6 µg/dL in 1988 – 1991 following the phase-out and elimination of Pb from gasoline in the US, and has continued to decline to current level of 1.3 µg/dL (Pirkle et al., 1994; Wheeler and Brown, 2013). Similar trends have been documented for PbB levels in children in other countries, including Chile (e.g., Pino et al., 2004). But current PbB levels in US and Chilean children are still several folds greater than the estimated natural PbB level (0.016 µg/dL) in humans (Flegal and Smith, 1992). Moreover, health impairments continue to be discovered at PbB levels that were previously considered harmless (WHO, 2010; Wheeler and Brown, 2013).

As previously indicated, efforts to reduce human exposure to Pb in many parts of the world, including the US and Chile, have been largely successful (Pino et al., 2004; Wheeler and Brown, 2013). However, the legacy of Pb contamination is still evident in the environment. For example, the average soil Pb concentration in Pasadena, California was approximately 6-fold greater than the natural crustal rock (baseline) level (~12.5 µg/g) ten years after Pb was eliminated from gasoline in the US (Harris and Davidson, 2005).

Anthropogenic emissions and associated health impairments of other trace elements that are less pervasive than Pb have also been documented (Buchauer, 1973;

Sweet et al., 1993). For example, concentrations of Co, Cu, and Zn as high as 610 mg/kg, 27,000 mg/kg, and 450 mg/kg, respectively, were measured in topsoil in the Copperbelt Province of Kitwe in Zambia and these were attributed primarily to mining and metal processing (Ettler et al., 2011). Much of those trace element deposits adhere to surface sediments, organic matter, and vegetation, where they could be remobilized by environmental processes, including wildfires (Harris and Davidson, 2005; Biswas et al., 2007; Friedli et al., 2009).

Pyrogenic Remobilization of Trace Elements

Forests are a large reservoir for trace element contaminants. Trace elements sequestered in forests sorb to organic matter and vegetation and are relatively immobilized (Biswas et al., 2007; Obrist et al., 2008; Friedli et al., 2009). However, the combustion and volatilization of vegetation and soil organic matter release these trace element contaminants in more labile forms (Biswas et al., 2007; Wiedinmyer and Friedli, 2007). In addition, wildfires could increase the rates of soil erosion by as much as two orders of magnitude, thus facilitating the rapid transport of remobilized contaminants to aquatic ecosystems (Cohen et al., 2005; Stein et al., 2012).

Climate and Changing Wildfire Regimes

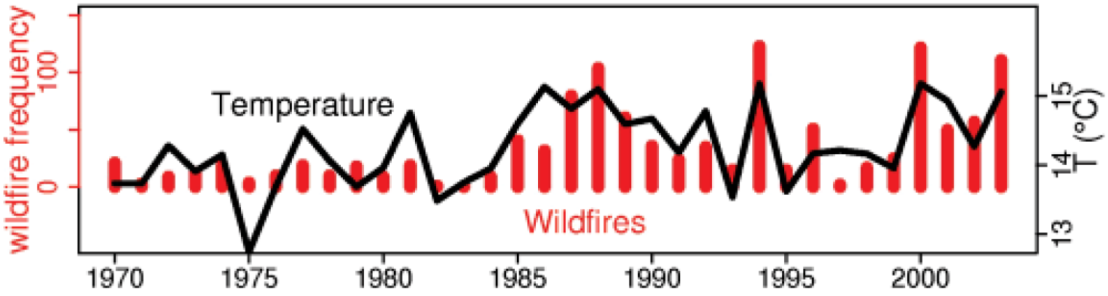

Figure 2. Relationship between wildfire frequency and spring-summer temperature in Western US (Figure from Westerling et al., 2006). Reprinted with permission from AAAS.

Recent studies have associated increases in wildfire frequency and area burned in many parts of the world with increase in surface temperature over the past few decades (e.g., Fig. 2, Westerling et al., 2006). California recently declared a drought state of emergency as it faced its driest period since the mid-19th century (Kostigen, 2014; State of California, 2014). Drought enhances fuel build up in forests, thus increasing the potential for bigger wildfires (Westerling et al., 2006; Ghimire et al., 2012). Moreover, the intensity and frequency of wildfires are expected to increase further with projected climate change (McKenzie et al., 2004; Flannigan et al., 2005; Schuur et al., 2008; IPCC, 2013).

Objectives of Study

The objectives of this study were to investigate the spatial and temporal changes in trace element fluxes associated with development, industrialization, and wildfires. Several studies have investigated the pyrogenic remobilization of Hg and its subsequent impacts on aquatic ecosystems (Kelly et al., 2006; Biswas et al., 2008; Witt et al., 2009), but similar studies on other toxic elements, e.g., Pb, are limited. Consequently, the central focus of this study was to investigate the pyrogenic remobilization of some of these other toxic elements, especially Pb, and their subsequent impacts on aquatic ecosystems. The project also aimed at investigating the sources of remobilized Pb by using Pb isotopic compositions. To address these objectives, four sites representing different levels of industrialization were chosen across three continents (Fig. 3).

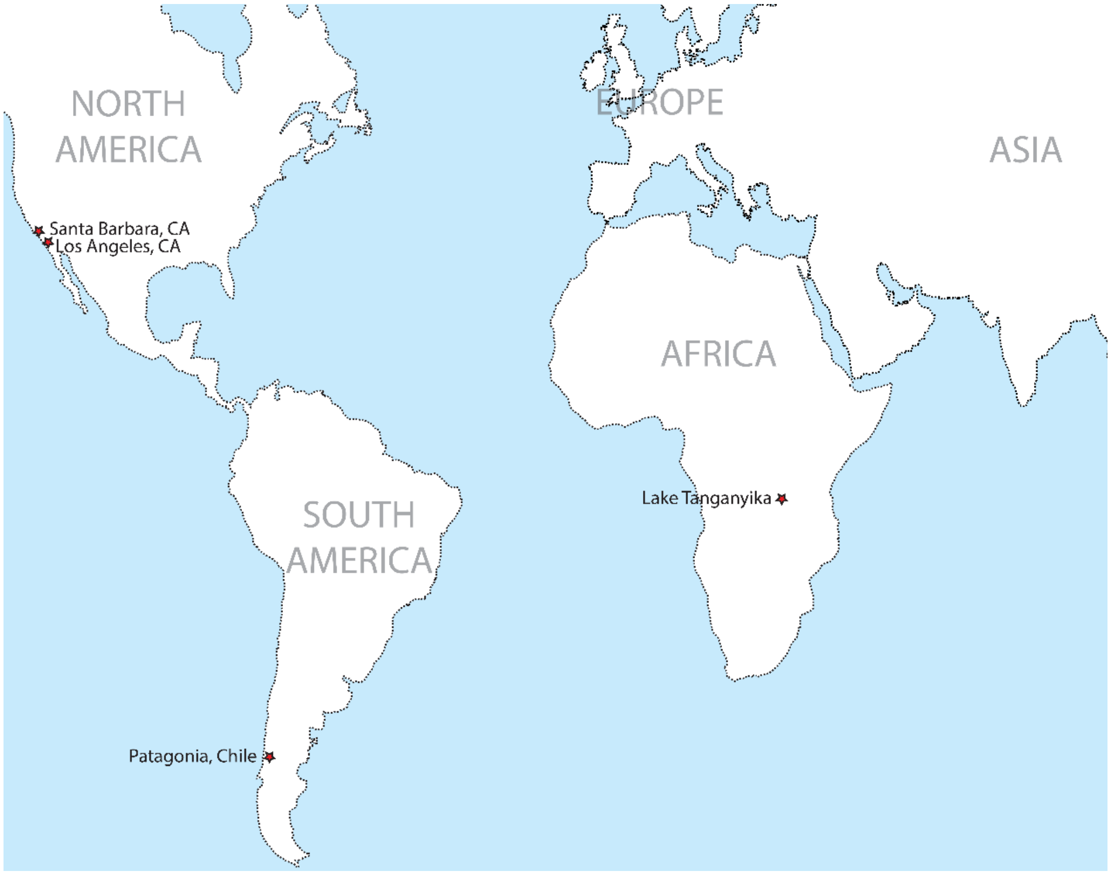

Figure 3. Map showing approximate locations of the study sites.

Site 1: Santa Barbara, California

Santa Barbara is a relatively pristine location in Southern California and the major source of anthropogenic contaminants to forests around the city is aeolian input (Odigie and Flegal, 2011). Santa Barbara provides an ideal location to study the impacts of wildfires on remobilization of toxic elements in a relatively pristine environment. The availability of trace element data, including Pb isotopic compositions, for the region (e.g., Bruland et al., 1974), makes it easy to distinguish between natural and anthropogenic sources of trace elements. The 2009 Jesusita Fire in Santa Barbara, which burned approximately 3,534 hectares of land in a largely mountainous forest, was selected for this study. Ash samples were collected from accessible areas within the burned perimeter using established trace metal clean techniques and transported to UC Santa Cruz for processing. Detailed description and results of this study are presented in Chapter 2.

Site 2: Los Angeles, California

In contrast to Santa Barbara, Los Angeles is a highly populated and industrialized metropolis that is often ranked as one of the most contaminated metropolises in the US (Su et al., 2009). Approximately 17 million people live in Los Angeles, Orange, San Bernardino, and Riverside Counties (US Census, 2013). The study site, the Angeles National Forest, abuts the Los Angeles Metropolitan Area and receives aeolian deposition of trace elements emitted in Los Angeles. Consequently, the study was aimed at investigating the impacts of wildfires on the remobilization of toxic elements in an industrialized and highly populated area, and comparing the data to those from the relatively pristine Santa Barbara, California. Like in Santa Barbara, trace element data, including Pb isotopic compositions, are available for Los Angeles. The September 2012 Williams Fire, which burned approximately 1,696 hectares of land in the Angeles National Forest, was selected for this study. Ash and soil (from unburned patches) samples were collected from different accessible locations within the burned perimeter of the fire site using established trace metal clean techniques and transported to UC Santa Cruz for processing. Detailed description and results of this study are presented in Chapter 3.

Site 3: Patagonia, Chile

Patagonia, Chile is a relatively pristine region known for its extensive freshwater reservoir and important wildlife. However, the region has been experiencing increased pressure from human activities in the past several decades (Vince, 2010; Araneda et al., 2013). For example, approximately three million hectares of land was burned in the Aysén region in Northern Patagonia from 1930 to 1950 (Araneda et al., 2013). Consequently, Northern Patagonia provides an ideal location to investigate the impacts of wildfires on the influx of toxic elements to an aquatic ecosystem. A dated sediment core collected from Lake Thompson in Northern Patagonia, Chile was used for this study (Araneda et al., 2013). Detailed description and results of the study are presented in Chapter 4.

Site 4: Lake Tanganyika, Africa

Lake Tanganyika, the world's second largest (by volume) and second deepest lake, is a source of livelihood and food for millions of people, making it a strategically important resource in East Africa (Coulter and Spigel, 1991; Molsa et al., 1999; Tierney et al., 2010). However, the lake has been facing increasing pressure from human activities over the past several decades in addition to changes attributed to climate change (O'Reilly et al., 2003; Tierney et al., 2010). Some northern parts of the lake catchment have experienced up to 100% deforestation (Cohen et al., 1993). Consequently, efforts aimed at protecting the lake have resulted in the generation of large data sets on the lake (Cohen et al., 1993; Alin and Cohen, 2003). However, studies on the impacts of human activities on the deposition of trace elements in the lake are few (e.g., Brucker et al., 2011). Therefore, this study was aimed at complementing those efforts and investigating the impacts of human activities, especially land-use changes, on the remobilization of toxic elements to the lake. Dated sediment cores collected from two contrasting sites in the lake were used for this study. Detailed description and results of this study are presented in Chapter 5.

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Chapter 2: Pyrogenic Remobilization of Historic Lead Depositions

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Pyrogenic Remobilization of Historic Industrial Lead Depositions

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ABSTRACT: Relatively high levels (4.3 to 51 μg/g) of labile lead (Pb) in ash from the 2009 Jesusita Fire in Santa Barbara County, California attest to the pyrogenic remobilization of historic industrial lead depositions in this relatively pristine area in Southern California, USA. The primarily industrial origin of that lead was evidenced by its poor correlations (simple linear regressions) with lithogenic aluminum (r = 0.18, p = 0.354, n = 30) and iron (r = 0.21, p = 0.270, n = 30) concentrations and by its associated enrichment factors (EFs): EF using aluminum as conservative element (f-Al) vs lead concentration [Pb] (r = 0.79, p < 0.001, n = 30), and EF using iron as conservative element (f-Fe) vs [Pb] (r = 0.83, p < 0.001, n = 30). The industrial origins of much of that lead were corroborated by its isotopic compositions (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb), which fell between those of natural lead in the Santa Barbara Basin and previous leaded gasoline emissions in Southern California. This apparent pyrogenic remobilization of legacy lead pollution indicates that it—and other persistent pollutants—will increase with the projected increase in the frequency and intensity of forest fires in the Southwest U.S. and elsewhere as a consequence of climate change.

INTRODUCTION

Historic Emissions of Industrial Lead. Massive anthropogenic emissions of lead (Pb) have greatly perturbed its natural biogeochemical cycle.[1] These industrial emissions have included exhaust from the combustion of leaded gasoline, which accounted for approximately 75% of atmospheric lead contamination in the world[1] and 90% of that contamination in California—where other sources of industrial lead emissions were relatively low—during the latter half of the previous century.[2,3] Most of the contamination from leaded gasoline emissions has been localized in urban areas, such as the Los Angeles Basin in Southern California, USA. There, during the late 1960s and early 1970s, the amount of lead used in gasoline was ~24 000 kg/day; two-thirds (~67%) of that lead (~18 000 kg/day) was aerosolized; and two-thirds (~67%) of those aerosols (~12 000 kg/day) were deposited within the basin.[4]

Atmospheric depositions of those and other industrial lead aerosols markedly increased lead concentrations of sediments in Southern California.[5,6] For example, Chow et al.[7] reported that subsequent to the introduction of leaded gasoline, lead fluxes into sediments increased from 1.0 to 2.1 μg/cm^2/year in the Santa Barbara Basin, 0.26 to 1.7 μg/cm^2/year in the San Pedro Basin and 0.24 μg/cm^2/year to 0.9 μg/cm^2/year in the Santa Monica Basin. Similarly, Harris and Davidson[8] reported that the average (mean ± SD, Standard Deviation) soil lead concentration in Southern California (Los Angeles and suburbs) increased from a 1919–1933 value of 16 ± 0.5 to 79 ± 23 μg/g between 1967 and 1970. Those temporal increases are consistent with increases in proximate, age-dated sediments in Northern California[9] and Northern Mexico[10] that have also been correlated with the use of leaded gasoline in the North American Southwest.

This massive contamination of the geosphere by industrial lead was associated with corresponding increases of lead in the biosphere: most notably in the blood lead (PbB) concentrations of humans.[11] Both occurred at the same time the threshold for sublethal lead toxicity in humans was being lowered.[12–14] Consequently, industrial uses of lead—including leaded gasoline—were reduced and/or eliminated in the U.S. and most other countries.[11]

The positive effects of those remedial actions were documented in subsequent reductions of lead contamination in the environment and in humans. The former included decreases in remote oceanic surface waters, where aeolian depositions of industrial lead were dominant;[15,16] the latter included decreases in the average PbB of children (ages 1–5 years) in the U.S. from 15 μg/dL in 1976–1980 to 3.6 μg/dL in 1988–1991, which corresponded with the phase out of leaded gasoline in the U.S.[17] Since then, PbB concentrations of children in the U.S. have continued to decrease to ~2 μg/dL.[18] Nevertheless, that current baseline level is still 2 orders of magnitude above the estimated natural PbB level (~0.016 μg/dL) in humans, and the threshold for lead toxicity in humans has yet to be established.[19]

The legacy of historic industrial lead contamination is evident in the geosphere. For example, a decade after the elimination of leaded gasoline in California, soil lead concentrations in Pasadena (77 ± 19 μg/g) were still 6-fold greater than the preindustrial crustal lead (baseline) level of ~12.5 μg/g.[8] Likewise, it has been

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Figure 1. Photograph of the 2009 Jesusita Fire burned area in Santa Barbara, California showing the relatively remote and mountainous terrain where the fire occurred (Photo by Kingsley O. Odigie).

calculated that it will take decades, if not centuries, to flush historic leaded gasoline depositions from surface sediments in California's Central Valley to San Francisco Bay.[2,3] Moreover, much of those historic depositions have been retained in terrestrial sediments, soils and vegetation in forests throughout the state where they may be remobilized by anthropogenic and natural processes—including forest fires.

Pyrogenic Remobilization of Heavy Metals. One of the potentially most important processes for the global remobilization of inorganic legacy pollutants is forest fires. While there is little information about the remobilization of lead from forest fires, there is a substantial amount of information on the pyrogenic remobilization of other pollutants, including mercury.[20] Forests are a reservoir for trace metals sequestered in sediments, soil organic matter, and vegetation, where they are relatively immobile.[21,22] The combustion of soil organic matter and vegetation releases those sequestered trace metals and increases their bioavailability.[21,23,24] Forest fires also increase soil erosion by as much as 2 orders of magnitude,[25] accelerating the transport of those mobilized trace metals to water bodies and further increasing their bioavailability.[26]

Therefore, this work was conducted to determine the amount and sources of potentially labile lead in ash from a large forest fire that occurred in Southern California in 2009. In that year, when there were several large forest fires in Southern California, we focused on ash from the Jesusita Fire in Santa Barbara because (1) emissions of industrial lead in that relatively pristine area have been primarily limited to those from leaded gasoline combustion and (2) there are data on isotopic compositions of both natural lead and leaded gasoline in the region. Consequently, we expected it would be simpler to distinguish natural and industrial sources of lead in ash from that area than in more industrial areas of Southern California (e.g., Los Angeles and San Diego).

MATERIALS AND METHODS

Sample Collection Sites. Samples were collected from the burned area of the May 2009 Jesusita Fire in Santa Barbara, California (Figures 1 and 2). The fire burned about 3534 ha (8733 acres) of land.[27] Twenty-six ash samples were collected from different accessible areas around the burned perimeter (Figure 2), using trace metal clean techniques.[9] The samples were immediately double bagged in plastic containers to prevent contamination, and then stored in sealed containers at room temperature until analysis.[28]

Analytical Methods. Ash samples from the 26 sites, including two sites that were sampled in triplicate (SB11 and SB22), were processed in a trace metal clean laboratory in a filtered HEPA (Class-100) hood using established techniques.[28] All reagents were either trace metal or ultrapure (2× sub-boiling quartz distilled) grade. High purity (18.2 MΩ cm) water (Milli-Q) was used for dilutions and cleaning. Three procedural blanks and 3 samples of 2 National Institute of Standards and Technology (NIST) standard reference materials (SRMs) were processed concurrently: SRM 1547 (peach leaves) and SRM 1633b (coal fly ash).

A concentrated nitric acid digestion was used to derive a measure of the acid-leachable (labile) lead in the samples and reference materials.[29−32] Approximately 0.3 to 0.5 g of ash sample or reference material was transferred to a trace metal clean Teflon digestion vial and dried overnight at 65 °C. Ten milliliters (mL) of concentrated nitric acid (HNO_3) was then added to each sample vial and kept at room temperature for ~18 h. Next, the solutions were heated and refluxed for ~18 h. After the refluxed material was cooled and dried, a second 10 mL of concentrated HNO_3 was added, and the digestion process was repeated. The digests were then dried, cooled and redissolved in 10 mL of 1 M ultrapure HNO_3 for elemental and isotopic composition analyses.[33]

The digests were analyzed for their lead concentration and isotopic composition with a Finnigan ELEMENT 2 high resolution—inductively coupled plasma mass spectrometer (HR ICP-MS), using established techniques that have been intercalibrated with measurements on both a Finnigan NEPTUNE multiple collector magnetic sector inductively coupled mass spectrometer[34] and a VG Sector 54-WARP thermal ionization mass spectrometer.[35]

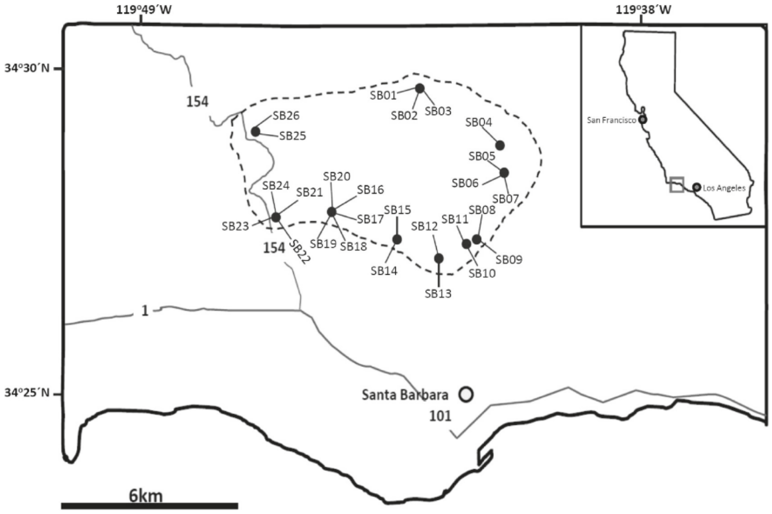

Figure 2. Map showing approximate sample collection sites within the boundary (---) of the 2009 Jesusita Fire in Southern California. Coordinates of the sites are listed in Table 1.

Bismuth (Bi) was used as an internal standard to correct for instrumental drifts, and NIST SRM 981 (common lead) was used as standard to correct for the fractionation of isotopic composition. One sample (SB01) was analyzed multiple times ($n = 7$) to assess reproducibility of the isotopic measurements. The analytical precisions (RSDs, Relative Standard Deviation) for $^{208}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, and $^{207}Pb/^{204}Pb$ were 0.22%, 0.38%, and 0.30%, respectively. Aluminum (Al) and iron (Fe) concentrations of the digests were measured with a PerkinElmer Optima 4300 DV inductively coupled plasma−optical emission mass spectrometer (ICP-OES), using established techniques, to determine the enrichment factor (EF) of lead in the ash.[36,37]

The detection limit (3 x SD of the blanks, $n = 3$) of lead concentration for this project was 0.03 ng/g of sample. Average recoveries (mean ± RSD, $n = 3$) of lead for SRM 1547 and SRM 1633b were 105 ± 2.5% and 52.1 ± 1.1% of their certified values, respectively. The RSD values for the concentrations of lead in the replicate samples ($n = 3$) of ash (SB11 and SB22) were 0.8% and 1.3%, respectively. Recoveries for aluminum and iron in SRM 1547 were 83.2% and 87.9%, respectively; those of aluminum and iron in SRM 1633b were 24.2% and 68.1%, respectively. Differences in the percent recoveries of the elements in the different SRMs were consistent with previous measurements in our laboratory, and reflect the different lability of those elements in the two matrices. The normalization to $[Fe]_{Baseline}$ is considered more appropriate for samples digested with strong acids other than hydrofluoric acid (HF) because the lead in aluminosilicates, which require an HF digestion, is extremely refractory.[36,38] That is illustrated by differences in our recoveries of aluminum (24%) and iron (68%) in coal fly ash (SRM 1633b), compared to our recoveries of aluminum (83%) and iron (88%) in peach leaves (SRM 1547) because coal fly ash (SRM 1633b) would require digestion with concentrated HF to dissolve metals bound in its aluminosilicate lattices. The peach leaves (SRM 1547), therefore, provided better estimates of recoveries of metals in our ash samples, which are predominantly derived from soil organic matter and vegetation.

■ RESULTS AND DISCUSSION

Lead Concentrations. Lead concentrations (μg/g dry weight) of the ash ranged from 4.3 to 51 μg/g (Table 1). As previously noted, these concentrations are conservative because they did not include a concentrated HF digestion of refractory aluminosilicates, and may also not account for all of the lead volatized by the fire. Also included in the table are the concentrations (mg/g dry weight) of labile aluminum and iron, which were used to derive the enrichment factor (EF) for lead for both of those relatively conservative, lithogenic elements. The relatively low and insignificant ($p > 0.05$) correlations (simple linear regressions) between [Pb] and [Al] ($r = 0.18$, $p = 0.354$, $n = 30$), and [Pb] and [Fe] ($r = 0.21$, $p = 0.270$, $n = 30$) indicate that lead in the ash samples was primarily from anthropogenic, rather than natural, sources. Metals of predominantly natural origin, e.g., aluminum and iron—which are difficult to contaminate because of their relatively high natural abundance, correlate better than metals enriched by anthropogenic processes.[39]

Enrichment Factors. The predominantly industrial component of lead in the ash was further indicated by calculations of its enrichment factor (EF) relative to aluminum and iron.[36,39−41] EF is defined as follows:

$$\mathrm{EF} = \frac{\dfrac{[\mathrm{Pb}]_{\mathrm{Sample}}}{[\mathrm{Al}]_{\mathrm{Sample}}}}{\dfrac{[\mathrm{Pb}]_{\mathrm{Baseline}}}{[\mathrm{Al}]_{\mathrm{Baseline}}}} \text{ or } \frac{\dfrac{[\mathrm{Pb}]_{\mathrm{Sample}}}{[\mathrm{Fe}]_{\mathrm{Sample}}}}{\dfrac{[\mathrm{Pb}]_{\mathrm{Baseline}}}{[\mathrm{Fe}]_{\mathrm{Baseline}}}}$$

For our calculations, we normalized $[Pb]_{Sample}$, $[Al]_{Sample}$, and $[Fe]_{Sample}$ of our ash samples to $[Pb]_{Baseline}$, $[Al]_{Baseline}$, and $[Fe]_{Baseline}$ of Pb-210 dated preindustrial sediments deposited in a Santa Barbara Basin[5] because sediments from the study site are deposited in that basin.

The correlations ($r = 0.99$, simple linear regressions) of lead EFs calculated using aluminum (*f*-Al) and iron (*f*-Fe) for the ash samples were highly significant ($p < 0.001$), as were the

Table 1. Data from the Analyses of Ash Samples Collected from the 2009 Jesusita Fire in Southern California: Coordinates of Sample Collection Sites; Concentrations of Lead, Aluminum, And Iron; And Enrichment Factors (*f*-Al and *f*-Fe) and Isotopic Ratios of Lead

sample collection sites and results										
	collection sites		concentration			enrichment factor		isotopic ratios		
sample ID	latitude	longitude	[Pb] (μg/g)	[Al] (mg/g)	[Fe] (mg/g)	*f*-Al	*f*-Fe	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{207}Pb/^{204}Pb
SB01	34°29′40.10″N	119°42′49.30″W	9.60	16.39	12.66	2.8	2.3	2.480	1.212	15.637
SB02	34°29′40.00″N	119°42′48.90″W	26.75	18.33	12.00	7.1	6.8	2.471	1.205	15.689
SB03	34°29′37.60″N	119°42′51.10″W	29.35	18.20	14.67	7.8	6.1	2.464	1.204	15.710
SB04	34°28′51.50″N	119°41′05.50″W	24.33	19.86	17.72	6.0	4.2	2.436	1.161	15.609
SB05	34°28′27.60″N	119°40′55.20″W	28.21	18.02	14.66	7.6	5.9	2.461	1.209	15.649
SB06	34°28′27.60″N	119°40′55.20″W	24.89	22.32	16.13	5.4	4.7	2.469	1.209	15.649
SB07	34°28′27.60″N	119°40′54.90″W	27.65	22.33	17.04	6.0	5.0	2.464	1.210	15.716
SB08	34°27′27.30″N	119°41′43.80″W	32.12	22.51	19.52	6.9	5.0	2.465	1.210	15.692
SB09	34°27′27.30″N	119°41′43.80″W	14.85	26.87	22.85	2.7	2.0	2.464	1.210	15.680
SB10	34°27′21.30″N	119°41′56.70″W	6.51	10.97	8.71	2.9	2.3	2.467	1.206	15.624
SB11A	34°27′21.50″N	119°41′57.10″W	18.66	36.01	31.11	2.5	1.8	2.481	1.207	15.576
SB11B	34°27′21.50″N	119°41′57.10″W	18.95	31.23	25.33	2.9	2.3	2.479	1.204	15.682
SB11C	34°27′21.50″N	119°41′57.10″W	18.81	25.75	20.91	3.6	2.8	2.480	1.206	15.636
SB12	34°27′12.10″N	119°42′27.40″W	13.85	9.89	8.07	6.8	5.2	2.466	1.200	15.578
SB13	34°27′12.10″N	119°42′27.40″W	10.48	7.45	5.82	6.8	5.5	2.467	1.202	15.621
SB14	34°27′30.30″N	119°43′24.30″W	12.37	23.96	19.03	2.5	2.0	2.476	1.206	15.644
SB15	34°27′30.80″N	119°43′25.00″W	14.57	14.20	11.19	5.0	4.0	2.473	1.214	15.668
SB16	34°27′55.00″N	119°44′58.20″W	48.96	7.39	7.60	32.2	19.7	2.458	1.217	15.629
SB17	34°27′55.00″N	119°44′58.20″W	36.19	15.29	13.44	11.5	8.2	2.461	1.215	15.648
SB18	34°27′56.00″N	119°44′50.90″W	17.04	14.40	13.88	5.8	3.8	2.460	1.193	15.688
SB19	34°27′56.00″N	119°44′50.90″W	9.08	27.20	23.64	1.6	1.2	2.474	1.209	15.609
SB20	34°27′55.60″N	119°44′51.00″W	4.71	12.72	10.65	1.8	1.4	2.466	1.203	15.586
SB21	34°27′50.10″N	119°46′16.70″W	4.29	5.70	5.00	3.7	2.6	2.464	1.201	15.632
SB22A	34°27′50.00″N	119°46′16.70″W	4.78	8.29	7.15	2.8	2.0	2.458	1.199	15.581
SB22B	34°27′50.00″N	119°46′16.70″W	4.68	9.26	7.46	2.5	1.9	2.455	1.197	15.637
SB22C	34°27′50.00″N	119°46′16.70″W	4.80	8.43	7.34	2.8	2.0	2.459	1.197	15.563
SB23	34°27′50.00″N	119°46′16.70″W	5.40	10.38	8.40	2.5	2.0	2.469	1.203	15.600
SB24	34°27′48.50″N	119°46′16.20″W	23.76	13.57	11.57	8.5	6.3	2.470	1.218	15.581
SB25	34°29′02.10″N	119°46′33.80″W	17.82	8.59	8.98	10.1	6.1	2.465	1.214	15.615
SB26	34°29′02.10″N	119°46′34.20″W	51.02	14.85	14.13	16.7	11.0	2.464	1.214	15.631

correlations ($r = 0.98$, simple linear regressions) between concentrations of those two conservative metals (aluminum and iron) in the ash ($p < 0.001$). Using the more conservative EF (*f*-Fe) and the classification proposed by Sutherland,[42] the normalizations conservatively indicate that of the 26 samples analyzed: 2 were not measurably contaminated (EF < 2); 14 were moderately contaminated (EF = 2−5); and 10 were significantly contaminated (EF = 5−20).

Isotopic Compositions. The industrial origins of that enrichment are indicated in Figure 3, which shows a plot of the lead isotopic ratios (^{208}Pb/^{207}Pb: ^{206}Pb/^{207}Pb) of the ash samples. Also included in the plot are the ranges of lead isotopic compositions of natural and contaminated sediments deposited in the Santa Barbara Basin,[6] as well as those reported for leaded gasoline used in California during the latter half of the previous century.[3]

The plot shows that the amount of natural lead in the ash samples is relatively small compared to that of industrial lead, based on isotopic composition of preindustrial sediments in the Santa Barbara Basin.[6,7] It also indicates that most of the lead in the ash samples is a mixture of industrial emissions from the 1960s-1970s and the 1980s, which have been primarily attributed to the combustion of alkyl-lead in gasoline in Southern California.[6,7,43]

Temporal variations of the isotopic composition of leaded gasoline in California correspond with temporal differences in ores used to manufacture alkyl-lead in the U.S. during that period. In the 1960s, the ores were obtained primarily from Australia, Canada, Mexico, and Peru, which had ^{206}Pb/^{207}Pb ratios of about 1.037, 1.064, 1.192, and 1.200, respectively.[6] The use of lead from the Missouri deposits (^{206}Pb/^{207}Pb = 1.28 to 1.33) subsequently increased from 9% in 1962 to 82% in 1976. This change in lead sources was reflected in the lead isotopic compositions of aerosols in Southern California, where the ^{206}Pb/^{207}Pb ratio changed from ~1.15 before 1967 to ~1.20 by 1974 and to 1.23 by 1977.[44] It is, therefore, assumed that the isotopic composition of those aerosols reflects a mixture of contemporary and previous industrial lead emissions that have been resuspended, as observed in Los Angeles[8] and the San Francisco Bay area.[28]

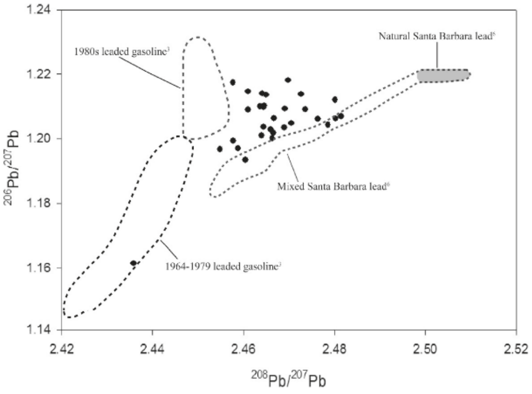

Figure 3. Lead isotopic composition ($^{208}Pb/^{207}Pb$: $^{206}Pb/^{207}Pb$) of ash samples (●) collected from the 2009 Jesusita Fire site in Southern California. Also included in the plot are the ranges of previous reports of the isotopic composition of leaded gasoline in California[3] and Pb-210 dated sediment cores in the Santa Barbara Basin.[6]

Potential Impact of Climate Change. The present findings have broad implications because climate change is increasing the global frequency and intensity of wildfires.[45−50] For example, a recent study by Westerling et al.[47] showed a significant correlation ($r = 0.76$, $p < 0.001$, $n = 34$) between wildfire frequency and regional spring and summer temperatures in the Western U.S. They also observed that wildfires in the Western U.S. increased in frequency (~4 times) and total area burned (~7 times) in the mid-1980s, compared to wildfires from 1970 to 1986; this corresponded with a temperature rise of <0.9 °C. Several studies have reported similar associations between wildfires and temperature.[45,51,52] Moreover, the IPCC[48] projects that global surface temperature will increase by 1.5 to 5.8 °C by the end of the 21st century, and others have proposed there will be a corresponding increase in the frequency and intensity of wildfires during that period.[51−53] While the associated remobilization of legacy pollutants has recently been highlighted by concerns that forest fires in Russia could volatize radioactive pollutants in Chornobyl,[54,55] our preliminary study indicates forest fires are already remobilizing large amounts of lead, a much more pedestrian but pervasive pollutant and that the mobilization of lead and other refractory legacy pollutants will increase with climate change.

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Chapter 3. Trace Metal Inventories and Lead Isotopic Composition Chronicle a Forest Fire's Remobilization of Industrial Contaminants Deposited in the Angeles National Forest

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ABSTRACT

The amounts of labile trace metals: [Co] (3 to 11 μg g^{-1}), [Cu] (15 to 69 μg g^{-1}), [Ni] (6 to 15 μg g^{-1}), [Pb] (7 to 42 μg g^{-1}), and [Zn] (65 to 500 μg g^{-1}) in ash collected from the 2012 Williams Fire attest to the role of fires in remobilizing industrial metals deposited in forests. These remobilized trace metals may be dispersed by winds, increasing human exposures, and they may be deposited in water bodies, increasing exposures to aquatic ecosystems. Correlations between the concentrations of these trace metals normalized to Fe, in ash from the fire suggest that Co, Cu, and Ni in most of those samples were predominantly from natural sources, whereas Pb and Zn were enriched in some ash samples. The mainly anthropogenic source of Pb in that ash was further evidenced by its isotopic ratios ($^{206}Pb/^{207}Pb$: $^{208}Pb/^{207}Pb$) that fell between those of natural Pb and leaded gasoline sold in California during the previous century. This attests to current human and environmental health concerns with the pyrogenic remobilization of toxic metals, which are compounded by projections of increases in the intensity and frequency of wildfires associated with climate change.

INTRODUCTION

Historic Emissions of Trace Metals

Extensive anthropogenic emissions of environmentally persistent contaminants have substantially altered the natural biogeochemical cycles of some trace metals in the biosphere over the past century (Nriagu, 1996; Dunlap et al., 2008; Flegal et al., 2013). For example, ~90% and 75% of atmospheric lead (Pb) in California and the world, respectively, during the second half of the previous century were attributed to anthropogenic sources, predominantly the combustion of leaded gasoline (Dunlap et al., 2008).

These industrial emissions extensively contaminated aerosols and sediments in Southern California, where enormous amounts of leaded gasoline were combusted during the previous century. For example, Pb concentrations in surface soil in Los Angeles Metropolitan Area increased from 16±0.5 µg/g (mean ± SD) between 1919 and 1933 to 79±23 µg/g between 1967 and 1970 (Harris and Davidson, 2005); and the flux of Pb to sediments in the coastal San Pedro Basin, which abuts the Los Angeles Metropolitan Area, increased by ~7-fold, compared to the natural rate, following the introduction of alkyl-lead gasoline additives in Southern California (Chow et al., 1973). Similar temporal increases in fluxes of Pb in age-dated sediments that were attributed to the use of leaded gasoline have been documented in adjacent areas both north and south of Southern California, albeit at lower levels (Ritson et al., 1999; Soto-Jimenez et al., 2006). Substantial temporal increases in the fluxes of other trace metals, e.g., zinc (Zn), associated with anthropogenic inputs have also been measured in Southern California (Finney and Huh, 1989).

However, efforts to reduce industrial metal contamination, especially Pb contamination, over the past half century have been quite successful in much of the world, notably the US and specifically Los Angeles. For example, the burden of emissions from the past combustion of leaded gasoline on humans was indicated by the relatively high average blood Pb levels (PbB) of children (ages 1 – 5 years) in the US, which declined from 15 µg/dL in 1976 – 1980 to 3.6 µg/dL in 1988 – 1991, during the phase-out and subsequent elimination of leaded gasoline in the US, and then to current level of 1.3 µg/dL (Pirkle et al., 1994; Wheeler and Brown, 2013). But the current average PbB level in the US is still about 80-fold greater than the estimated natural PbB (0.016 µg/dL) level in humans (Flegal and Smith, 1992), and health impairments are being reported at Pb levels that were previously considered harmless (WHO, 2010; Wheeler and Brown, 2013). Similarly, sublethal toxicities of other trace metals (e.g., Cu and Zn) continue to be documented at increasingly lower levels (McGeer et al., 2000).

Moreover, the legacy of historic anthropogenic Pb emissions is evident in terrestrial and aquatic sediments in California and elsewhere (Ritson et al., 1999; Harris and Davidson, 2005). Ten years after Pb was phased out from gasoline in California, concentrations of Pb (77±19 µg/g) in soil in Pasadena, California were 6-

fold greater than the natural (baseline) Pb level (~12.5 µg/g) of crustal rock (Harris and Davidson, 2005). This persistence of industrial Pb deposits was summarized by Steding et al. (Steding et al., 2000) and Dunlap et al. (Dunlap et al., 2008), who predicted that it could take decades to centuries to flush alkyl-lead depositions from surface sediments in California’s Central Valley to San Francisco Bay.

Remobilization of Trace Metals by Forest Fires

As previously noted, wildfires remobilize legacy trace metal contaminants deposited in grasslands and forests. Metals are sequestered in sediment, soil organic matter, and vegetation in forests, where they are relatively immobile (Biswas et al., 2007; Obrist et al., 2008; Friedli et al., 2009). However, the combustion of vegetation and soil organic matter releases these trace metals in more labile forms (Biswas et al., 2007; Wiedinmyer and Friedli, 2007). In addition, forest fires increase erosion rates by as much as 100-fold and facilitate the rapid transport of remobilized trace metals to draining water bodies, raising contamination levels in aquatic ecosystems (Cohen et al., 2005; Stein et al., 2012).

While there have been several investigations of the remobilization of mercury by forest fires (Biswas et al., 2008; Witt et al., 2009), there have been few similar studies on the remobilization of Pb and other trace metals (e.g., Co and Zn). The latter include a recent study in the relatively unpopulated and relatively pristine Santa Barbara area north of Los Angeles (Odigie and Flegal, 2011). In contrast, this study was conducted in the Angeles National Forest, which is adjacent to the Los Angeles Metropolitan Area, which has a population of ~17 million (US Census, 2013), has many large sources of industrial contaminants (Singh et al., 2002; Sardar et al., 2005; Smail et al., 2012), and ranks as one of the nation's most contaminated metropolitan areas (Su et al., 2009). Moreover, "car is king" in Los Angeles, where leaded gasoline emissions were the dominant source of atmospheric Pb during the previous century and resuspension of that legacy pollution continues to be the principal component of atmospheric Pb today, as documented in mass balance studies of atmospheric Pb contamination in the Los Angeles Air Basin (Harris and Davidson, 2005). Therefore, we hypothesized that forest fires within that Basin would remobilize relatively large amounts of industrial Pb and other industrial metals, and that remobilization would add to the already large amounts of legacy gasoline Pb deposits that now constitute the major source of atmospheric Pb in Los Angeles.

MATERIALS AND METHODS

Samples Collection Sites

The Los Angeles Metropolitan Area is one of the most populated metropolitan areas in the US, and its air basin is often ranked among the most contaminated in the nation (Su et al., 2009). Approximately 17 million people live in Los Angeles, Orange, San Bernardino, and Riverside Counties (US Census, 2013). The Angeles National

Forest, which covers ~660,000 acres, abuts the Los Angeles Metropolitan Area (USDA, 2013). The September 2012 Williams Fire scorched about 1,696 hectares (4,192 acres) of land in Angeles National Forest from approximately September 2nd to 13th. The fire occurred in a very steep (~ 30 – 80% slope, Fig. 1) area of the forest that is covered with medium to heavy brush. The fuels, mostly chaparral, brush, and mixed conifers, were approximately 15 to 20 years old (InciWeb, 2012). Fourteen ash and 6 soil (from unburned patches) samples were collected from different accessible locations within the burned perimeter of the fire site (Figs. 1 and 2) using established trace metal clean techniques (Odigie and Flegal, 2011). The samples were then transported in plastic containers to the University of California, Santa Cruz for processing. The approximate collection location (GPS coordinates) for each sample is presented in Table S1 in Appendix 1. No specific permissions were required to access and collect samples from the fire site, and the sampling did not involve interactions with endangered or protected species.

Analytical Methods

Trace metal or ultra-pure (2x sub-boiling quartz distilled) grade reagents and high purity (18.2 MΩ cm) water (Milli-Q®) were used for cleaning labware and processing samples. Fourteen ash and 6 soil samples, 3 procedural blanks, and triplicates of 3 National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs), SRM 1547 (peach leaves), SRM 2709 (San Joaquin soil), and SRM 1633b (coal fly ash), were processed concurrently in a Class-100 HEPA-filtered trace metal clean laboratory. Three ash samples (CWA-1, CWA-8, and CWA-14) and 2 soil samples (CWS-1 and CWS-6) were processed in triplicate.

A concentrated aqua regia (HNO_3: HCl, 1:3 v/v) digestion was used to extract the acid-leachable (labile) trace (Co, Cu, Ni, Pb, and Zn) and major (Al and Fe) metals in the samples and reference materials (Kober et al., 1999; Emmanuel and Erel, 2002) using established methods (Soto-Jimenez et al., 2006). Briefly, approximately 0.3 to 0.5 g of ash, soil or reference material was transferred to a clean Teflon® digestion vial, dried overnight at 65°C, refluxed in hot (~130°C) aqua regia for about 6 hours, dried, weighed and redissolved in 10 mL of 1M ultrapure HNO_3.

The digests were analyzed for trace metal (Co, Cu, Ni, Pb, and Zn) concentrations with a Finnigan ELEMENT 2 high resolution – inductively coupled plasma mass spectrometer (HR ICP-MS), and for Al and Fe concentrations with a PerkinElmer Optima 4300™ DV inductively coupled plasma – optical emission mass spectrometer (ICP-OES). The concentrations of Fe were used to compute the enrichment factors of trace metals in the samples. The digests were then analyzed for stable lead isotopic composition after optimizing their concentrations with a Finnigan ELEMENT 2 HR ICP-MS. Internal standards (Bi, Ga, In, Rh, Sc, and Y) were used to correct for instrumental drifts during analysis, and NIST SRM 981 (common lead) was used as standard to correct for instrumental fractionation of lead isotopic composition. The detection limit (3 x standard deviation of procedural blanks), reproducibility, and recoveries of each analyte are presented in Tables 1 to 4. The recoveries of metals in the NIST SRM 1547 (peach leaves) are assumed to be more representative of the recoveries of metals in the ash samples since they were derived predominantly from vegetation and soil organic matter.

RESULTS AND DISCUSSION

Metal Concentrations

The “acid-leachable” concentrations of Al, Co, Cu, Fe, Ni, Pb, and Zn, and lead isotopic ratios (^{206}Pb/^{207}Pb, ^{208}Pb/^{204}Pb, and ^{208}Pb/^{207}Pb) of the ash and soil samples are listed in Table 5. The enrichment factors of the trace metals (Co, Cu, Ni, Pb, and Zn) normalized to Fe are listed in Table S2 in Appendix 1. These concentrations and enrichment factors are considered conservative because they may not include metals volatilized during the fire and those contained in refractory aluminosilicate lattices, which require dissolution with concentrated HF (Hornberger et al., 1999; Schiff and Weisberg, 1999).

Concentrations of Co (3.1 to 11 µg g^{-1}), Cu (15 to 69 µg g^{-1}), Ni (5.9 to 15 µg g^{-1}), Pb (7.4 to 42 µg g^{-1}), and Zn (65 to 500 µg g^{-1}) in the ash varied substantially. But the ranges of these concentrations are consistent with those measured in ash collected from the 2009 Jesusita Forest Fire site in Santa Barbara, California (Table 5). The concentrations are also comparable to concentrations of these metals in ash sourced primarily from the experimental combustion of ponderosa pines in Montana (Gabet and Bookter, 2011).

Variations in the amounts of these remobilized metals potentially reflect variations in baseline concentrations of the metals, anthropogenic input, and levels of volatilization of organic matter during the fire (Ranali, 2004; Simpson et al., 2011). The concentrations of Co (6.3 to 13 μg g^{-1}), Cu (17 to 32 μg g^{-1}), Ni (6.0 to 21 μg g^{-1}), Pb (8.6 to 140 μg g^{-1}), and Zn (32 to 61 μg g^{-1}) in the soil samples are also comparable to previously reported values of soils in Southern California (Shacklette and Boerngen, 1984; Holmgren et al., 1993; Wu et al., 2010). The concentrations of some metals (e.g., Co and Ni) in the soils approximate their baseline concentrations in Southern California, but the 2-fold increase in Pb concentrations (e.g., 140 μg g^{-1}) indicated that the Angeles National Forest site had received substantial Pb inputs from anthropogenic sources.

Enrichment Factors

The amounts of anthropogenic trace metals in the ash are indicated by the enrichment factors of the metals normalized to Fe: Co (0.9 to 2.5), Cu (0.9 to 6.2), Ni (0.3 to 1.0), Pb (1.9 to 29), and Zn (0.9 to 19) (Table S2 in Appendix 1).

$$EF = \frac{\dfrac{[X]_{Sample}}{[Fe]_{Sample}}}{\dfrac{[X]_{Baseline}}{[Fe]_{Baseline}}}$$

We calculated the enrichment factor of each metal by normalizing the concentrations of the metal ($[X]_{Sample}$) and iron ($[Fe]_{Sample}$) in the sample to the baseline concentrations of each metal ($[X]_{Baseline}$) and iron ($[Fe]_{Baseline}$) of ^{210}Pb-dated preindustrial sediment deposited in San Pedro Basin, which drains parts of the Los Angeles Metropolitan Area. Normalization of trace metals to Fe is considered more appropriate than normalization to Al for samples that were not treated with HF because of the recalcitrance of aluminosilicates as indicated by the difference in the recoveries of these metals in the NIST SRMs (Table 2). Using the enrichment classification proposed by Sutherland (Sutherland, 2000), the ratios indicate that most of the Co, Cu, and Ni are predominantly from natural sources while Pb and Zn were enriched in some ash samples. These industrial enrichments were further indicated by the correlations between the concentrations of the metals and the concentrations of Fe: [Co] ($r = 0.576$, $p = 0.031$, $n = 14$), [Cu] ($r = 0.058$, $p = 0.844$, $n = 14$), [Ni] ($r = 0.612$, $p = 0.020$, $n = 14$), [Pb] ($r = -0.158$, $p = 0.590$, $n = 14$), and [Zn] ($r = -0.221$, $p = 0.448$, $n = 14$) in the ash. Metals that are primarily from natural origin, e.g., aluminum and iron ($r = 0.909$, $p < 0.001$, $n = 14$), which are relatively abundant and not easy to contaminate, correlate better than those enriched by anthropogenic inputs (Daskalakis and O'Connor, 1995). These varying enrichments are also generally consistent with those of these metals in ash collected from the 2009 Jesusita Fire (e.g., Odigie and Flegal, 2011).

Lead Isotopic Compositions

The apparent anthropogenic enrichment of Pb in some of the samples is further evidenced in Figure 3, which is a plot of the lead isotopic ratios ($^{206}Pb/^{207}Pb$: $^{208}Pb/^{207}Pb$) of the ash and soil samples. The plot also includes the lead isotopic compositions of pre-industrial and contaminated sediment deposited in the San Pedro Basin, which drains parts of the Los Angeles Metropolitan Area as previously mentioned, and those of leaded gasoline sold in California during the second half of the previous century.

The plot indicates that the Pb in the ash is mainly from anthropogenic sources, predominantly the past combustion of leaded gasoline. The plot also indicates that the portion of anthropogenic Pb from the leaded gasoline used between 1964 to1979 was substantially larger than that from the 1980s leaded gasoline in the ash, which contrasts the results from the Santa Barbara study that indicate that the predominant source of anthropogenic Pb was the combustion of the 1980s leaded gasoline (Odigie and Flegal, 2011). The predominantly alkyl-lead in the samples is further corroborated by the isotopic compositions of Pb in most (4) of the soil samples (Fig. 3). Two soil samples (CWS-4 and CWS-5) have distinct lead isotopic compositions compared to the other samples and are assumed to be representative of mixtures between baseline and anthropogenic Pb or are variants of baseline Pb.

The apparent leaded gasoline signature of Pb in the samples attests to the persistence of industrial Pb deposits in the Los Angeles Basin that is consistent with the results of the mass balance studies by Harris and Davidson (Harris and Davidson, 2005). It is also consistent with previous reports on the persistence of industrial Pb deposits in California's Central Valley, which is north of Los Angeles, based on both mass balance and lead isotopic composition analyses (Steding et al., 2000; Dunlap et al., 2008). The latter has been principally traced to atmospheric depositions from the combustion of leaded gasoline in California (Dunlap et al., 2008).

This attribution is based on the temporal changes in the isotopic compositions of leaded gasoline in California in the previous century. Before 1960, alkyl-lead in the US was primarily manufactured with ores from Australia, Canada, Mexico, and Peru, which had $^{206}Pb/^{207}Pb$ ratios of 1.037, 1.064, 1.192, and 1.200, respectively (Ng and Patterson, 1982). Then, the proportion of Pb sourced from the Missouri deposits ($^{206}Pb/^{207}Pb$ = 1.28 to 1.33) increased from 9% in 1962 to 82% in 1976. This change in the sources of Pb in alkyl-lead was subsequently reflected in the lead isotopic compositions of aerosols in Southern California. There, the $^{206}Pb/^{207}Pb$ ratio of aerosol, which was ~1.15 before 1967, changed to 1.20 by 1974, and then to 1.23 by 1977 (Shirahata et al., 1980).

Accelerated Transport of Contaminants to Water Bodies and Atmosphere

In addition to atmospheric contamination, wildfires increase the load of contaminants in aquatic ecosystems. This was recently documented in a study (Stein et al., 2012) that examined the impact of wildfires on contaminant loadings in Southern California – the same area where the Williams Fire occurred. The results from that study show that the mean fluxes of Cu, Pb, Ni, and Zn from burned sites were 110-fold, 740-fold, 82-fold, and 110-fold greater than their respective fluxes at similar unburned (control) sites. They also found that the mean post-fire concentrations of Cu, Pb, Ni, and Zn in the first stormwater collected from an area that was ~20 km from the closest fire site were each 3 times their pre-fire levels, which they attributed to ash fallout. Similarly, Sabin et al. reported 4-fold, 6-fold, 8-fold, and 13-fold post-fire increases in fluxes of Cu, Zn, Pb, and Ni, respectively, over their mean fluxes in an unburned site in Southern California, which were likewise attributed to forest fires in nearby mountains (Sabin et al., 2005). Those attributions are consistent with results from a study by Young and Jan (Young and Jan, 1977), who showed that trace metals (Cu, Ni, Pb, and Zn) fallout increased by ~3 to 4-fold in a 10,000 km^2 unburned area that was impacted by smoke plumes and ash from wildfires in the Angeles National Forest in Southern California.

Potential Impact of Climate Change

The mobilization of contaminants by wildfires is a concern, especially in western US where climate change is expected to further alter fire regimes (Westerling et al., 2006). Recent studies have linked increases in fire intensity, frequency, and burned area to climate change (Gillett et al., 2004; Wang et al., 2010; Westerling et al., 2011). For example, wildfire frequency has been positively linked ($r = 0.76$, $p < 0.0001$, $n = 34$) to regional spring and summer temperatures in western US (Westerling et al., 2006). The frequency of wildfires and total area burned in western US in the mid-1980s were ~4 times and ~7 times, respectively, higher than their mean values from 1970 to 1986, and this interval was marked by a rise in temperature of $<0.9^{o}$C (Westerling et al., 2006). Furthermore, the Intergovernmental Panel on Climate Change has projected that global surface temperature could increase by up to 5.8^{o}C by the end of this century, and many researchers have predicted a corresponding increase in the frequency and intensity of wildfires (McKenzie et al., 2004; Flannigan et al., 2005; IPCC, 2007; Schuur et al., 2008). Consequently, it is hypothesized that the remobilization and volatilization of contaminants from forests and grasslands will increase in response to projected climate change. The expected increase in the pyrogenic remobilization of contaminants is a concern, especially in forests contaminated with radioactive pollutants and at sites used for nuclear waste storage, as recently highlighted for Chornobyl, Russia and Los Alamos National Laboratory, US, respectively (Charles, 2010; Gilbert, 2010; Weinhold, 2011). The results from this and complementary studies provide empirical evidence that wildfires are already remobilizing and volatilizing contaminants – albeit more pedestrian ones that constitute a greater global health problem (e.g., Pb).

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TABLES AND FIGURES

Table 1: Method detection limits of analytes.

	Detection Limit (3 x SD, Standard Deviation of 3 blanks)						
	(ng/g)					(µg/g)	
Element	[Co]	[Cu]	[Ni]	[Pb]	[Zn]	[Al]	[Fe]
Detection Limit	0.002	0.010	0.002	0.008	0.148	0.015	0.035

Table 2: Digestion recoveries (concentrations) for elements in standard reference materials (SRMs).

	% Recovery (Mean ± SD, n = 3)						
SRM	Co	Cu	Ni	Pb	Zn	Al	Fe
NIST SRM 1547 (Peach Leaves)	82.6 ± 3.0	89.3 ± 0.7	74.5 ± 2.8	104 ± 0.8	98.7 ± 1.2	65.7 ± 5.2	86.7 ± 4.7
NIST SRM 2709 (San Joaquin Soil)	52.0 ± 0.4	49.1 ± 0.6	49.1 ± 0.4	77.5 ± 0.7	53.2 ± 0.7	55.6 ± 1.1	93.7 ± 0.5
NIST SRM 1633b (Coal Fly Ash)	43.7 ± 0.7	38.6 ± 0.5	42.6 ± 0.6	62.5 ± 0.3	41.2 ± 0.0	25.6 ± 0.8	76.7 ± 1.9

Table 3: Analytical (instrumental) precision.

	% RSD (n = 5)					% RSD (n = 4)	
SRM	[Co]	[Cu]	[Ni]	[Pb]	[Zn]	[Al]	[Fe]
SRM 1640a	0.9	1.1	0.9	0.5	1.6	-	-
Consistency Standard A	2.3	1.6	2.3	0.2	0.9	0.3	0.5
Consistency Standard B	-	-	-	-	-	0.3	0.6

Table 4: Analytical (instrumental) precision for lead isotopic compositions.

	% RSD (n = 5)		
Sample	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{207}Pb/^{204}Pb$
CWA-2	0.07	0.04	0.09

Table 5: Concentrations (µg g^{-1}) of trace metals: Co, Cu, Ni, Pb, and Zn; concentrations (mg g^{-1}) of Al and Fe; and lead isotopic composition of ash (CWA) and soil (CWS) samples collected from the 2012 Williams Fire in Angeles National Forest in Southern California. Samples marked with (*) were processed in triplicates and are reported as mean ± (standard deviation, SD). Also listed in the table are the ranges and mean concentrations of metals and lead isotopic compositions of ash collected from the 2009 Jesusita Fire in Santa Barbara, California. Data marked with (‡) were summarized from Odigie and Flegal (Odigie and Flegal, 2011).

Sample ID	Concentrations [mean ± *(standard deviation, SD)*]							Lead Isotopic Ratios [mean ± *(SD)*]		
	[Co] (µg g^{-1})	[Cu] (µg g^{-1})	[Ni] (µg g^{-1})	[Pb] (µg g^{-1})	[Zn] (µg g^{-1})	[Al] (mg g^{-1})	[Fe] (mg g^{-1})	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{207}Pb/^{204}Pb
CWA-1*	3.90	15.4	6.77	16.0	216	13.8	10.9	2.454	1.189	15.673
	(0.05)	*(0.24)*	*(0.25)*	*(0.04)*	*(2.92)*	*(0.55)*	*(0.29)*	*(0.001)*	*(0.001)*	*(0.004)*
CWA-2	7.54	68.5	10.6	24.0	128	18.4	25.0	2.461	1.185	15.635
CWA-3	3.59	41.3	9.21	42.2	83.0	5.79	6.94	2.438	1.178	15.656
CWA-4	6.76	30.8	10.6	14.8	85.0	18.7	24.4	2.457	1.190	15.633
CWA-5	3.81	38.6	9.72	20.8	65.3	7.86	10.8	2.454	1.192	15.659
CWA-6	8.75	56.0	12.5	27.2	414	13.6	16.2	2.463	1.213	15.684
CWA-7	5.17	65.5	14.3	38.5	203	14.3	13.8	2.451	1.195	15.711
CWA-8*	10.9	58.2	13.3	8.95	374	13.0	17.0	2.457	1.193	15.660
	(0.74)	*(3.24)*	*(0.52)*	*(1.02)*	*(15.7)*	*(0.36)*	*(0.55)*	*(0.001)*	*(0.002)*	*(0.011)*
CWA-9	4.32	17.3	10.5	9.68	96.5	14.3	16.2	2.471	1.186	15.662
CWA-10	7.47	26.3	14.6	20.0	73.6	24.4	31.5	2.458	1.187	15.672
CWA-11	3.13	17.0	5.86	8.23	74.2	7.42	8.71	2.450	1.189	15.733
CWA-12	6.05	20.5	11.2	17.3	65.5	18.6	18.1	2.462	1.183	15.669
CWA-13	6.30	56.8	9.17	11.5	503	7.85	10.7	2.472	1.188	15.664
CWA-14*	6.66	43.3	12.9	7.38	66.6	20.7	19.2	2.450	1.189	15.686
	(0.27)	*(0.23)*	*(0.15)*	*(0.25)*	*(0.68)*	*(0.53)*	*(0.39)*	*(0.001)*	*(0.001)*	*(0.017)*
CWS-1*	7.31	20.0	6.04	20.7	44.5	29.2	52.4	2.459	1.181	15.635
	(0.10)	*(3.89)*	*(0.14)*	*(0.76)*	*(0.46)*	*(2.11)*	*(1.84)*	*(0.002)*	*(0.000)*	*(0.011)*
CWS-2	8.65	19.6	21.1	143	61.2	35.1	46.8	2.461	1.204	15.647
CWS-3	12.5	32.1	16.8	20.3	41.5	32.1	43.5	2.455	1.178	15.614
CWS-4	6.26	25.9	11.8	8.62	32.0	20.7	28.1	2.506	1.196	15.684
CWS-5	8.82	17.0	15.0	10.9	37.3	34.9	40.1	2.491	1.185	15.643
CWS-6*	9.98	20.0	13.1	16.4	44.2	33.5	46.4	2.443	1.160	15.581
	(0.67)	*(0.89)*	*(1.21)*	*(1.81)*	*(0.65)*	*(5.00)*	*(1.37)*	*(0.001)*	*(0.006)*	*(0.024)*
Jesusita Fire ash, Santa Barbara, California (Data Summary, n = 30)										
Mean, [x̄]	4.46	-	22.7	18.8‡	151	16.7‡	13.9‡	2.466‡	1.205‡	15.635‡
Range (Min to Max)	1.95	-	8.88	4.29‡	41.6	5.70‡	5.00‡	2.436‡	1.161‡	15.563‡
	-	-	-	-	-	-	-	-	-	-
	7.23	-	49.1	51.0‡	433	36.0‡	31.1‡	2.481‡	1.218‡	15.716‡

Figure 1: Photograph of the 2012 Williams Fire in Angeles National Forest, California showing the relatively remote and mountainous terrain where the fire occurred. Photo by Freddie W. Duncan, US Forest Service.

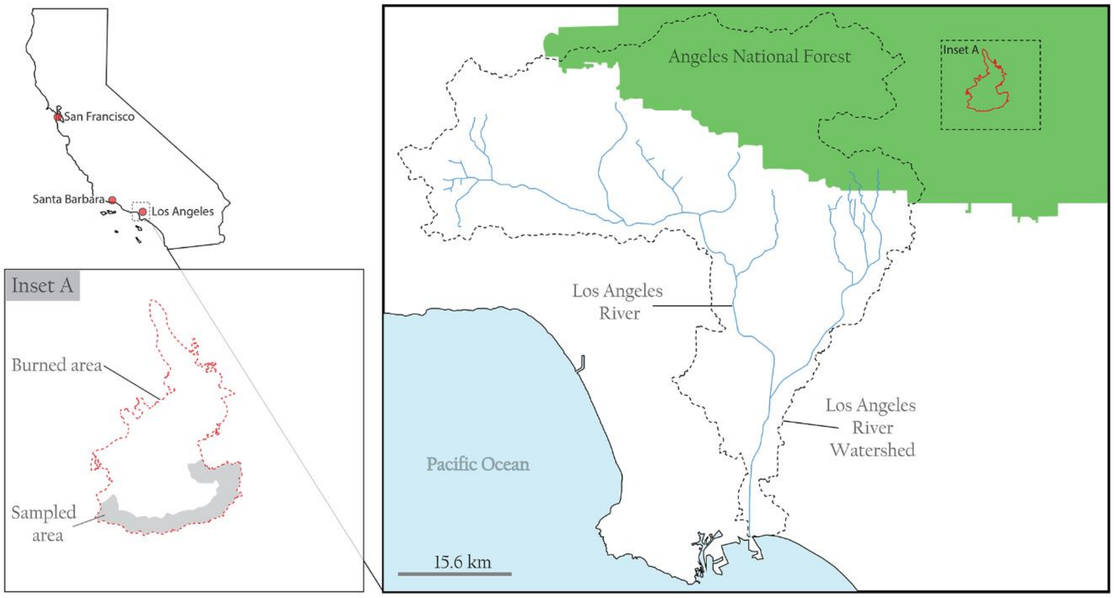

Figure 2: Map showing approximate samples collection sites within the boundary of the 2012 Williams Fire in Angeles National Forest, California.

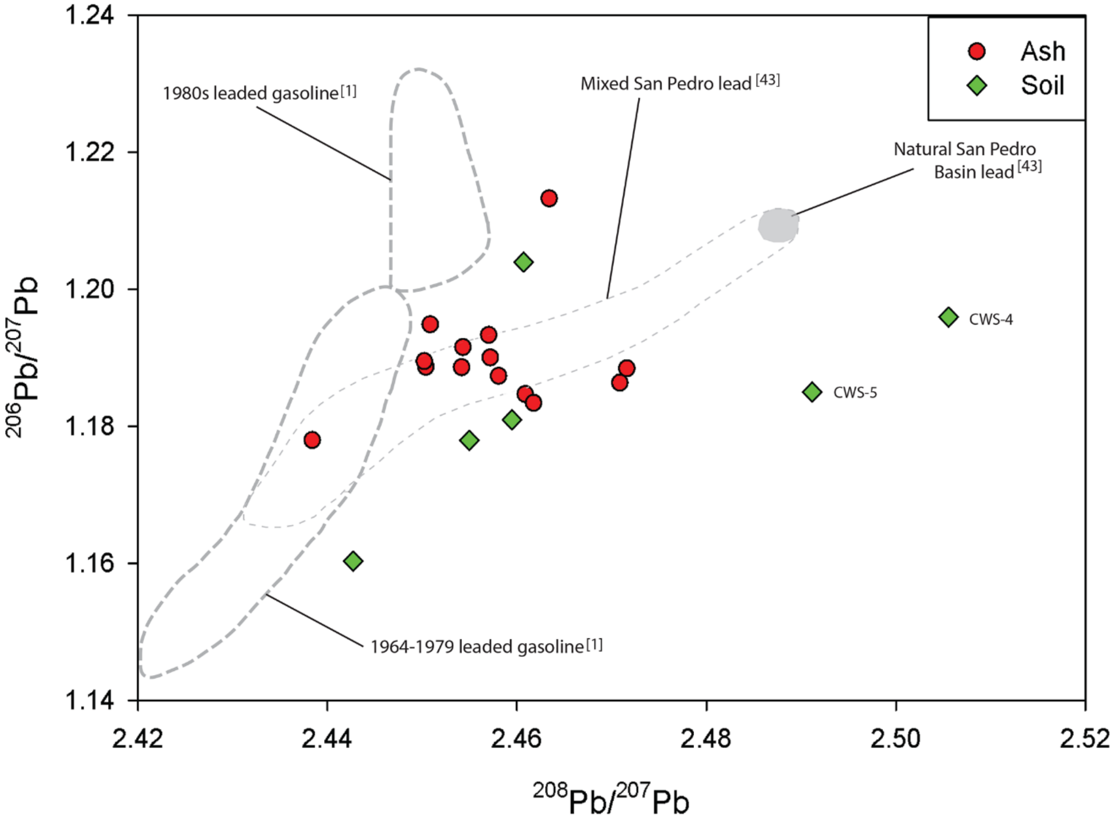

Figure 3: Lead isotopic composition ($^{208}Pb/^{207}Pb$: $^{206}Pb/^{207}Pb$) of ash and soil samples collected from the 2012 Williams Fire site in Southern California. The plot also includes the ranges of isotopic composition of alkyl-lead used in California and those of ^{210}Pb dated sediment cores in the San Pedro Basin.

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Chapter 4: Sediment Records of Trace Elements and Lead Isotopic Composition Chronicle Historic Pyrogenic Remobilization of Contaminants in Patagonia, Chile

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ABSTRACT

Temporal changes in the amounts of trace elements (As, Co, Cu, Mn, Ni, Pb and Zn) and their correlations with temporal changes in charcoal abundance in age-dated sediments collected from Lake Thompson in Patagonia, Chile attest to the substantial pyrogenic mobilization of contaminants that occurred in Patagonia in the mid-1900s. This elemental mobilization was concurrent with the extensive historic slash and burn period in Patagonia during the last century. The changes in concentrations of Co, Cu, and Ni in relation to charcoal abundance in the lacustrine sediments over time were small compared to those of As, Mn, Pb and Zn. However, the relatively low enrichment factors of all those trace elements, normalized to Al and Fe, indicate that they were predominantly derived from natural – rather than industrial – sources. The predominantly natural source of Pb in the sediments was corroborated by the temporal consistency of its isotopic ratios (^{206}Pb/^{207}Pb: ^{208}Pb/^{206}Pb), which were similar to previously reported values for natural lead in Central and Southern Chile.

INTRODUCTION

Environmental and Health Impacts of Contaminant Emissions

Anthropogenic emissions of environmentally persistent contaminants have increased drastically since the industrial revolution (Ng and Patterson, 1982; Nriagu, 1996; Sen and Peucker-Ehrenbrink, 2012). Impacts of these emissions on environmental and human health have been extensive, including elevated levels of trace elements in air, surface waters, and terrestrial and lacustrine sediments – both in industrialized and remote uninhabited locations (Nriagu and Pacyna, 1988; Boutron et al., 1995; Boyle et al., 2005). For example, emissions from the combustion of leaded gasoline accounted for ~75% of global Pb aerosols during the second half of the twentieth century (Nriagu, 1990; Dunlap et al., 2008).

That contamination has been well documented in Chile. Air Pb concentrations as high as 1.1 µg/m^3 were measured in Santiago in 1994 (Böllhofer and Rosman, 2000), which were over 3 orders of magnitude higher than the estimated Pb concentration (0.0006 µg/m^3) in a relatively pristine atmosphere (Chow et al., 1972). Similarly, relatively high concentrations of trace elements (As, Co, Cu, Mn, Ni, Pb, and Zn) were found in snow collected from regions in the Chilean Andes that were impacted by atmospheric depositions of urban and industrial (e.g., mining and smelting) emissions compared to their concentrations in snow collected from more pristine sites in that mountain chain (e.g., Cereceda-Balic et al., 2012). Pb and Zn concentrations as high as 129 mg/kg and 1015 mg/kg, respectively, were measured in topsoil at an industrial site in Talcahuano, Chile (Tume et al., 2008). High levels of As in soil and water have been documented in some parts of Chile, which was the second largest As producer in the world in 2013 (Ferreccio et al., 2000; Hopenhayn-Rich et al., 2000; Edelstein, 2014).

The burden of these emissions on human health was evidenced by elevated blood Pb (PbB) levels in children in Chile (Tchernitchin et al., 2005). For example, PbB levels as high as 26 µg/dL were measured in children (ages 5 – 12 years) living near a Pb storage site in Antofagasta, Chile (Perez-Bravo et al., 2004). Similar high PbB levels (e.g., >20 µg/dL) in infants were associated with the combustion of leaded gasoline in Santiago, Chile (Pino et al., 2004). Fortunately, efforts to reduce human exposure to Pb, including the ban of leaded gasoline in Chile and elsewhere, have been very successful in reducing atmospheric Pb concentrations and PbB levels in children in most countries (Pino et al., 2004; US EPA, 2006; Wheeler and Brown, 2013). However, recently reported PbB levels in Chilean children (e.g., Sepulveda et al., 2000) are still several folds greater than the estimated preindustrial PbB level of 0.016 µg/dL in humans (Flegal and Smith, 1992), and health impairments continue to be reported at sublethal PbB levels that were previously considered harmless (Wheeler and Brown, 2013). Similarly, health impairments associated with exposure to As have been documented in some parts of Chile (Ferreccio et al., 2000; Hopenhayn-Rich et al., 2000).

Remobilization of Trace Elements by Forest Fires

Trace elements sorb to terrestrial sediments, vegetation, and soil organic matter in forests, where they are relatively immobile (Siccama et al., 1980; Friedland et al., 1984; Biswas et al., 2007; Obrist et al., 2008). However, these contaminants are released in more labile forms when vegetation and soil organic matter are burned and volatilized by fire (Young and Jan, 1977; Biswas et al., 2007; Wiedinmyer and Friedli, 2007). In addition, wildfires increase erosion rates by as much as two orders of magnitude, which subsequently increases the rates of transport of remobilized contaminants to water bodies (Cohen et al., 2005; Stein et al., 2012; Warrick et al., 2012). While the impacts of wildfires on Hg influx to aquatic systems have been relatively well documented (e.g., Kelly et al., 2006), there is much less information on other trace elements (e.g., Pb and Zn) mobilized by wildfires (Odigie and Flegal, 2011).

Wildfires in Patagonia, Chile

Patagonia, Chile is renowned for its relatively pristine environment, extensive freshwater resources, and wildlife (Araneda et al., 2013). However, human activities associated with development in the region began measurably impacting its ecosystems during the last century (Vince, 2010; Araneda et al., 2013). Most notably, settlers burned approximately three million hectares of forest between 1930 and 1950 in the Aysén region of Northern Patagonia in Chile, resulting in a loss of ~23 % of its original vegetation (Araneda et al., 2013).

Objectives of Study

The extensive forest burning in the Aysén region makes it an ideal environment to study the impacts of wildfires on aquatic ecosystems. Lacustrine sediments are a good archive of environmental changes, including cycling of environmentally persistent contaminants, in a lake's catchment area (Tierney et al., 2010; Brucker et al., 2011). In addition, Pb isotopic compositions (^{206}Pb/^{207}Pb: ^{208}Pb/^{206}Pb) may be used as tracers of natural and industrial sources of mobilized Pb in the environment (Ellam, 2010; Flegal et al., 2010). Therefore, the objectives of this study were to (1) investigate the temporal changes in the influx of trace elements (As, Co, Cu, Mn, Ni, Pb, and Zn) associated with wildfires to an aquatic ecosystem and (2) determine the sources of remobilized Pb using its isotopic ratios.

MATERIALS AND METHODS

Study Site

Lake Thompson (45^{o}38'26"S; 71^{o}47'07"W) is a small, relatively pristine lake located about 20 km southeast of Coyhaique in Northern Patagonia, Chile (Fig. 1). The lake has a surface area of ~1.18 km^{2}, maximum depth of ~15 m, and drainage area of ~15.43 km^{2} (Araneda et al., 2013).

A sediment core (172 cm) was collected from the deepest part of the lake with a gravity corer and subsampled at 1 cm intervals for analyses. Radiocarbon dating was done on a parallel core collected from the lake, and depths of both cores were correlated using magnetic susceptibility and organic content profiles. That dating, organic content measurement, and charcoal analysis are described in detail elsewhere (Bertrand et al., 2012; Araneda et al., 2013).

Analytical Methods

All samples were processed with trace metal grade or ultrapure (2X sub-boiling quartz distilled) reagents and high purity (18.2 MΩ cm) water (Milli-Q) using established trace metal clean techniques in a HEPA-filtered (Class 100) trace metal clean laboratory. Concentrations of trace elements (As, Co, Cu, Mn, Ni, Pb, and Zn), concentrations of major elements (Al and Fe), and Pb isotopic compositions (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) were determined in 41 age-dated sediment samples, including 4 samples in triplicate. Those samples, triplicate of procedural blanks, triplicate of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1645 (River Sediment), and triplicate of NIST SRM 1646a (Estuarine Sediment) were processed concurrently using established methods (Soto-Jimenez et al., 2006). Approximately 0.3 to 0.5 g of sediment or SRM was transferred to an acid-cleaned Teflon digestion vial and dried overnight at 65^{o}C. The sediment was then digested by refluxing in 10 mL of hot (~130^{o}C) concentrated aqua regia (HNO_3 + HCl, 1:3 v/v) overnight. The digest was dried and redissolved in 10 mL of 1 M ultrapure HNO_3. Concentrations of Co, Cu, Ni, Pb, and Zn of the digests, and then their Pb isotopic compositions, were determined with a Finnigan ELEMENT 2 high resolution inductively coupled plasma – mass spectrometer (HR ICP-MS). Concentrations of As were determined with a Thermo Scientific XSERIES 2 Quadrupole ICP-MS in collision cell mode. Concentrations of Al, Fe, and Mn of the digests were determined with a PerkinElmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES). Instrumental drifts during analyses were corrected with internal standards (Bi, Ga, In, Rh, Sc, Te, and Y), and instrumental fractionation of lead isotopic composition was corrected with NIST SRM 981 (common lead). The detection limit, digestion recovery, and analytical precision for each element are listed in Tables 1, 2, 3, and 4.

RESULTS AND DISCUSSION

The labile (acid-leachable) concentrations of trace elements (As, Co, Cu, Mn, Ni, Pb, and Zn), concentrations of Al and Fe, and lead isotopic ratios ($^{208}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, and $^{207}Pb/^{204}Pb$) of sediments collected from Lake Thompson, Patagonia are listed in Table 5. Also listed in Table 5 are the previously reported concentrations of charcoal particles in the sediments (Araneda et al., 2013).

Elemental Concentrations

Concentrations (dry weight) of As (1.4 – 3.7 µg/g), Co (7.0 – 12 µg/g), Cu (12 – 17 µg/g), Mn (0.87 – 2.3 mg/g), Ni (6.1 – 7.9 µg/g), Pb (4.3 – 7.1 µg/g), and Zn (36 – 57 µg/g) in the sediments (Fig. 2) were generally comparable to reported basal levels of these elements measured in other relatively pristine lacustrine sediments in Chile (Urrutia et al., 2002; Fagel et al., 2010; Palma-Fleming et al., 2012), but were substantially lower (~10-fold) than those measured in lacustrine and river sediments from more industrialized and populated areas in the country (Segura et al., 2006; Fagel et al., 2010). For example, the concentrations of Pb and Zn were as high as 60 µg/g and 1300 µg/g, respectively, in sediments collected from Mapocho River, which runs through and receives anthropogenic inputs from Santiago in Chile (Segura et al., 2006). Concentrations of Al (16.4 – 26.8 mg/g) and Fe (21.9 – 46.6 mg/g) in the sediments were also comparable to previously reported levels of these elements in Central and Southern Chile (Urrutia et al., 2002; Chirinos et al., 2005). Therefore, those concentrations are considered to represent background or ~natural levels.

Temporal changes in the concentrations of trace elements (Fig. 2) and their correlations with charcoal abundance (Table 6) in the sediments attest to the impacts of the extensive slash and burn that occurred in Aysén region of Patagonia during the last century. For example, from ~1920 (depth of 19.5 cm) to ~1945 (depth of 13.5 cm), charcoal abundance increased by ~300% and during this period, the concentrations of As, Co, Cu, Mn, Ni, Pb, and Zn increased by 38%, 13%, 13%, 40%, 11%, 27%, and 33%, respectively. The changes in concentrations of Co, Cu, and Ni in relation to charcoal abundance in the lacustrine sediments over time were small (e.g., <20% from ~1920 to ~1945) compared to those of As, Mn, Pb, and Zn, which increased by more than 20% over the same period. The concentrations of Zn in the sediments peaked with charcoal abundance (~1940-1960), but the concentrations of Al, Fe, Mn, and Pb in the sediments continued to be relatively elevated for years after that (e.g., levels of Pb appear to be above baseline concentrations in the sediments deposited in the 1990s).

Differences in the rates of transport of remobilized trace elements to the lake could be due to several factors. These include their different affinities to sediments (i.e., partition coefficients), sensitivities to redox conditions, and solubilities at different pH (Charlatchka and Cambier, 2000; Allison and Allison, 2005). Differences in the apparent fluxes of the trace elements to Lake Thompson are consistent with their median partition coefficients (log K_d, L/kg) between soil and water: Pb (4.2) > Ni (3.1) = Zn (3.1) > Cu (2.7) > Co (2.1) (Allison and Allison, 2005); and previous studies have shown that the flux of Pb could be up to two orders of magnitude slower than those of other trace elements in soil (e.g., Pang et al., 2004). Correlations of the concentrations of the first row transition elements, except Zn, with charcoal abundance were low and not statistically significant ($p > 0.05$, $n = 30$), which are potentially due to the complexing properties of these elements, including those listed above. For example, the adsorption of Zn in acidic solutions is much greater than those of the other transition elements (Kraus and Moore, 1953).

Pre-1880 levels of some of the elements, including the major elements (Al and Fe), were relatively high – before charcoal abundance started increasing (Fig. 2), suggesting that processes that potentially mobilized bulk terrestrial sediments, e.g., mining and other land-use changes, could have impacted influx of elements to the lake during this period. But the concentrations of most of those elements decreased substantially (to their lowest levels) after this period before they started increasing in tandem with increase in charcoal abundance. The temporal trend of charcoal abundance in the sediments, which peaked during the middle of the previous century, is consistent with the period of intentional forest fires in the region (Araneda et al., 2013).

Enrichment Factors

Enrichment factors (EFs) of the trace elements were calculated by normalizing the concentrations of trace elements and major elements (Al and Fe) in each sample to their respective average background concentrations in the sediments. These EFs are considered conservative because the samples were not treated with concentrated hydrofluoric acid, which is required to completely dissolve aluminosilicates (Hornberger et al., 1999; Schiff and Weisberg, 1999). The relatively low enrichment factors of the trace elements, which were less than 5, and their relative consistency over the past century (Figs. 3a and 3b) indicate that all of them – including Pb were predominantly derived from natural sources.

Those enrichment levels were consistent with reported enrichment levels of these elements measured in other relatively pristine lakes in Chile (e.g., Urrutia et al., 2002) and the level of industrialization in Patagonia during the study period (Araneda et al., 2013). The predominantly natural source of most of those trace elements was further indicated by the significant ($p < 0.05$) positive correlations of their concentrations with concentrations of Al (Table 7), a conservative element that is naturally very abundant (~8% of continental crust) and relatively difficult to contaminate (Taylor and McLennan, 1985; Faure, 1991; Daskalakis and O'Connor, 1995). The correlations of the concentrations of trace elements with those of Fe, another major element, were generally lower than their correlations with the concentrations of Al.

Lead Isotopic Composition

The predominantly natural source of Pb in the sediments was further indicated by their Pb isotopic ratios (^{206}Pb/^{207}Pb vs ^{208}Pb/^{206}Pb), which have remained relatively constant over the past century and are consistent with previously reported natural ranges of Pb isotopic ratios for Central Chile (Figs. 4 and 5) (e.g., Fagel et al., 2010). The Pb isotopic ratios of these sediments are distinct from those of alkyl lead aerosols measured in Santiago and other cities in Chile. For example, ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios were ~1.064 and ~2.336, respectively, in Punta Arenas and Puerto Natales in Southern Chile and ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios were 1.150 – 1.182 and 2.413 – 2.436, respectively, in Santiago in the mid-1990s (Böllhofer and Rosman, 2000). These spatial variations in Pb isotopic compositions of aerosols reflect the extent of mixing of natural Pb, alkyl Pb, and industrial Pb emissions and the different sources of alkyl Pb used in the region (Fagel et al., 2010). The replacement of leaded gasoline with unleaded gasoline in Chile began in 1993 and leaded gasoline was banned there in 2001 (Pino et al., 2004; Tchernitchin et al., 2005).

The Pb isotopic ratios plots indicate that the fraction of anthropogenic Pb in the sediments is small. This relative homogeneity is consistent with the results of an earlier study of sediments in Lago Puyehue, a relatively pristine lake in the Andes in Chile, which determined that anthropogenic Pb accounted for <5% of the Pb deposited in the lake (Fagel et al., 2010). Consequently, increases in the flux of Pb, and – by association – other trace elements, to Lake Thompson are predominantly attributed to increased weathering and increased rates of erosion associated with the extensive slash and burn that occurred in the region, rather than temporal increases of industrial emissions in the region over the last century. Notably, these Pb isotopic ratios show that the increase in Pb concentrations at the middle of last century and then the slow decline are not due to the introduction and subsequent phase out of leaded gasoline in Chile – in spite of the similarity of the temporal variability of the Pb concentration profile in sediments in Lake Thompson to those in sediments of lakes and rivers elsewhere that corresponded with the use of leaded gasoline during the previous century (Callender and vanMetre, 1997; Renberg et al., 2001; Van Metre and Mahler, 2004; Lima et al., 2005).

Potential Impacts of Climate Change and Development

The remobilization of toxic contaminants by forest fires is a concern because those fires are expected to increase in frequency and intensity in many parts of the world with climate change (Flannigan et al., 2005; Westerling et al., 2006). Though wildfires in Central–South Chile over the past century have been largely (~99%)

anthropogenic in origin, future forest fires in that region are projected to be exacerbated by climate change (Gonzalez et al., 2011). Temperatures have increased by ~0.4 to 1.4°C and annual precipitations have decreased by up to 40% over the past century in Central–South Chile (Rignot et al., 2003; Glasser et al., 2011; Gonzalez et al., 2011; IPCC, 2013). Therefore, it is hypothesized that pyrogenic remobilization of toxic elements will increase in response to increasing fire intensity and frequency associated with climate change in Chile, especially in its more contaminated forests. That remobilization of toxic elements by fires would be exacerbated by ongoing and planned developments in Southern Chile, which are expected to cause substantial increases in sediment erosion and deforestation (Vince, 2010).

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TABLES AND FIGURES

Table 1: Method detection limits of analytes.

	Detection Limit (3 x SD, Standard Deviation of 3 blanks)								
	(ng/g)						(µg/g)		
Element	[As]	[Co]	[Cu]	[Ni]	[Pb]	[Zn]	[Al]	[Fe]	[Mn]
Detection Limit	0.015	0.005	0.005	0.066	<0.001	0.179	0.005	0.001	0.001

Table 2: Digestion recoveries (concentrations) for elements in standard reference materials (SRMs).

	% Recovery (Mean ± SD, n = 3)								
SRM	As	Co	Cu	Mn	Ni	Pb	Zn	Al	Fe
NIST SRM 1646A (Estuarine Sediment)	52.3 ± 0.8	68.2 ± 1.1	78.3 ± 4.3	88.7 ± 3.5	72.8 ± 1.9	76.5 ± 2.6	68.0 ± 0.7	51.4 ± 3.1	95.7 ± 0.8
NIST SRM 1645 (River Sediment)	97.2 ± 2.1	75.4 ± 0.2	94.6 ± 3.8	95.1 ± 1.8	86.4 ± 0.9	92.2 ± 1.1	92.2 ± 0.9	36.5 ± 1.2	89.1 ± 1.4

Table 3: Analytical (instrumental) precision.

	% RSD (n = 6 or 7 or 8)*						% RSD (n = 5)		
SRM	[As]	[Co]	[Cu]	[Ni]	[Pb]	[Zn]	[Al]	[Fe]	[Mn]
SRM 1640a	4.6	0.9	1.1	0.9	1.1	1.1	5.2	2.1	0.9
Consistency Standard A	5.4	0.9	1.1	1.2	1.4	1.2	1.5	1.1	1.2

*n = 7 for SRM 1640a and n = 8 for Consistency Standard A; n = 6 for As

Table 4: Analytical (instrumental) precision for lead isotopic compositions.

	% RSD (n = 5)		
Sample	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{207}Pb/^{204}Pb$
PT01	0.10	0.11	0.15
PT39	0.08	0.09	0.16

Table 5: Table showing the average depth, charcoal abundance, elements concentrations, and lead isotopic compositions of sediments collected from Lake Thompson in Patagonia, Chile. Samples marked with (*) were processed in triplicates and are reported as mean ± (standard deviation). Charcoal data were provided by Araneda et al. 2013.

			Concentrations [mean ± *(standard deviation, SD)*]									Lead Isotopic Ratios [mean ± *(SD)*]		
sample ID	ave depth (cm)	charcoal abundance (particles/cm^3)	[As] (µg g^{-1})	[Co] (µg g^{-1})	[Cu] (µg g^{-1})	[Ni] (µg g^{-1})	[Pb] (µg g^{-1})	[Zn] (µg g^{-1})	[Mn] (mg g^{-1})	[Al] (mg g^{-1})	[Fe] (mg g^{-1})	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{207}Pb/^{204}Pb
PT01	0.5	35	3.3	9.3	14.5	7.5	6.0	41.9	2.2	23.7	46.6	2.466	1.187	15.616
PT02*	1.5	29	2.8	9.3	14.5	7.7	6.2	41.2	2.0	22.8	43.6	2.467	1.188	15.597
			(0.32)	*(0.19)*	*(0.24)*	*(0.03)*	*(0.14)*	*(0.43)*	*(0.14)*	*(0.7)*	*(0.8)*	*(0.000)*	*(0.002)*	*(0.017)*
PT03	2.5	36	2.8	9.2	14.6	7.6	6.4	41.2	1.6	22.6	38.9	2.468	1.187	15.570
PT04	3.5	34	2.8	9.5	15.5	7.8	6.8	42.8	1.7	24.0	36.4	2.465	1.187	15.597
PT05	4.5	24	2.6	9.4	17.2	7.6	6.6	41.5	2.0	23.1	32.7	2.464	1.187	15.590
PT06	5.5	28	3.0	7.8	16.5	7.7	6.9	43.0	1.0	25.0	33.1	2.469	1.188	15.610
PT07	6.5	46	2.8	8.4	15.0	7.5	6.6	42.1	1.7	26.8	37.3	2.466	1.188	15.610
PT08	7.5	55	2.9	8.5	14.8	7.1	6.2	41.6	1.4	23.2	29.1	2.467	1.190	15.591
PT09	8.5	68	3.1	7.9	13.5	6.6	6.0	38.6	1.2	21.4	28.1	2.465	1.187	15.639
PT10	9.5	82	3.4	9.6	15.0	7.2	6.6	45.5	1.5	24.7	30.7	2.470	1.188	15.616
PT11	10.5	117	3.4	8.9	15.8	7.4	7.1	47.6	1.4	23.8	30.3	2.468	1.188	15.628
PT12	11.5	93	3.5	9.1	15.9	7.3	7.1	47.6	1.4	25.8	31.0	2.469	1.188	15.596
PT13	12.5	113	2.6	9.1	16.2	7.1	6.3	51.8	1.5	25.6	29.2	2.473	1.190	15.600
PT14*	13.5	143	3.3	8.6	15.5	7.1	6.2	56.6	1.4	22.7	28.9	2.467	1.190	15.594
			(0.10)	*(0.06)*	*(0.31)*	*(0.01)*	*(0.02)*	*(2.4)*	*(0.03)*	*(0.9)*	*(0.6)*	*(0.001)*	*(0.001)*	*(0.013)*
PT15	14.5	100	3.0	8.3	15.2	6.9	5.7	49.0	1.3	21.4	27.3	2.469	1.191	15.596
PT16	15.5	83	3.1	8.0	14.5	6.7	5.7	57.3	1.3	20.6	26.0	2.468	1.189	15.623
PT17	16.5	98	3.2	7.9	14.6	6.9	5.4	54.8	1.2	20.3	26.8	2.468	1.189	15.593

Table 5 (*continued*)

			Concentrations [mean ± *(standard deviation, SD)*]									Lead Isotopic Ratios [mean ± *(SD)*]		
sample ID	ave depth (cm)	charcoal abundance (particles/cm^3)	[As] (µg g^{-1})	[Co] (µg g^{-1})	[Cu] (µg g^{-1})	[Ni] (µg g^{-1})	[Pb] (µg g^{-1})	[Zn] (µg g^{-1})	[Mn] (mg g^{-1})	[Al] (mg g^{-1})	[Fe] (mg g^{-1})	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{207}Pb/^{204}Pb
PT18	17.5	77	2.7	8.5	15.7	7.3	5.6	48.1	1.2	21.2	26.7	2.470	1.189	15.610
PT19	18.5	55	2.7	7.9	14.7	6.7	5.2	45.2	1.1	19.1	24.5	2.469	1.191	15.600
PT20	19.5	36	2.4	7.6	13.7	6.4	4.9	42.6	1.0	17.6	24.9	2.467	1.187	15.649
PT21	20.5		3.7	9.0	15.5	7.3	5.4	44.2	1.3	19.5	29.6	2.470	1.190	15.591
PT22	21.5	27	3.2	8.3	14.2	7.0	5.1	42.8	1.3	18.5	28.2	2.467	1.188	15.601
PT23	22.5		1.4	7.9	13.0	6.6	5.0	39.5	1.1	18.6	26.3	2.470	1.188	15.608
PT24	23.5	22	2.7	8.6	14.8	7.1	5.1	42.4	1.3	18.6	25.1	2.469	1.191	15.583
PT25	24.5		2.5	8.6	14.7	6.9	5.2	43.3	1.2	18.8	25.8	2.469	1.190	15.549
PT26	25.5	11	2.6	8.3	15.2	7.6	5.0	41.1	1.0	17.6	25.5	2.469	1.194	15.575
PT27*	26.5		2.6	8.0	15.0	7.0	5.0	41.5	1.1	18.3	24.9	2.468	1.190	15.602
			(0.15)	*(0.42)*	*(0.46)*	*(0.26)*	*(0.17)*	*(1.5)*	*(0.10)*	*(0.4)*	*(1.0)*	*(0.001)*	*(0.001)*	*(0.029)*
PT28	27.5	17	2.3	7.4	13.5	6.3	4.5	37.4	1.0	17.5	22.7	2.466	1.190	15.572
PT29	28.5		2.6	7.7	14.5	6.6	4.7	43.6	1.1	19.2	25.8	2.466	1.189	15.623
PT30	29.5	3	2.2	7.0	13.2	6.1	4.3	37.4	0.9	16.4	21.9	2.466	1.190	15.587
PT31	30.5		1.8	7.5	13.1	6.1	4.5	37.8	1.0	18.5	26.3	2.468	1.190	15.597
PT32	31.5	3	2.2	7.5	12.9	6.4	4.4	36.8	1.1	17.1	25.1	2.467	1.190	15.581
PT33	32.5		2.5	8.0	13.2	6.5	4.9	39.0	1.3	19.6	27.8	2.471	1.190	15.569
PT34	33.5	5	2.3	9.0	13.3	6.5	4.7	39.2	1.3	20.8	31.6	2.470	1.188	15.598
PT35	34.5		2.1	8.5	13.1	6.3	4.8	39.8	1.3	20.7	32.4	2.470	1.190	15.604
PT36	35.5	12	2.3	9.3	13.8	6.9	5.1	41.5	1.5	20.9	34.9	2.469	1.190	15.598
PT37	36.5		2.5	9.1	13.6	6.6	5.3	57.2	1.6	22.4	33.7	2.465	1.189	15.608
PT38	37.5	7	2.5	12	14.7	7.9	5.1	42.3	2.3	21.0	33.1	2.467	1.188	15.635
PT39	38.5		2.2	8.6	12.4	6.2	5.0	36.2	1.6	20.0	32.2	2.465	1.189	15.610
PT40*	39.5	5	2.1	9.3	13.6	6.7	5.1	41.2	1.5	22.4	34.3	2.465	1.190	15.598
			(0.01)	*(0.24)*	*(0.16)*	*(0.04)*	*(0.03)*	*(0.57)*	*(0.06)*	*(0.9)*	*(0.7)*	*(0.000)*	*(0.001)*	*(0.009)*
PT41	40.5		1.5	8.8	12.7	6.3	4.9	41.6	1.5	24.1	35.9	2.469	1.191	15.565

Table 6: Correlations of trace and major elements concentrations with charcoal abundance (particles/cm^3, n = 30) in sediments collected from Lake Thompson in Patagonia.

	[As] (µg/g)	[Co] (µg/g)	[Cu] (µg/g)	[Mn] (mg/g)	[Ni] (µg/g)	[Pb] (µg/g)	[Zn] (µg/g)	[Al] (mg/g)	[Fe] (mg/g)
r	0.71	-0.05	0.47	-0.06	0.08	0.54	0.83	0.44	-0.13
p-value	<0.01	0.79	0.01	0.76	0.67	<0.01	<0.01	0.02	0.50

Table 7: Correlations of trace element concentrations with Al and Fe concentrations in sediments collected from Lake Thompson in Patagonia.

	Correlations of element concentrations, r (p-value), n = 41	
Element	with Al concentrations (mg/g)	with Fe concentrations (mg/g)
[As] (µg/g)	0.36 (0.019)	0.13 (0.407)
[Co] (µg/g)	0.50 (0.001)	0.60 (<0.001)
[Cu] (µg/g)	0.49 (0.001)	0.10 (0.543)
[Mn] (mg/g)	0.57 (<0.001)	0.81 (<0.001)
[Ni] (µg/g)	0.54 (<0.001)	0.49 (0.001)
[Pb] (µg/g)	0.84 (<0.001)	0.47 (0.002)
[Zn] (µg/g)	0.34 (0.031)	-0.04 (0.811)

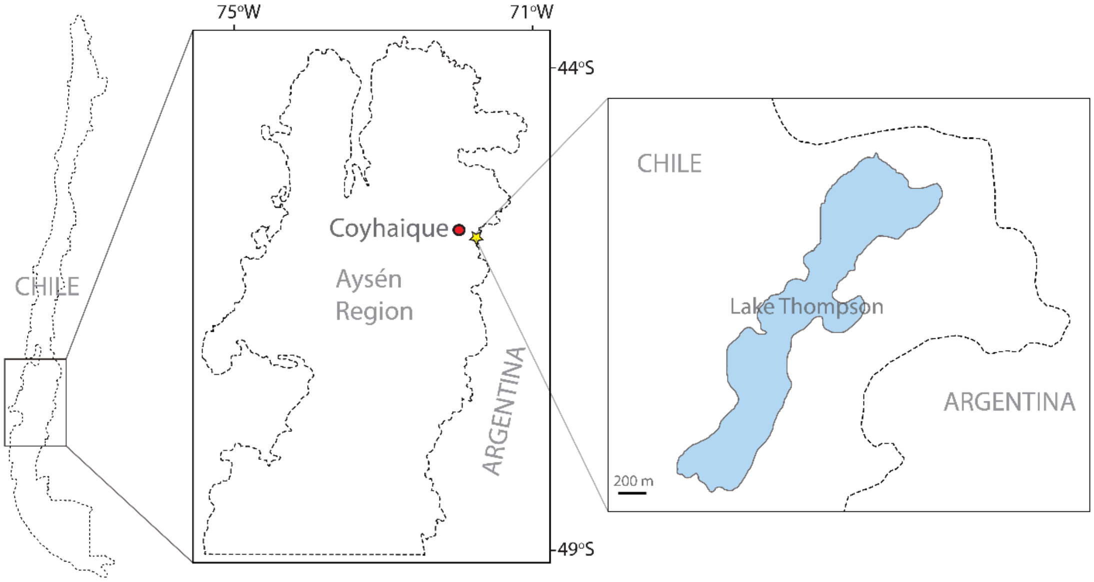

Figure 1. Map showing the approximate location of the study site, Lake Thompson, in Patagonia, Chile.

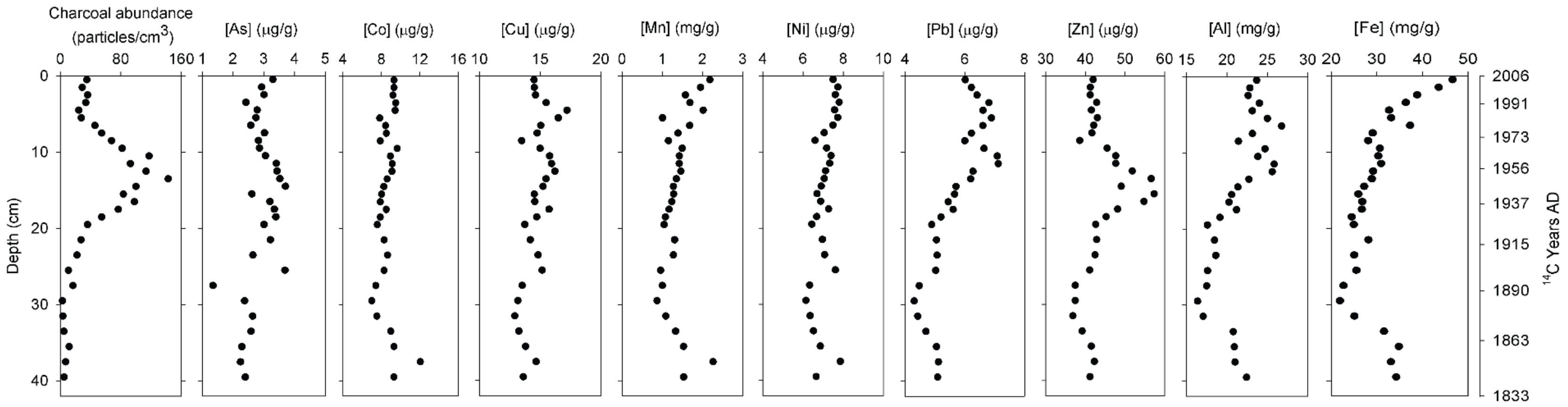

Figure 2. Charcoal abundance, trace elements (As, Co, Cu, Mn, Ni, Pb, and Zn) concentrations, and major elements (Al and Fe) concentrations profiles of sediments collected from Lake Thompson in Patagonia, Chile.

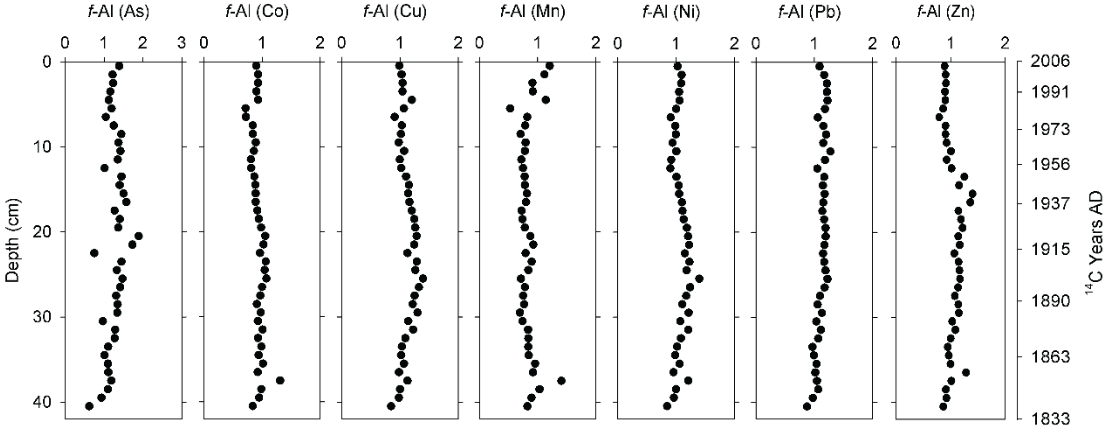

Figure 3a. Enrichment factors (EFs, normalized to Al) of trace elements in sediments collected from Lake Thompson in Patagonia, Chile.

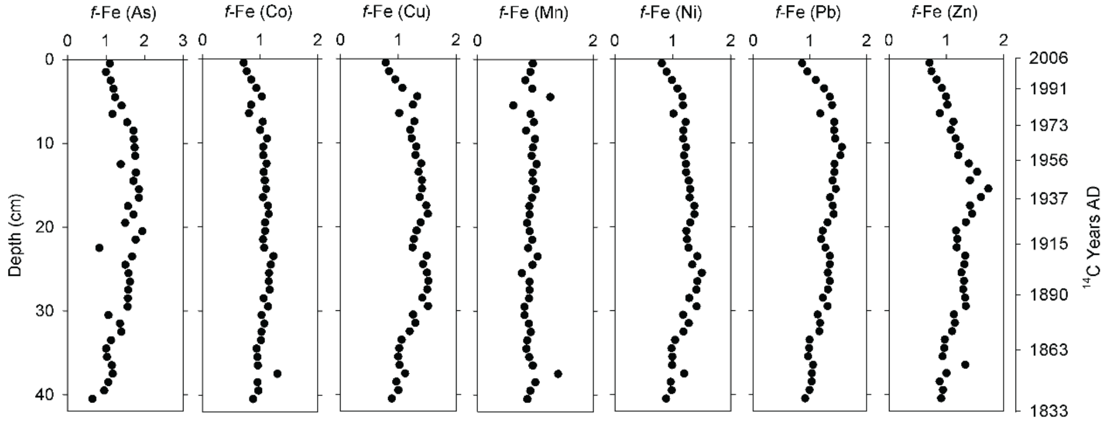

Figure 3b. Enrichment factors (EFs, normalized to Fe) of trace elements in sediments collected from Lake Thompson in Patagonia, Chile.

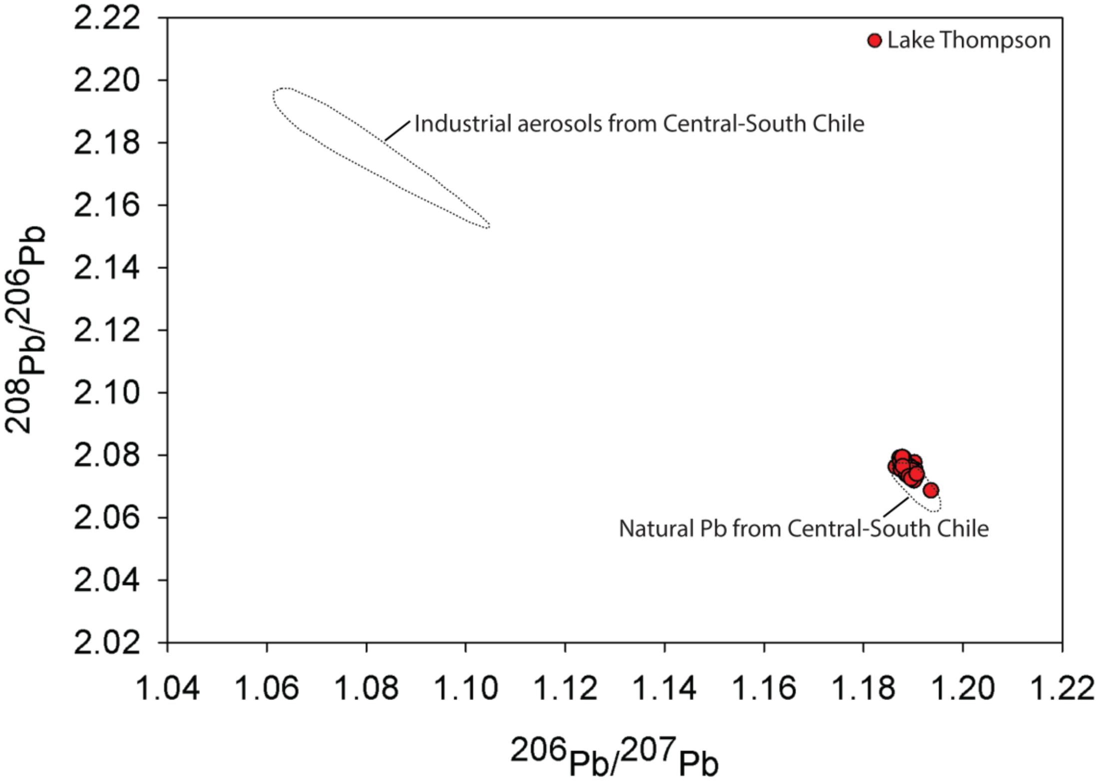

Figure 4. Lead isotopic ratios ($^{206}Pb/^{207}Pb$: $^{208}Pb/^{206}Pb$) of sediments collected from Lake Thompson in Patagonia, Chile. Also included in the plot are the ranges of natural and industrial lead isotopic ratios of aerosols collected from Central-South Chile (Böllhofer and Rosman, 2000; De Vleeschouwer et al., 2008).

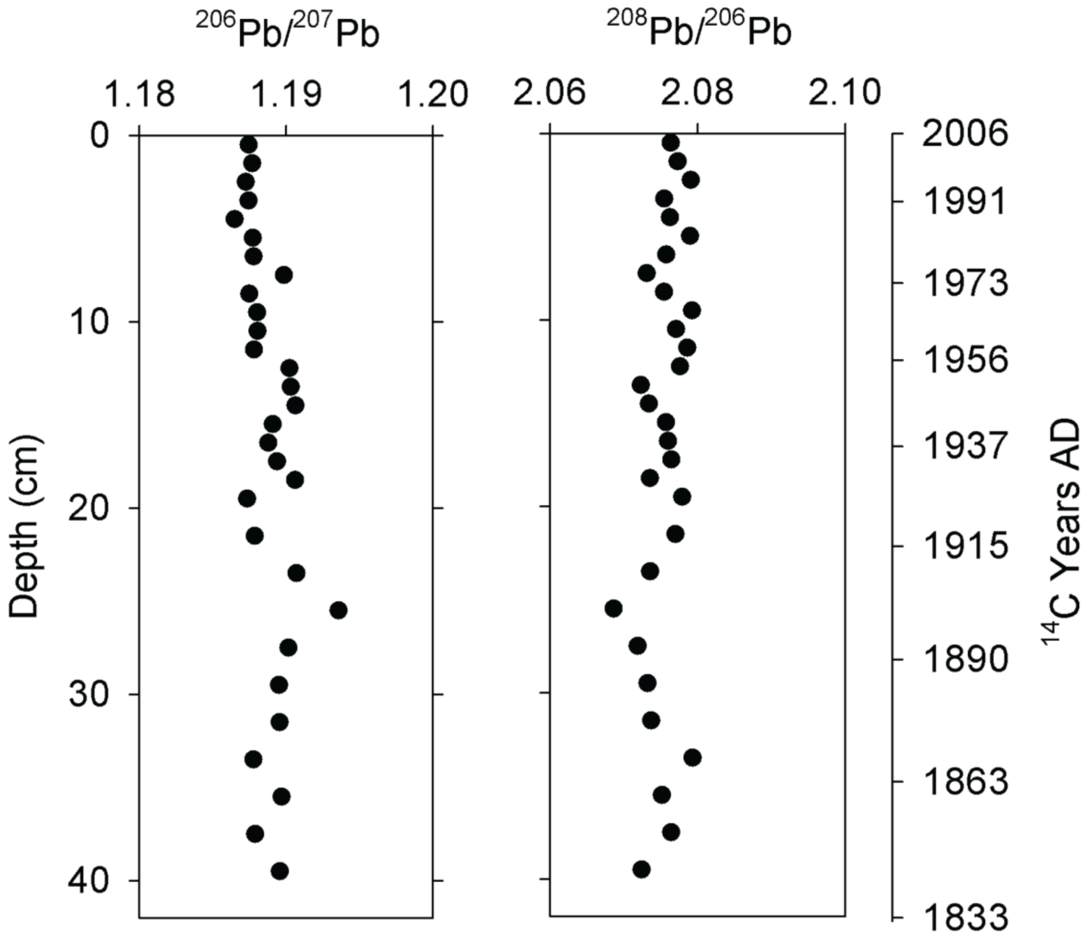

Figure 5. Depth profiles of lead isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) of sediments collected from Lake Thompson in Patagonia, Chile.

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Chapter 5: Using Lead Isotopes and Trace Element Records from Two Contrasting Lake Tanganyika Sediment Cores to Assess Watershed – Lake Exchange

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ABSTRACT

Lead isotopic and trace element records from 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) that is directly downstream from the Kahama and Nyasanga River watersheds and adjacent to Gombe Stream National Park. Trace element fluxes at LT-98-58 did not measurably change over the last two centuries (1815 to 1998), while the distal, mid-lake site recorded 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. Such accelerated weathering and detrital mobilization of lithogenic trace elements were further evidenced by (i) positive correlations ($r = 0.77$ to 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 ($r = 0.82$ to 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 normalized to Fe, and (iv) the temporal consistencies of the isotopic composition of Pb in the sediment. The aforementioned 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 results also indicate that the mid-lake sediment core is a much more sensitive and useful recorder of environmental changes than the nearshore sediment core. 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 sources at the two locations.

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 directly 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 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, such as widespread 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 poorly 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 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, agriculture, and rapid urbanization – may all contribute to elevated trace element releases into the environment via enhanced weathering and erosion. For example, deforestation (with rates of up to 100% already 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; Wells et al., 1999; Cohen et al., 2005a; 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 may increase in much of the world, including large parts of Africa, which will further impact trace element flux trends (Yang et al., 2003; IPCC, 2013).

Consequently, current and 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 in measurements of blood Pb (BPb) levels in children in Kabwe, Zambia (Blacksmith Institute, 2007). On average, their BPb levels were 10 to 20 times the current US CDC 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, the air and water temperatures at Lake Tanganyika have also been increasing in recent time. For example, average annual air temperatures around the lake have increased by 0.5 to 0.7^{o}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^{o}C between 1913 and 2000 (Tierney et al., 2010). Moreover, it has been predicted that surface temperature in Central Africa could rise by 1.25 to 1.5^{o}C by the end of this century (IPCC, 2013). Wildfires and soil erosion, which effectively mobilize trace elements and enhance their bioavailability, are thus expected to increase in response to projected 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, could further increase soil erosion rates and exacerbate release of sediment-bound trace elements (Eva and Lambin, 2000). 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 more recently, 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). Among those new data are the recently published 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) associated with mining and smelting operations and land-use changes around the lake.

Moreover, stable lead isotopic compositions ($^{207}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) are a useful tool for determining the sources and studying the fate of Pb contamination in the environment (Ellam, 2010; Flegal et al., 2010). For example, lead isotopic composition data were successfully 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 watershed-lake exchange.

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 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 multicorer 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 discussed elsewhere (Cohen et al., 2005a). The nearshore core (4.6883^{o}S, 29.6167^{o}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 protected 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^{o}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 dated with excess ^{210}Pb using the constant rate of supply (CRS) method and ^{14}C using accelerator mass spectrometry. The age model and determination of sedimentation rate 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 whereas the offshore site integrates more dispersed inputs.

2.2. Sample Processing and Analysis

High purity (18.2 MΩ cm) water (Milli-Q) and trace metal or ultrapure (2X sub-boiling quartz distilled) grade reagents were used for cleaning labware and processing samples. Thirty-seven (37) samples, including four 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 to 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 redissolved in 10 mL of 1 M ultrapure HNO_3. 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 (Odigie and Flegal, 2011). 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. 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 (Bi, Ga, In, Rh, Sc, and Y) 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. The detection limit, digestion recovery, and analytical precision for each analyte are presented in Tables 1 to 4. We calculated the enrichment factors (EFs) by normalizing the concentrations of the trace elements to those of Fe, which is naturally very abundant (~7% of continental crust) (Taylor and McLennan, 1985; Faure, 1991), difficult to contaminate, and considered more appropriate than Al because the aqua regia digestion did not include treatment with concentrated HF. Treatment of samples with HF is required for complete dissolution of Al and trace elements bound in aluminosilicate lattices (Hornberger et al., 1999; Schiff and Weisberg, 1999) as evidenced by the substantially higher recoveries for Fe (79.0 to 81.5%) compared to those for Al (28.9 to 30.3%) in our analyses. Consequently, we consider the element concentrations, fluxes, and enrichment factors as conservative. The fluxes of elements (µg 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 (µg g^{-1} or mg g^{-1}). 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 5. 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 6. Temporal profiles for the concentrations of the elements and lead isotopic ratios are presented in Appendix 2. Fluxes of trace elements at the offshore site (MC1) were consistently lower (up to 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 elements at both sites had comparable levels of enrichment, which were close to 1, except for Zn, which showed recent increased input, although its enrichment factors (EFs) were still less than 5 and within the range of natural variability.

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

The “near total” concentrations of Cu (15.77 ± 2.43 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 2002, but the concentrations of Pb (5.32 ± 0.86 µg g^{-1}, mean ± standard deviation, n = 28) and Zn (16.09 ± 1.89 µg g^{-1}, mean ± standard deviation, n = 28) in our nearshore 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 (252.52 ± 44.02 µg g^{-1}, mean ± standard deviation, n = 28) in our nearshore sediment core are 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 (29.97 ± 5.57 mg g^{-1}, mean ± standard deviation, n = 28) and Fe (32.59 ± 5.18 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 ($r = 0.77$ to 0.88, $p < 0.01$, $n = 28$) at the nearshore site (Table 7). None of the fluxes systematically changed over the last two centuries (1815 to 1998) (Fig. 2a); and all of their EFs, normalized to Fe, 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 attributed primarily 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). Organic matter sequesters trace elements and influences their mobility 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; Cohen et al., 2005b; O'Reilly et al., 2005).

In contrast to the element fluxes, there were pronounced temporal changes in charcoal fluxes (e.g., it increased by ~500% between 1935 to 1998, Fig. 3b) to sediment at the nearshore site that do not appear to be from local inputs (Palacios-Fest et al., 2005). The charcoal fluxes were relatively high (2574 – 19473 fragments per gram) throughout the core, 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, the increase in charcoal fluxes is 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 ($r = -0.35$ to 0.49, $n = 10$, $p > 0.1$). Consequently, the naturally high rates of sedimentation at the nearshore site (MAR = 0.13 to 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 to 9.7 mg cm^{-2} yr^{-1}), as discussed in section 3.3 (Offshore Site).

The isotopic compositions of Pb in sediment at the nearshore site (Figs. 4 and 5), which are assumed to be predominantly characteristic of 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 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 7). 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 (23.40 ± 2.86 $\mu g\ g^{-1}$, mean ± standard deviation, $n = 9$), Pb (15.89 ± 2.19 $\mu g\ g^{-1}$, mean ± standard deviation, $n = 9$), and Zn (48.56 ± 36.70 $\mu g\ g^{-1}$, mean ± standard deviation, $n = 9$) in the offshore sediment core are similar to those of Cu (21 $\mu g\ g^{-1}$), Pb (14 $\mu g\ g^{-1}$), and Zn (28 $\mu g\ g^{-1}$) measured in nearshore sediment from Lake Tanganyika by Chale 2002, but are substantially higher than the concentrations of Cu (3.6 $\mu g\ g^{-1}$), Pb (1.4 $\mu g\ g^{-1}$), and Zn (2.2 $\mu g\ g^{-1}$) he measured in offshore sediment. The Mn concentrations (269.12 ± 58.21 $\mu g\ g^{-1}$, 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 (59.78 ± 7.93 mg g^{-1}, mean ± standard deviation, n = 9) and Fe (39.90 ± 5.50 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 of the concentrations of the other elements with 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 ($r = 0.77$ to 0.99, $p \leq 0.02$, $n = 9$) at the offshore site (Table 7). But in contrast to the nearshore site, those fluxes systematically varied over the past four centuries (1641 to 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. Still, the strong positive and statistically significant correlations between the fluxes of Co, Cu, Mn, Ni, and Pb and those of Fe ($r = 0.95$ to 1.00, $p < 0.02$, $n = 5$) over the past two centuries (1871 to 1991) as well as the low EF (< 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 to 1991). Still, the recent (1931 to 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 to 1991, Fig. 3a), presumably from accelerated erosion rates associated with substantial deforestation (~40 to 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 ($r = 0.82$ to 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. Consequently, we attribute the pronounced temporal increases in trace element fluxes at the offshore site primarily to increase 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 Pb (and most of the other trace elements by association) originated predominantly from local, natural sources. The apparent local sources of the trace elements were further evidenced by the positive correlations between the fluxes of those elements and 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) all suggest that these trace elements were predominantly derived from local sources. The spatial differences between the fluxes of respective trace elements (Figs. 2a and 2b) at the nearshore (LT-98-58) and offshore (MC1) sites are likely 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).

The spatially different, but predominantly consistent lead isotopic compositions at the sites over time indicate that the Pb (and other trace elements by association) originated from distinct sources at the two locations. This spatial difference in Pb isotopic compositions could have resulted from atmospheric contribution of Pb to the offshore site. The 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).

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 it was pronounced at the offshore site. The results indicate that the offshore core is a more sensitive and reliable recorder of environmental changes within the lake's basin. The temporal changes in trace element fluxes at the offshore site appear to be primarily due to land use changes. 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).

The results from this study also 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. Consequently, studies aimed at further characterizing the different sources, including regional versus local and natural versus anthropogenic, of Pb and other trace elements around Lake Tanganyika using Pb isotopic ratios may be necessary in order to improve our understanding of the extent of anthropogenic perturbations in the lake and its basin.

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TABLES AND FIGURES

Table 1: Method detection limits of analytes.

	Detection Limit (3 x SD, Standard Deviation of 3 blanks)							
	(ng/g)					(µg/g)		
Element	[Co]	[Cu]	[Ni]	[Pb]	[Zn]	[Mn]	[Al]	[Fe]
Detection Limit	0.000	0.011	0.006	0.002	0.066	0.009	0.046	0.060

Table 2: Digestion recoveries (concentrations) for elements in standard reference materials (SRMs).

SRM	% Recovery (Mean ± SD, n = 3)							
	Co	Cu	Ni	Pb	Zn	Mn	Al	Fe
SRM 1645 (River Sediment)	72.2 ± 3.5	89.3 ± 3.0	86.8 ± 9.8	88.8 ± 3.0	89.5 ± 1.6	79.6 ± 2.1	28.9 ± 1.4	79.0 ± 1.8
SRM 2704 (Buffalo River Sediment)	82.2 ± 0.6	89.1 ± 1.0	84.2 ± 1.3	98.1 ± 2.2	92.3 ± 2.1	85.5 ± 2.7	30.3 ± 5.5	81.5 ± 0.8

Table 3: Analytical (instrumental) precision.

SRM	% RSD (n = 7)					% RSD (n = 5)		
	[Co]	[Cu]	[Ni]	[Pb]	[Zn]	[Mn]	[Al]	[Fe]
SRM 1640a	0.86	0.89	0.98	0.31	0.56	–	–	–
Consistency Standard (1 ng/g)	1.18	1.25	2.67	0.23	1.24	–	–	–
Consistency Standard A	–	–	–	–	–	1.24	0.92	1.22

Table 4: Analytical (instrumental) precision for lead isotopic compositions.

Sample	% RSD (n = 5)		
	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{207}Pb/^{204}Pb$
MC02	0.17	0.14	0.21
LT07	0.09	0.15	0.16

Table 5: Table showing depth; age; concentrations of Co, Cu, Ni, Pb, and Zn (measured by HR ICP-MS after near total digestion); and concentrations of Mn, Al, and Fe (measured by ICP-OES) of sediment core samples (LT-98-58 and MC1) collected from Lake Tanganyika. Samples marked with asterisk (*) were digested in triplicate and are reported as mean (± standard deviation, SD).

Sample ID	Average Depth (cm)	Year (AD)	Concentrations							
			[Co] ($\mu g\ g^{-1}$) (± SD)	[Cu] ($\mu g\ g^{-1}$) (± SD)	[Ni] ($\mu g\ g^{-1}$) (± SD)	[Pb] ($\mu g\ g^{-1}$) (± SD)	[Zn] ($\mu g\ g^{-1}$) (± SD)	[Mn] ($\mu g\ g^{-1}$) (± SD)	[Al] ($mg\ g^{-1}$) (± SD)	[Fe] ($mg\ g^{-1}$) (± SD)
LT-98-58										
LT01	0.5	1998	9.35	13.96	17.13	6.21	15.89	337.33	28.09	33.55
LT02	1.5	1988	9.44	13.87	16.73	5.64	15.56	312.80	24.10	31.64
LT03	2.5	1981	10.00	14.47	18.39	6.08	16.31	294.85	25.06	33.02
LT04	3.5	1975	10.22	15.45	18.37	6.53	16.94	295.24	30.35	35.08
LT05	4.5	1968	10.89	17.42	19.87	6.42	18.52	277.23	26.88	33.87
LT06	5.5	1961	8.74	13.77	16.34	5.75	15.20	240.12	31.09	29.95
LT07	6.5	1955	8.60	13.35	16.12	5.45	14.24	244.27	30.44	30.20
LT08	7.5	1948	9.90	15.24	18.16	4.97	15.67	226.62	24.08	29.58
LT09	8.5	1941	8.99	13.94	16.64	4.98	13.87	265.04	29.80	32.45
LT10	9.5	1935	10.50	18.27	18.73	4.65	16.76	270.99	27.98	33.37
LT11	10.5	1928	7.60	12.17	14.31	3.65	13.17	179.54	21.73	22.37
LT12 *	11.5	1921	7.27 (0.19)	11.21 (0.28)	13.67 (0.48)	3.93 (0.08)	12.40 (0.37)	189.15 (3.24)	22.36 (1.72)	23.65 (0.61)
LT13	12.5	1915	9.57	15.49	18.28	4.79	16.29	226.54	25.10	29.40
LT14	13.5	1908	8.57	14.24	17.29	5.24	15.85	213.76	27.93	28.46
LT15	14.5	1901	7.71	12.81	15.11	4.25	13.99	180.74	23.80	24.19
LT16	15.5	1895	9.10	14.91	17.07	4.43	14.45	222.94	27.78	30.00
LT17	16.5	1888	11.56	19.74	22.23	5.10	17.98	286.02	31.84	36.59
LT18	17.5	1881	11.16	20.31	22.44	6.06	18.48	312.64	37.78	43.71
LT19	18.5	1875	9.28	16.85	18.98	4.53	15.64	212.52	28.49	31.16
LT20	19.5	1868	8.17	14.52	16.60	4.96	14.23	224.94	32.17	31.69
LT21	20.5	1861	10.59	18.40	20.87	6.00	18.00	278.49	37.67	37.73
LT22	21.5	1855	11.19	19.48	21.94	6.90	19.77	313.87	42.98	42.30
LT23 *	22.5	1848	8.93 (0.59)	15.60 (1.04)	18.08 (1.14)	4.75 (0.44)	15.87 (1.17)	231.91 (18.12	30.56 (2.72)	31.32 (2.15)
LT24	23.5	1841	8.99	16.34	18.75	5.14	16.19	219.44	31.51	32.29
LT25	24.5	1835	10.23	18.19	20.87	5.44	18.81	258.60	28.89	35.54
LT26	25.5	1828	8.20	14.77	17.29	4.37	14.40	195.92	29.57	28.99
LT27	26.5	1821	9.50	17.55	20.00	6.02	16.79	262.57	40.49	40.54
LT28	27.5	1815	10.42	19.34	21.41	6.69	19.13	296.38	40.65	39.98

Table 5 (*continued*)

Sample ID	Average Depth (cm)	Year (AD)	Concentrations							
			[Co] (µg g^{-1}) (± SD)	[Cu] (µg g^{-1}) (± SD)	[Ni] (µg g^{-1}) (± SD)	[Pb] (µg g^{-1}) (± SD)	[Zn] (µg g^{-1}) (± SD)	[Mn] (µg g^{-1}) (± SD)	[Al] (mg g^{-1}) (± SD)	[Fe] (mg g^{-1}) (± SD)
MC1										
MC01 *	0.5	1991	9.59 (0.70)	23.11 (1.65)	21.05 (1.47)	20.13 (0.81)	143.04 (9.67)	373.82 (7.66)	66.56 (1.78)	43.50 (0.41)
MC02	1.5	1971	9.21	22.29	20.71	16.11	61.36	314.89	67.08	43.19
MC03	3.5	1931	8.79	25.09	21.71	15.80	32.53	283.42	66.25	45.43
MC04	4.5	1911	9.23	29.25	23.29	16.77	37.01	294.01	63.74	45.98
MC05	6.5	1871	8.15	24.31	21.02	15.09	33.75	241.93	57.37	40.56
MC06	8.5	1831	7.32	22.79	19.40	13.55	35.74	190.34	48.30	33.29
MC07	10.5	1791	6.88	19.39	18.05	12.82	30.24	198.55	45.54	29.80
MC08	14.0	1721	6.81	20.33	18.47	15.00	30.42	287.16	61.64	37.71
MC09 *	18.0	1641	7.93 (0.19)	24.00 (0.22)	21.04 (0.52)	17.71 (1.38)	32.91 (0.55)	237.96 (6.51)	61.53 (2.84)	39.62 (1.22)

Table 6: Table showing depth; age; MAR (mass accumulation rate); fluxes of Co, Cu, Ni, Pb, Zn, Mn, Al, and Fe; and lead isotopic ratios of sediment core samples (LT-98-58 and MC1) collected from Lake Tanganyika.

Sample ID	Average Depth (cm)	Year (AD)	MAR ($g\ cm^{-2}\ yr^{-1}$)	Fluxes								Lead Isotopic Ratios		
				Co Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Cu Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Ni Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Pb Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Zn Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Mn Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Al Flux ($mg\ cm^{-2}\ yr^{-1}$)	Fe Flux ($mg\ cm^{-2}\ yr^{-1}$)	$^{208}Pb/^{207}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
LT-98-58														
LT01	0.5	1998	0.1360	1.27	1.90	2.33	0.84	2.16	45.9	3.82	4.56	2.697	15.946	1.302
LT02	1.5	1988	0.1477	1.39	2.05	2.47	0.83	2.30	46.2	3.56	4.67	2.691	15.961	1.298
LT03	2.5	1981	0.1484	1.48	2.15	2.73	0.90	2.42	43.8	3.72	4.90	2.699	15.929	1.306
LT04	3.5	1975	0.1548	1.58	2.39	2.84	1.01	2.62	45.7	4.70	5.43	2.715	15.921	1.316
LT05	4.5	1968	0.1471	1.60	2.56	2.92	0.94	2.72	40.8	3.95	4.98	2.711	15.959	1.320
LT06	5.5	1961	0.1394	1.22	1.92	2.28	0.80	2.12	33.5	4.33	4.17	2.730	15.959	1.338
LT07	6.5	1955	0.1328	1.14	1.77	2.14	0.72	1.89	32.4	4.04	4.01	2.742	15.974	1.347
LT08	7.5	1948	0.1406	1.39	2.14	2.55	0.70	2.20	31.9	3.39	4.16	2.743	15.931	1.329
LT09	8.5	1941	0.1505	1.35	2.10	2.50	0.75	2.09	39.9	4.48	4.88	2.810	15.994	1.364
LT10	9.5	1935	0.1572	1.65	2.87	2.94	0.73	2.63	42.6	4.40	5.25	2.889	15.958	1.371
LT11	10.5	1928	0.1631	1.24	1.99	2.33	0.60	2.15	29.3	3.54	3.65	2.778	15.981	1.346
LT12	11.5	1921	0.1692	1.23	1.90	2.31	0.67	2.10	32.0	3.78	4.00	2.752	15.950	1.337
LT13	12.5	1915	0.1743	1.67	2.70	3.19	0.83	2.84	39.5	4.38	5.13	2.748	15.970	1.328
LT14	13.5	1908	0.1751	1.50	2.49	3.03	0.92	2.78	37.4	4.89	4.98	2.741	15.960	1.340
LT15	14.5	1901	0.1762	1.36	2.26	2.66	0.75	2.46	31.8	4.19	4.26	2.745	16.003	1.342
LT16	15.5	1895	0.1770	1.61	2.64	3.02	0.78	2.56	39.5	4.92	5.31	2.799	15.991	1.354
LT17	16.5	1888	0.1685	1.95	3.33	3.75	0.86	3.03	48.2	5.36	6.17	2.790	15.978	1.345
LT18	17.5	1881	0.1600	1.79	3.25	3.59	0.97	2.96	50.0	6.04	6.99	2.787	15.947	1.339
LT19	18.5	1875	0.1527	1.42	2.57	2.90	0.69	2.39	32.5	4.35	4.76	2.781	15.977	1.329
LT20	19.5	1868	0.1530	1.25	2.22	2.54	0.76	2.18	34.4	4.92	4.85	2.749	15.990	1.318
LT21	20.5	1861	0.1533	1.62	2.82	3.20	0.92	2.76	42.7	5.77	5.78	2.777	15.984	1.327
LT22	21.5	1855	0.1536	1.72	2.99	3.37	1.06	3.04	48.2	6.60	6.50	2.778	16.010	1.329
LT23	22.5	1848	0.1508	1.35	2.35	2.73	0.72	2.39	35.0	4.61	4.72	2.763	15.955	1.321
LT24	23.5	1841	0.1481	1.33	2.42	2.78	0.76	2.40	32.5	4.67	4.78	2.764	15.992	1.322
LT25	24.5	1835	0.1457	1.49	2.65	3.04	0.79	2.74	37.7	4.21	5.18	2.753	15.898	1.315
LT26	25.5	1828	0.1451	1.19	2.14	2.51	0.63	2.09	28.4	4.29	4.21	2.771	15.959	1.322
LT27	26.5	1821	0.1445	1.37	2.54	2.89	0.87	2.43	37.9	5.85	5.86	2.799	15.952	1.328
LT28	27.5	1815	0.1440	1.50	2.79	3.08	0.96	2.76	42.7	5.85	5.76	2.769	15.897	1.323

Table 6 (*continued*)

Sample ID	Average Depth (cm)	Year (AD)	MAR (g cm^{-2} yr^{-1})	Fluxes								Lead Isotopic Ratios		
				Co Flux (µg cm^{-2} yr^{-1})	Cu Flux (µg cm^{-2} yr^{-1})	Ni Flux (µg cm^{-2} yr^{-1})	Pb Flux (µg cm^{-2} yr^{-1})	Zn Flux (µg cm^{-2} yr^{-1})	Mn Flux (µg cm^{-2} yr^{-1})	Al Flux (mg cm^{-2} yr^{-1})	Fe Flux (mg cm^{-2} yr^{-1})	^{208}Pb/^{207}Pb	^{207}Pb/^{204}Pb	^{206}Pb/^{207}Pb
MC1														
MC01	0.5	1991	0.0097	0.09	0.22	0.20	0.20	1.39	3.62	0.65	0.42	2.489	15.746	1.183
MC02	1.5	1971	0.0086	0.08	0.19	0.18	0.14	0.53	2.70	0.57	0.37	2.497	15.763	1.184
MC03	3.5	1931	0.0072	0.06	0.18	0.16	0.11	0.24	2.05	0.48	0.33	2.514	15.748	1.187
MC04	4.5	1911	0.0063	0.06	0.18	0.15	0.11	0.23	1.85	0.40	0.29	2.505	15.779	1.185
MC05	6.5	1871	0.0034	0.03	0.08	0.07	0.05	0.11	0.82	0.19	0.14	2.503	15.739	1.186
MC06	8.5	1831	0.0052	0.04	0.12	0.10	0.07	0.18	0.98	0.25	0.17	2.514	15.697	1.191
MC07	10.5	1791	0.0045	0.03	0.09	0.08	0.06	0.14	0.90	0.21	0.14	2.506	15.783	1.188
MC08	14.0	1721	0.0053	0.04	0.11	0.10	0.08	0.16	1.53	0.33	0.20	2.514	15.729	1.186
MC09	18.0	1641	0.0060	0.05	0.14	0.13	0.11	0.20	1.43	0.37	0.24	2.503	15.784	1.186

Table 7: Correlations between fluxes of elements and fluxes of Fe, a major element.

Core	Conservative Element	Correlation coefficient, r (p-value)					
		Co Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Cu Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Ni Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Pb Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Zn Flux ($\mu g\ cm^{-2}\ yr^{-1}$)	Mn Flux ($\mu g\ cm^{-2}\ yr^{-1}$)
LT-98-58 (n = 28)	Fe Flux ($mg\ cm^{-2}\ yr^{-1}$)	0.82 (<0.01)	0.88 (<0.01)	0.88 (<0.01)	0.77 (<0.01)	0.83 (<0.01)	0.79 (<0.01)
MC1 (n = 9)	Fe Flux ($mg\ cm^{-2}\ yr^{-1}$)	0.99 (<0.01)	0.98 (<0.01)	0.99 (<0.01)	0.96 (<0.01)	0.77 (<0.02)	0.97 (<0.01)

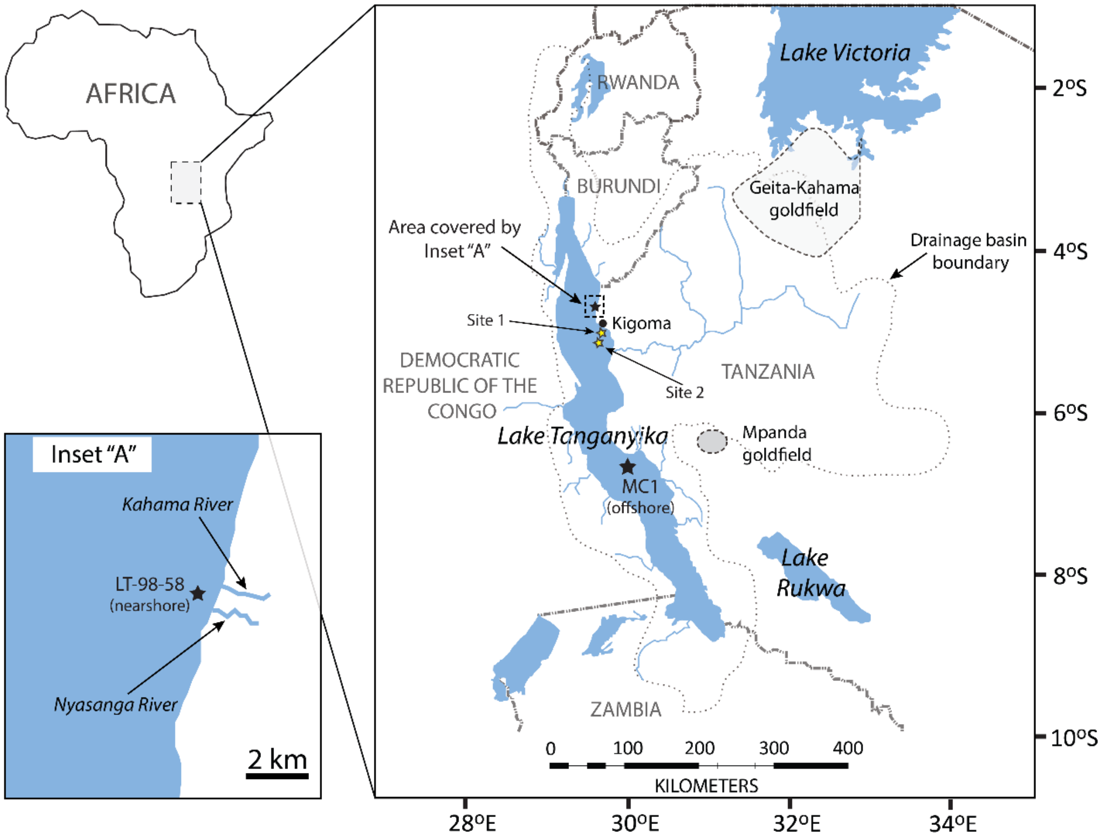


Fig. 1: Map showing sample collection sites from Lake Tanganyika in Africa and the approximate drainage basin of the lake (Adapted from Bergonzini et al. 1997 and Conaway et al. 2012). Also included on the map are the collection sites, Site 1 (72 m depth) and Site 2 (332 m depth), of sediment cores studied by Brucker et al. 2011.

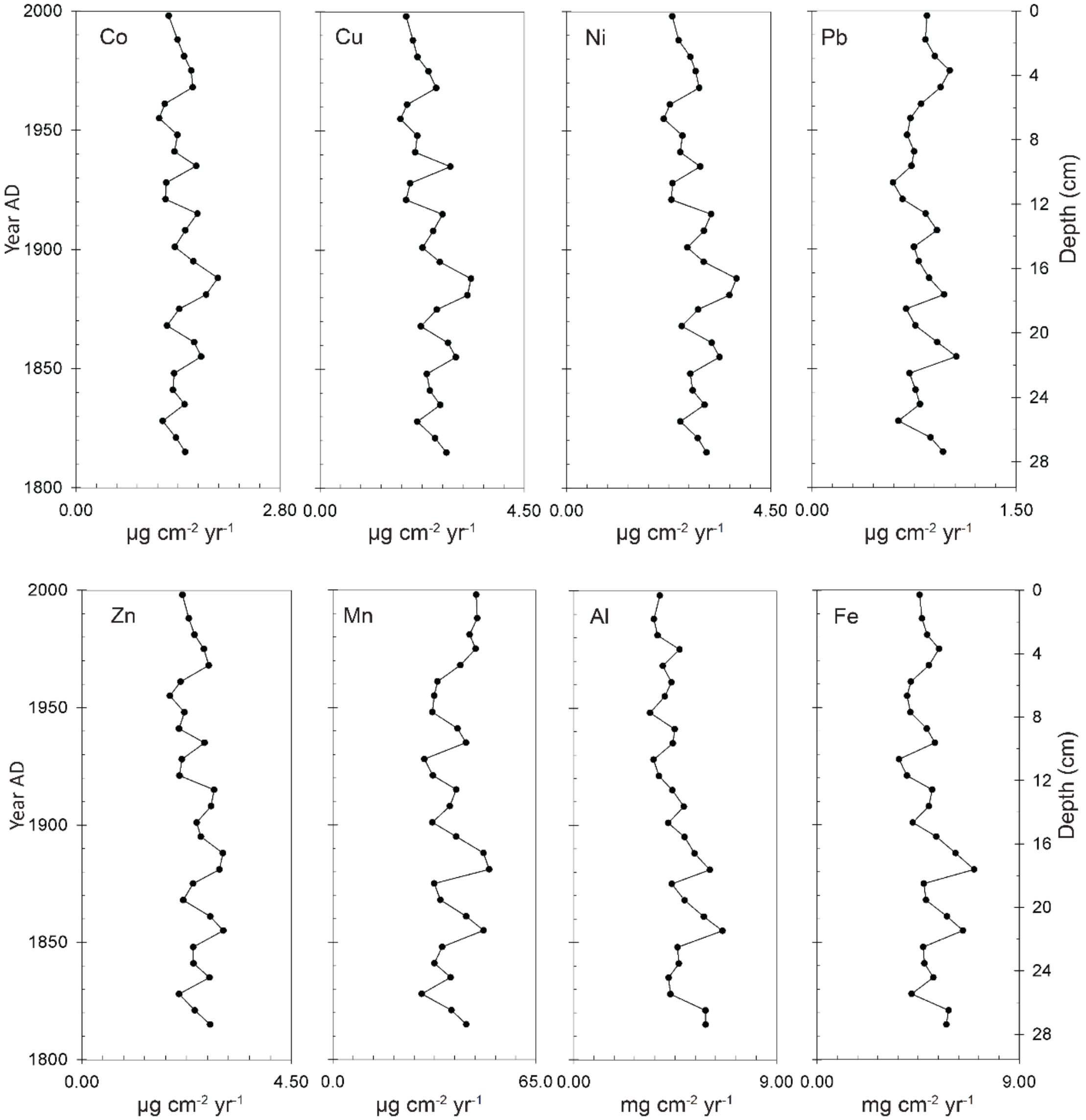


Fig. 2a: Down core fluxes of elements (Co, Cu, Ni, Pb, Zn, Mn, Al, and Fe) at the nearshore site, LT-98-58, in Lake Tanganyika.

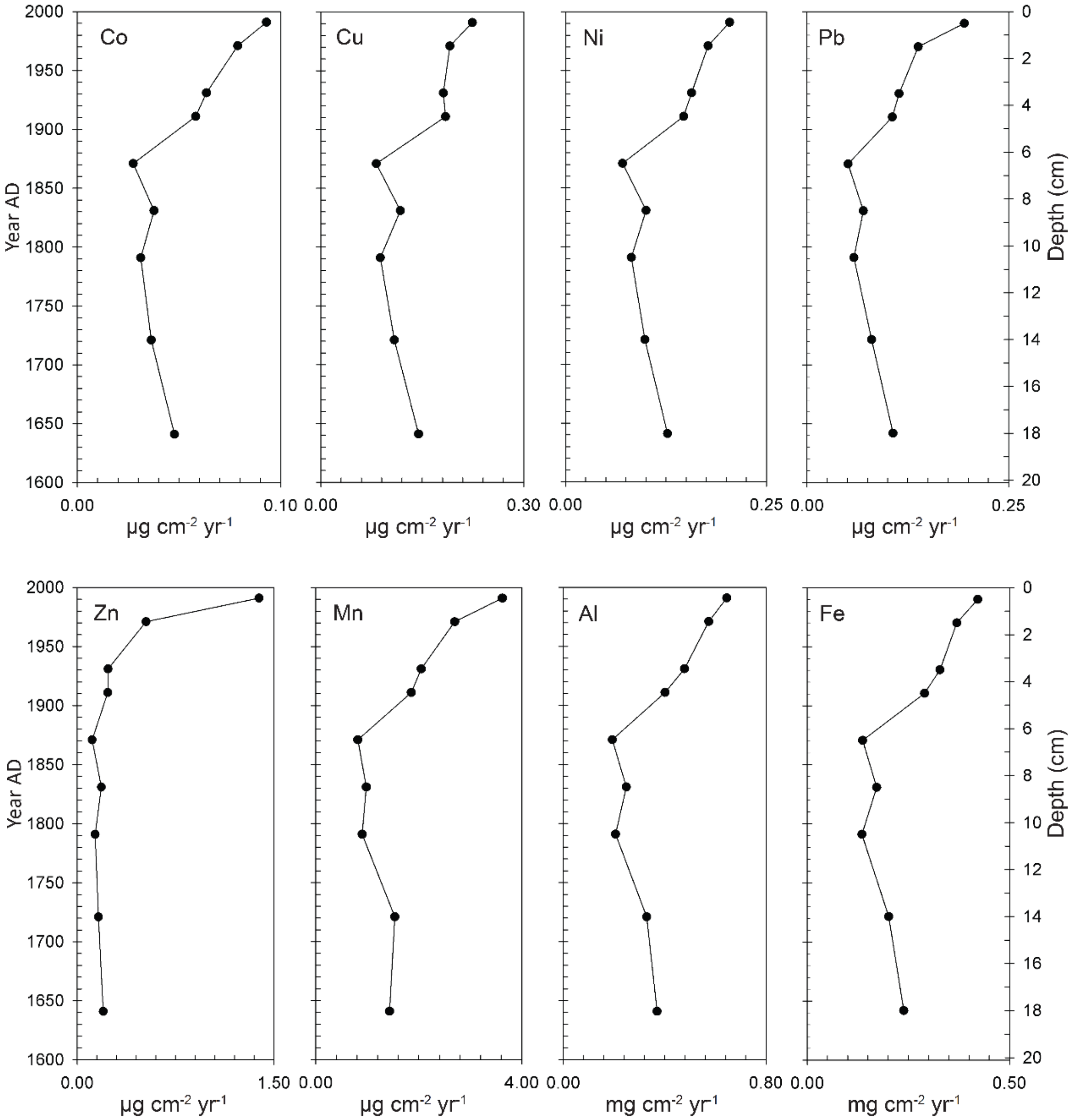
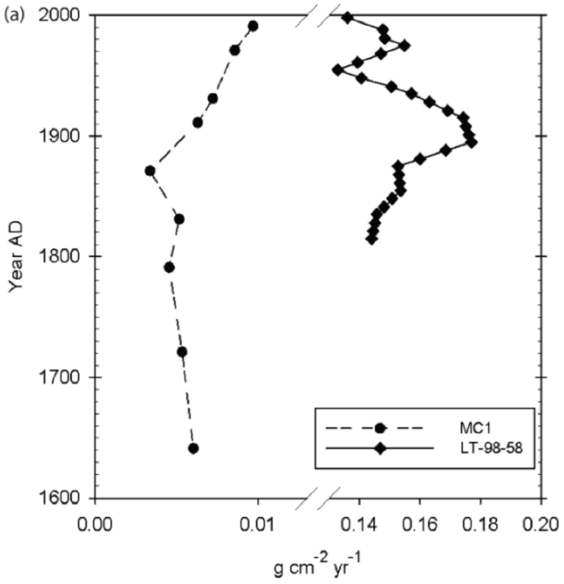


Fig. 2b: Down core fluxes of elements (Co, Cu, Ni, Pb, Zn, Mn, Al, and Fe) at the nearshore site, MC1, in Lake Tanganyika.



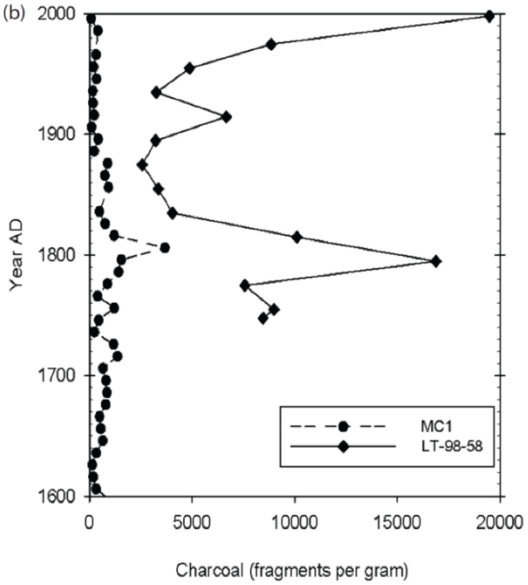


Fig. 3a: Mass accumulation rate (MAR, g cm^{-2} yr^{-1}) plots for cores MC1 (offshore) and LT-98-58 (nearshore) (Adapted from Conaway et al. 2012, data from Tierney et al. 2010 and McKee et al. 2005).

Fig. 3b: Charcoal abundance profiles for MC1 (offshore site) and LT-98-58 (nearshore site) (Adapted from Conaway et al. 2012, data from Palacios-Fes et al. 2005 and Tierney et al. 2010).

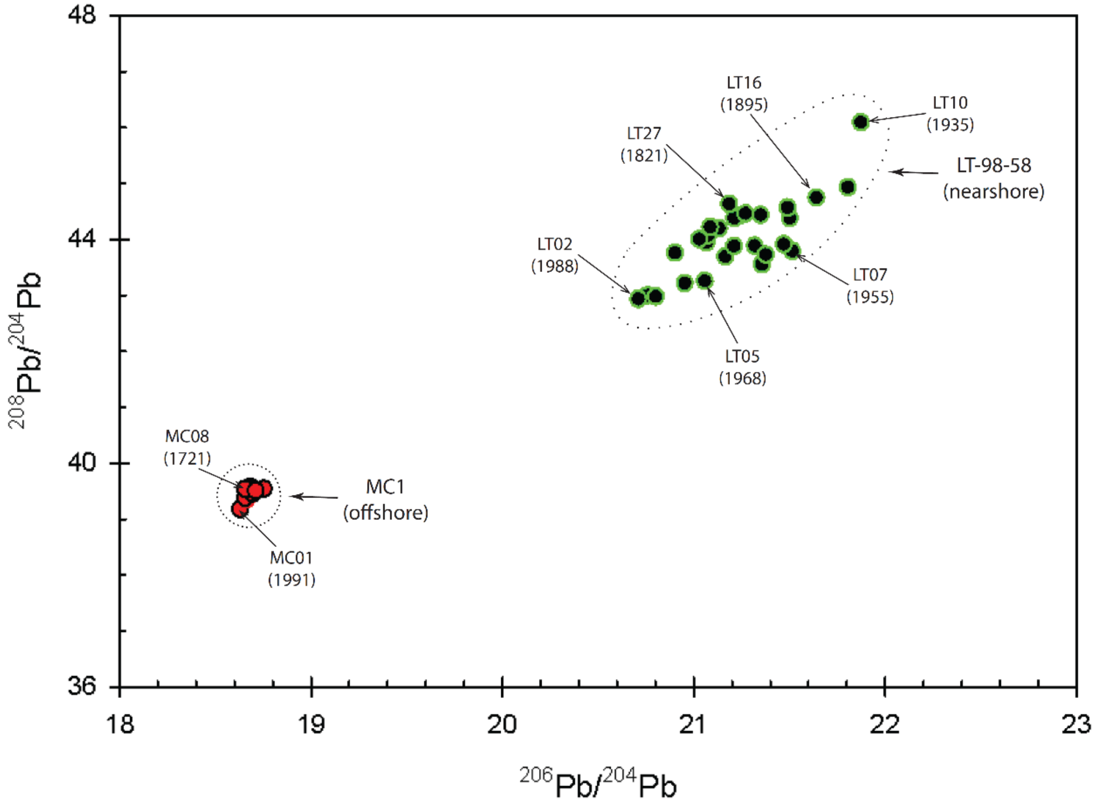


Fig. 4: Lead isotopic composition (^{206}Pb/^{204}Pb: ^{208}Pb/^{204}Pb) of sediment core samples (LT-98-58 and MC1) collected from Lake Tanganyika, Africa.

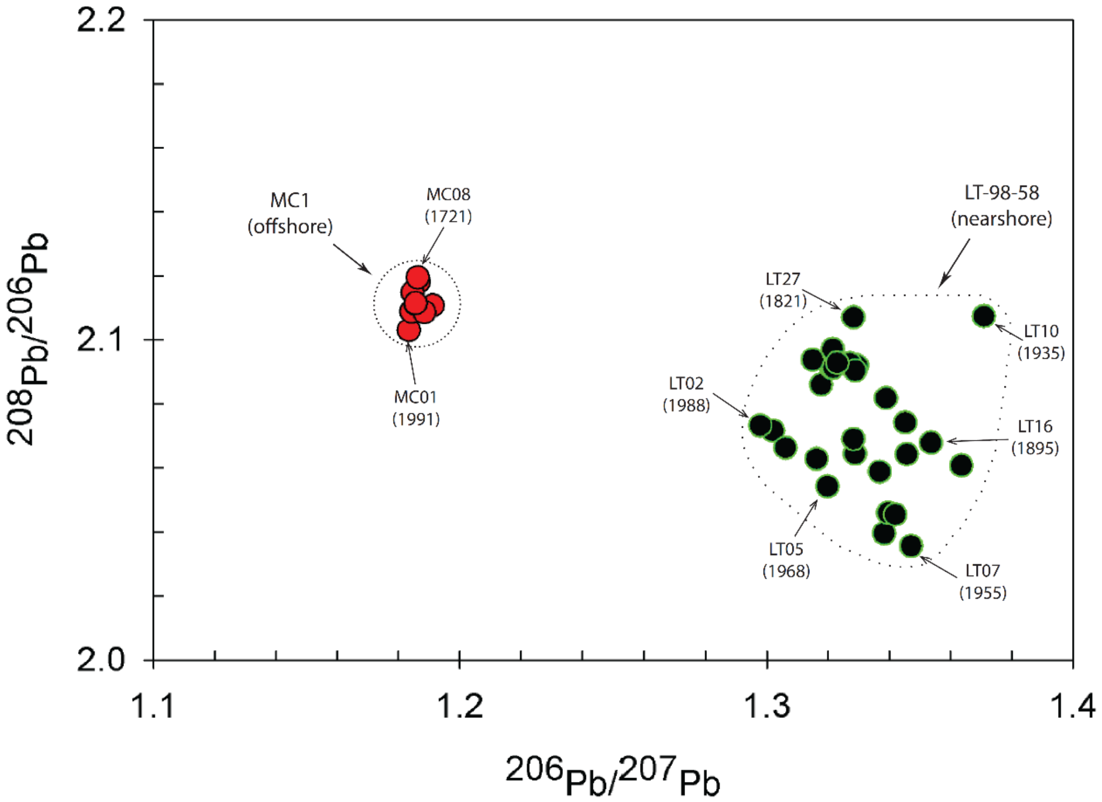


Fig. 5: Lead isotopic composition (^{206}Pb/^{207}Pb: ^{208}Pb/^{206}Pb) of sediment core samples (LT-98-58 and MC1) collected from Lake Tanganyika, Africa.

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CONCLUSIONS

The results of the investigations presented in this dissertation demonstrated that wildfires and land-use changes are mobilizing trace elements sequestered in forests. Chapter 2 provided insight to the substantial amounts of Pb (e.g., up to 50 μg/g of Pb in ash) that are remobilized by wildfires. Chapter 2 also indicated that the Pb remobilized in the relatively pristine forests near Santa Barbara, California was predominantly derived from the past combustion of leaded gasoline. Chapter 3, a complementary study to the Santa Barbara study (Chapter 2), provided insight to the amounts of trace elements and source of Pb remobilized at the Angeles National Forest, which abuts the more industrialized and highly populated Los Angeles Metropolitan Area. Somewhat surprisingly, the results from that study indicated that the amounts of trace elements and source of Pb remobilized in Los Angeles were generally comparable to those remobilized at the Santa Barbara site. Chapter 4 provided evidence that wildfires markedly increase the influx of trace elements (e.g., Pb and Zn) to aquatic ecosystems, including those in relatively pristine locations. In Chapter 5, it was demonstrated that land-use changes substantially increase the influx of trace element contaminants to aquatic ecosystems by simply increasing the rates of erosion. The results indicated that the trace elements mobilized to both Lake Thompson, Chile (Chapter 4) and Lake Tanganyika, Africa (Chapter 5) were predominantly derived from natural sources.

The data presented in this dissertation contribute to our understanding of how wildfires and land-use changes impact the cycling of toxic trace elements in the environment. Pyrogenic remobilization of trace elements is a concern, especially in forests contaminated with toxic elements. Forests are an important reservoir for trace elements, which sorb to vegetation and soil organic matter, but are released in more labile forms by wildfires. In addition to trace elements aerosolized during wildfires, ash is suspended by wind, thus increasing contaminant levels in air (Young and Jan, 1977).

The amounts of contaminants aerosolized by wildfires are substantial. For example, ~6–17% (60,000 – 3,800,000 kg) of total global Pb aerosols released from natural sources annually during the latter half of last century was attributed to wildfires (Nriagu, 1989). Those estimates of trace elements released by wildfires might have changed because the frequency and intensity of wildfires have been increasing over the past few decades (see Figure 2, Chapter 1) (Westerling et al., 2006). Aerosolized contaminants have been associated with health problems and deaths, especially in Asia and Africa (Smith et al., 2014; WHO, 2014b). For example, ~12.5% (7 million) of total global deaths in 2012 were attributed to air pollution, which is now ranked as the largest single environmental health hazard in the world (WHO, 2014b, a).

Furthermore, the predicted increase in the intensity and frequency of wildfires in response to projected climate change could increase the already high levels of toxic aerosols in many parts of the world (McKenzie et al., 2004; Flannigan et al., 2005; IPCC, 2013). While Chapters 2 and 3 provided insight on the pyrogenic remobilization of toxic trace elements, including past leaded gasoline depositions in the western US, more research is needed to quantify present and predict future contributions of wildfires to global air pollution and associated burden on human and wildlife health.

The contributions of wildfires to trace element influx to aquatic ecosystems and the impacts of remobilized contaminants on the health of aquatic organisms are not fully understood. Trace elements in ash and other mobilized debris, including fallouts from those aerosolized by wildfires, are flushed to water bodies (Stein et al., 2012). Chapter 4 improves our understanding of how this influx of mobilized trace elements increases the concentrations of contaminants in aquatic ecosystems, which is a concern, especially in sensitive ecosystems draining contaminated catchments. Recent studies have associated increase in Hg (total Hg and the toxic monomethylmercury) accumulation in fish with wildfires (e.g., Kelly et al., 2006). However, similar information on other trace elements (e.g., Pb and Zn) mobilized by wildfires is limited.

Deforestation and land-use changes expose topsoil to increased erosion, which accelerates the transport of mobilized trace elements to aquatic ecosystems as demonstrated in Chapter 5. In addition, suspension of soil particles is a major source of atmospheric trace element contaminants. For example, ~30% (300,000 –

7,500,000 kg) of total global Pb aerosols released from natural sources annually during the latter half of last century was attributed to suspension of soil particles (Nriagu, 1989). The potential impacts of climate change and land developments on dust suspension through vegetation loss are worth investigating in order to better understand and predict their subsequent effects on trace elements mobilization.

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Appendix 1: Supplementary materials for Chapter 3

Table S1: Collection locations (coordinates) for ash (CWA) and soil (CWS) samples collected from the 2012 Williams Fire site in the Angeles National Forest in California.

Sample ID	Longitude	Latitude	Remarks
CWA-1	117^{o} 48' 40" W	34^{o} 14' 15" N	
CWA-2	117^{o} 48' 36" W	34^{o} 14' 16" N	
CWA-3	117^{o} 48' 31" W	34^{o} 14' 21" N	
CWA-4	117^{o} 48' 01" W	34^{o} 14' 02" N	
CWA-5	117^{o} 47' 16" W	34^{o} 14' 09" N	
CWA-6	117^{o} 47' 15" W	34^{o} 14' 12" N	
CWA-7	117^{o} 47' 17" W	34^{o} 14' 14" N	
CWA-8	117^{o} 46' 13" W	34^{o} 14' 27" N	
CWA-9	117^{o} 45' 53" W	34^{o} 15' 06" N	
CWA-10	117^{o} 46' 05" W	34^{o} 14' 32" N	
CWA-11	117^{o} 48' 28" W	34^{o} 14' 12" N	
CWA-12	117^{o} - ' - " W	34^{o} - ' - " N	no complete GPS data
CWA-13	117^{o} 47' 18" W	34^{o} 14' 09" N	
CWA-14	117^{o} 48' 19" W	34^{o} 14' 11" N	
CWS-1	117^{o} 48' 01" W	34^{o} 14' 03" N	
CWS-2	117^{o} 47' 18" W	34^{o} 14' 08" N	
CWS-3	117^{o} 47' 17" W	34^{o} 14' 10" N	
CWS-4	117^{o} 47' 54" W	34^{o} 14' 01" N	
CWS-5	117^{o} 48' 14" W	34^{o} 14' 06" N	
CWS-6	117^{o} 48' 19" W	34^{o} 14' 11" N	

Table S2: Enrichment factors (*f*-Fe, normalized to Fe) of trace metals in ash (CWA) samples collected from the 2012 Williams Fire site in the Angeles National Forest in California.

	Enrichment Factors (*f*)				
Sample ID	*f*-Fe (Co)	*f*-Fe (Cu)	*f*-Fe (Ni)	*f*-Fe (Pb)	*f*-Fe (Zn)
CWA-1*	1.4	1.5	0.5	7.1	8.0
CWA-2	1.2	2.9	0.3	4.7	2.1
CWA-3	2.0	6.2	1.0	29	4.9
CWA-4	1.1	1.3	0.3	2.9	1.4
CWA-5	1.4	3.8	0.7	9.4	2.5
CWA-6	2.1	3.6	0.6	8.1	10
CWA-7	1.4	5.0	0.8	13	5.9
CWA-8*	2.5	3.6	0.6	2.6	9.0
CWA-9	1.0	1.1	0.5	2.9	2.4
CWA-10	0.9	0.9	0.4	3.1	0.9
CWA-11	1.4	2.0	0.5	4.6	3.5
CWA-12	1.3	1.2	0.5	4.6	1.5
CWA-13	2.2	5.6	0.7	5.2	19
CWA-14*	1.3	2.4	0.5	1.9	1.4
Min	0.9	0.9	0.3	1.9	0.9
Max	2.5	6.2	1.0	29	19

Appendix 2: Supplementary materials for Chapter 5

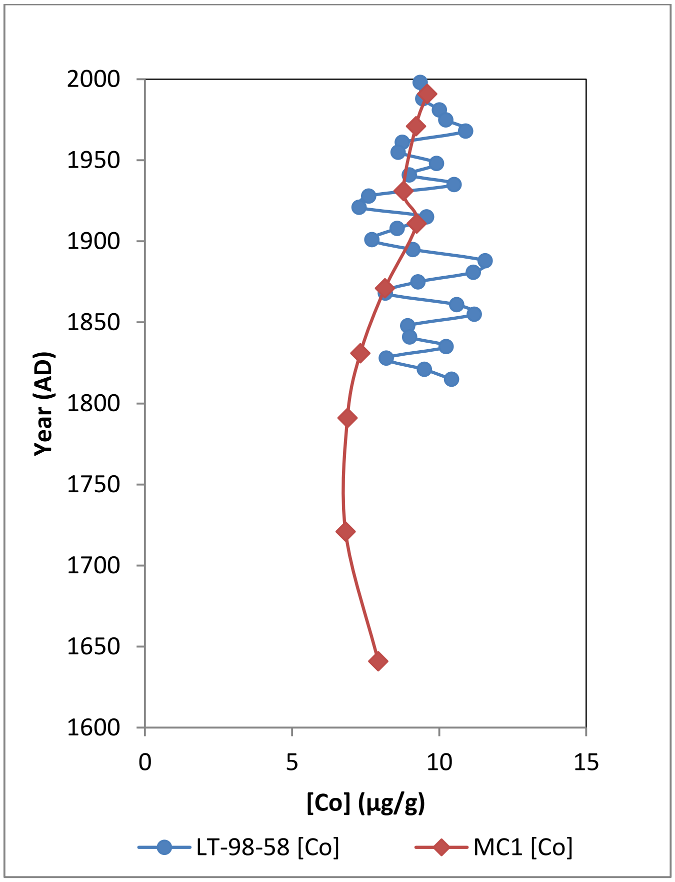

Fig. S1: Down core concentrations of Co at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

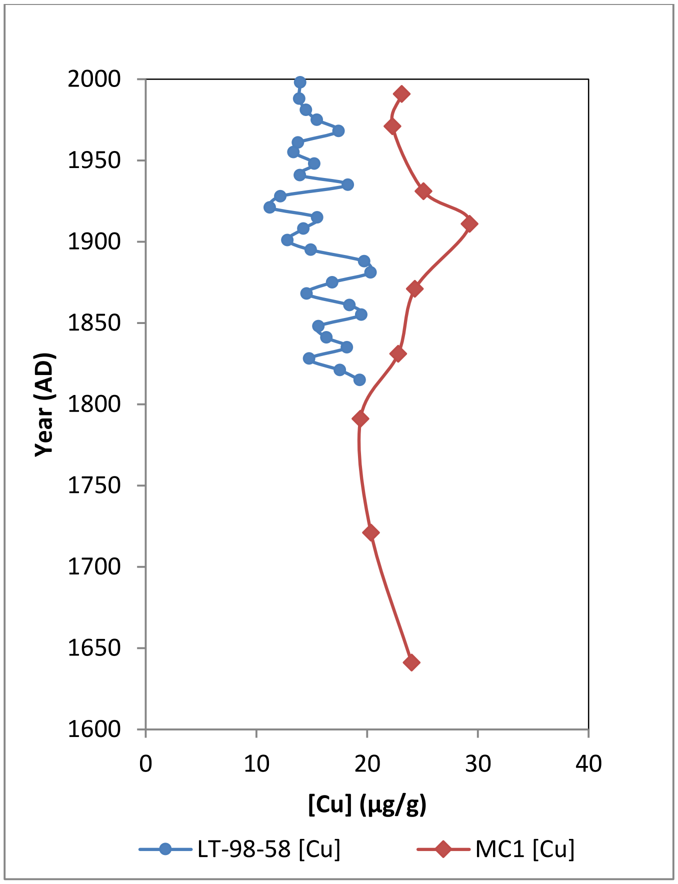

Fig. S2: Down core concentrations of Cu at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

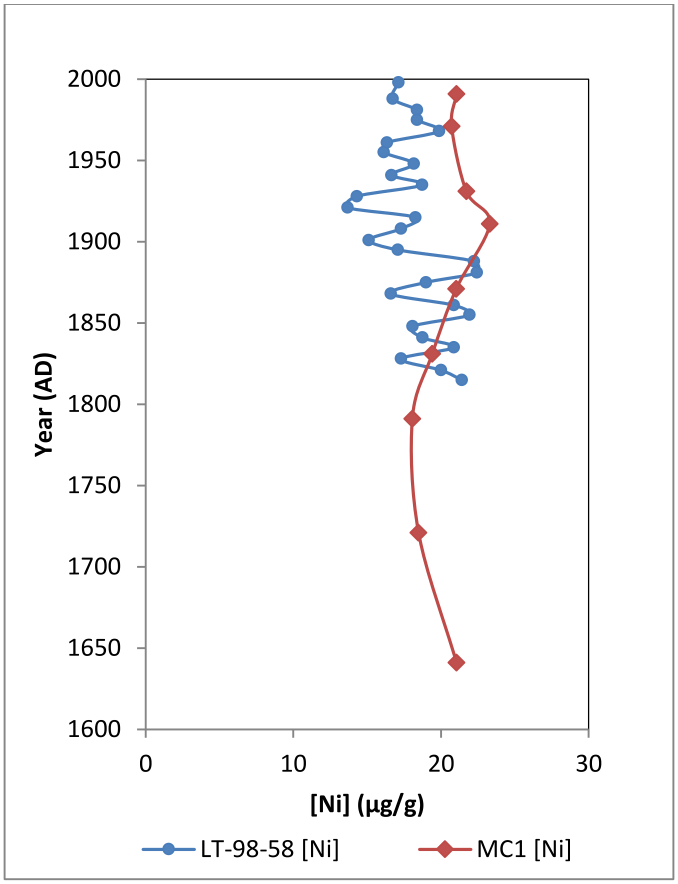

Fig. S3: Down core concentrations of Ni at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

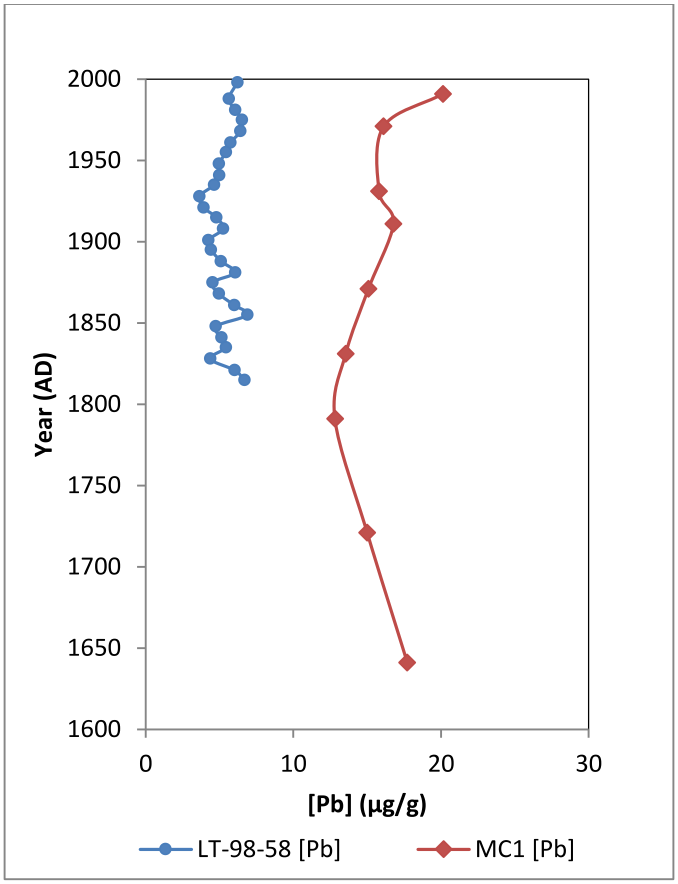

Fig. S4: Down core concentrations of Pb at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

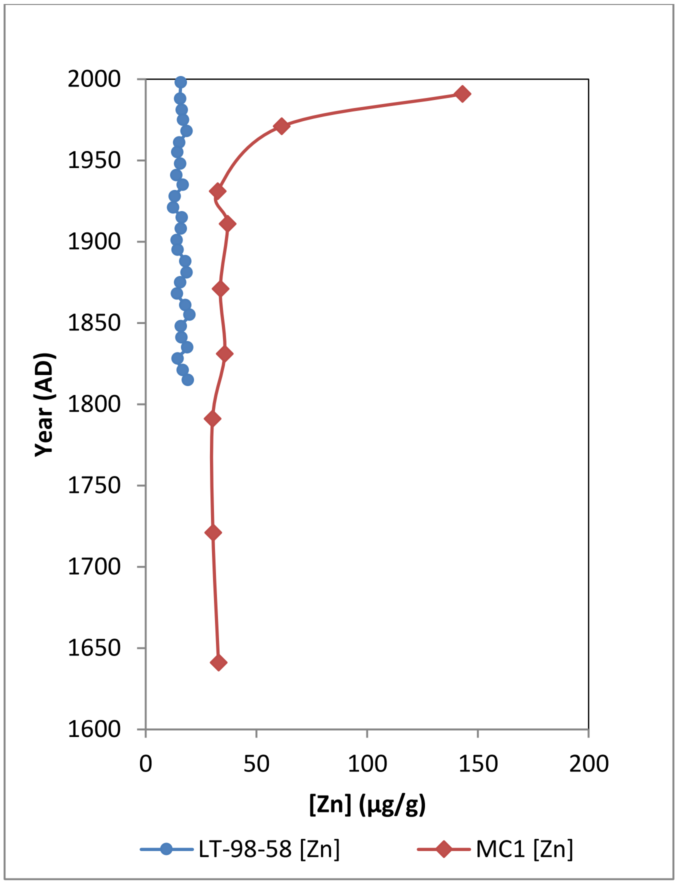

Fig. S5: Down core concentrations of Zn at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

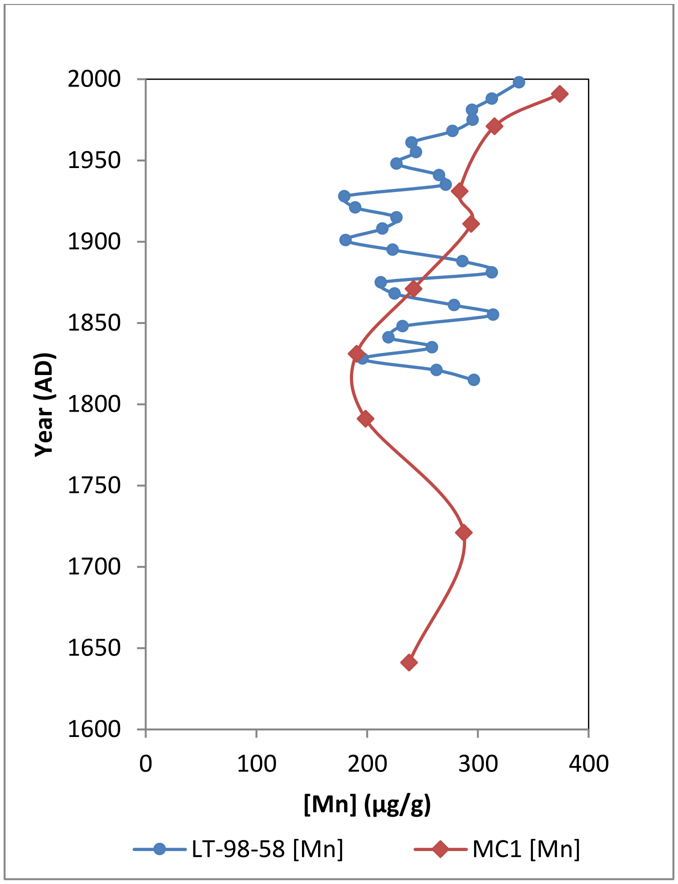

Fig. S6: Down core concentrations of Mn at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

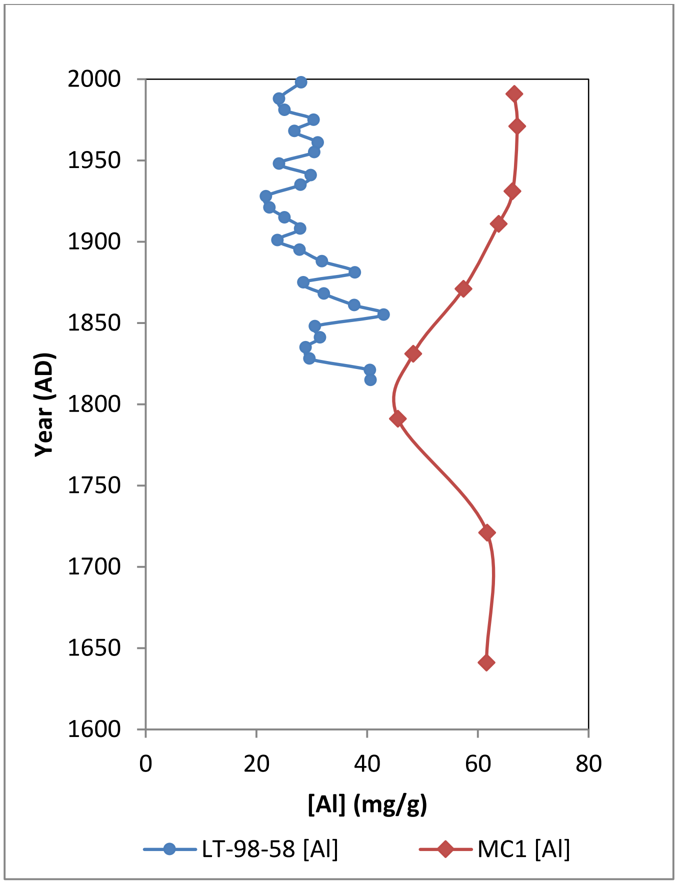

Fig. S7: Down core concentrations of Al at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

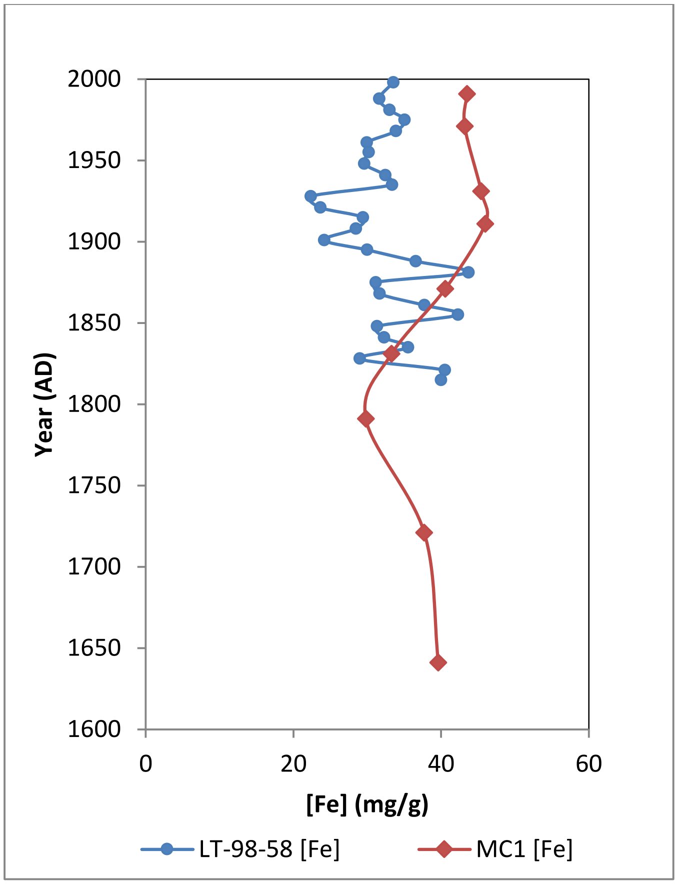

Fig. S8: Down core concentrations of Fe at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

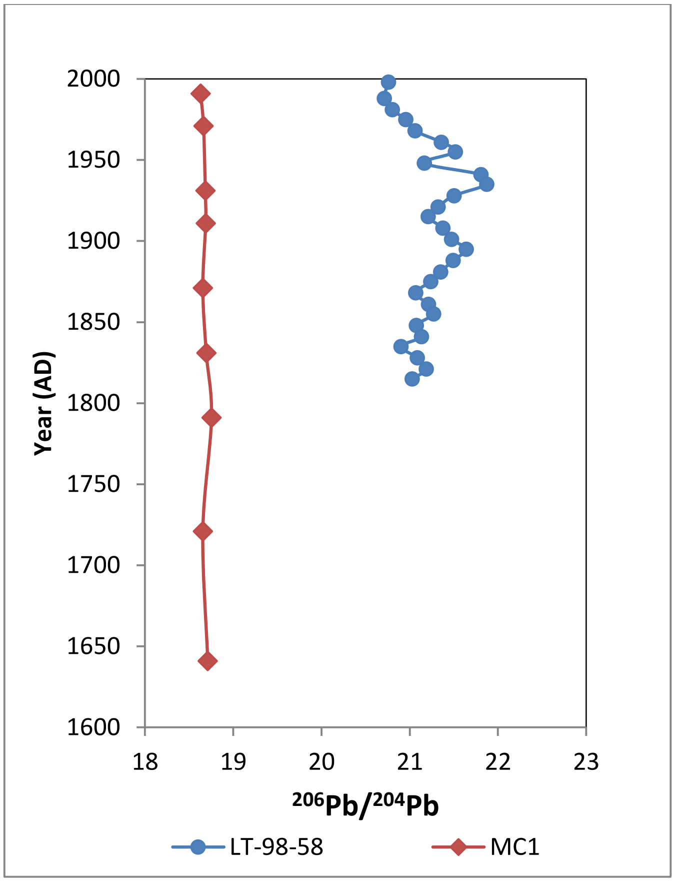

Fig. S9: Down core isotopic composition of Pb ($^{206}Pb/^{204}Pb$) at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.

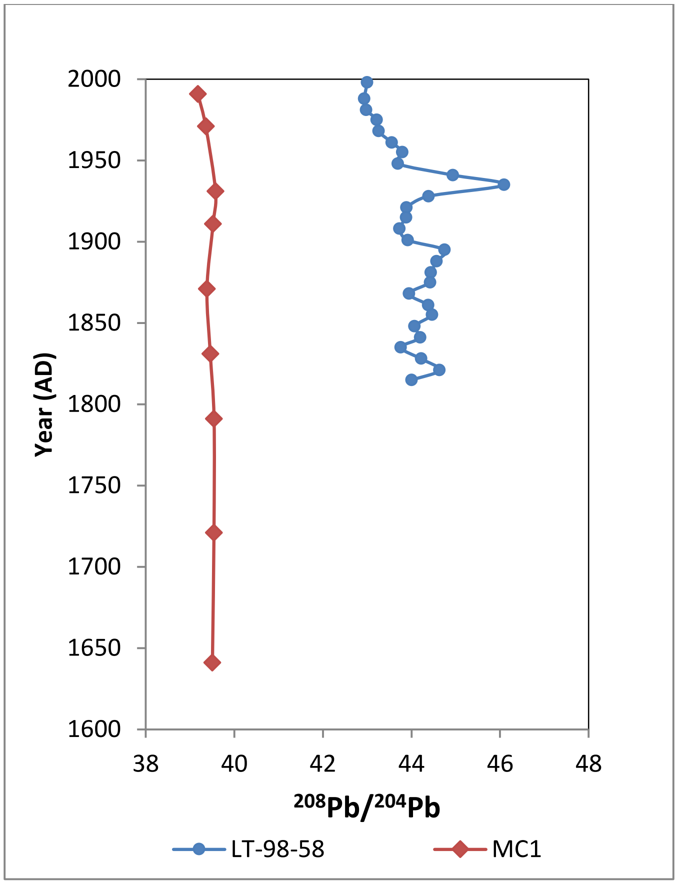

Fig. S10: Down core isotopic composition of Pb ($^{208}Pb/^{204}Pb$) at the nearshore (LT-98-58) and offshore (MC1) sites in Lake Tanganyika.