



Metal ratio mixing models clarify metal contamination sources to lake sediments in Yunnan, China

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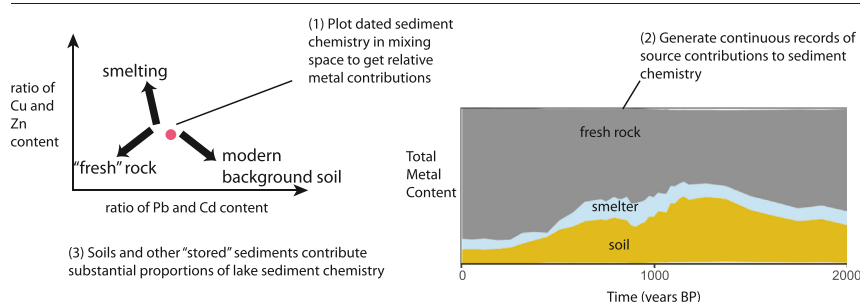
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HIGHLIGHTS

- Sediment storage and metal contamination interact to create metal delivery time lags
- Metal-ratio Bayesian mixing models clarify metal sources to lake sediments
- This approach accommodates cross-comparisons of distinct sediment extractions
- Yunnan lake record analysis demonstrates clarified metal delivery histories.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 October 2021

Received in revised form 10 January 2022

Accepted 14 January 2022

Available online xxxx

Editor: Filip M.G.Tack

Keywords:

Yunnan Province

Mixing models

Legacy contamination

Lake sediments

Basin sediment dynamics

Trace metals

ABSTRACT

Contaminated legacy sediments contribute to modern pollution loadings, particularly trace metals. These contributions are challenging to quantify as metal histories reconstructed from sediment records cannot be easily divided into legacy and concurrent contamination. In particular, the contribution from re-mobilization and delivery of legacy metals stored in catchment soil, colluvial, and fluvial environments are rarely considered or quantified when interpreting sediment records. Here, extended records of metals accumulation for a set of three lakes in Yunnan, China are compared with endmember chemistries using Monte Carlo-Markov Chain mixing models to help identify source contributions to the sediments. This approach allows attribution of metals transported by atmospheric and fluvial mechanisms in a region with a history of mining and metallurgy spanning millennia. These analyses reveal distinct source mixtures and demonstrate the sensitivity of lake records to basin sediment dynamics. In particular, substantial proportions of elevated metal concentrations in these lake systems seem to arise from soil contributions more than from atmospheric deposition of smelting emissions. The largest soil contributions seem to be in Erhai, a lake with erosion prone soils closely "connected" to the lake. Moreover, these investigations illustrate the potential for mixing approaches to accommodate and clarify uncertainties in metal source and extraction as differences in extraction efficiency can be incorporated into source uncertainty estimates. Ultimately, these approaches emphasize the need to account for fluvial metal transport in interpretation of sediment histories.

1. Introduction

Lake sediment records enable reconstruction of past conditions ranging from climate (Liu and Fearn, 1993; Colman et al., 1995; Smol et al., 2005) to vegetation (Hu et al., 1993; MacDonald et al., 1993; Whitlock and

Bartlein, 1997) to chemical contaminants (Splithoff and Hemond, 1996; Callender and Rice, 2000; Mahler et al., 2006). However, modern sediment chemistry analysis approaches are challenged in precisely attributing sediment metals among anthropogenic and background sources. The most common approaches are the use of lithogenic element normalization and enrichment factors, i.e., comparisons of sediment metal content to concentrations expected in the background sediment (Boës et al., 2011). If landscapes have numerous depositional environments, comparison of the

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record of interest with records dominated by atmospheric signal (i.e., large lake surface/catchment area ratios (Urban et al., 1990), ice cores (Beaudon et al., 2017), or peat cores (Shotyk et al., 2000)) can separate atmospheric contributions from non-atmospheric contributions. Finally, isotope compositional approaches can differentiate among ore bodies and human sources that 1) rely on single or limited ore bodies and 2) have metal compositions distinct from local geochemistries (Shi et al., 2021). However, none of these approaches alone can clarify the complicated mix of human activities that dictate the sediment chemistries observed in most systems with substantial human populations.

Denser human populations are more likely found in larger catchments, and metal contributions to lake sediments grow more ambiguous as multiple potential transport pathways and source variety (including legacy sediments) are integrated into the delivered signal. Other approaches generally quantitatively attribute the excess metal content to the disturbance (in this cases humans). This simple attribution precludes the apportionment of these materials to distinct human driven processes (e.g., are they enriched as soil? Enriched further (or even depleted) during alluvial storage?). Both soils and sediments accumulate contamination, and create a distinct and additional source of metal contamination to lake sediments once they are mobilized. This accumulation cannot be resolved by normalization approaches without substantial additional sampling and analysis. In the literature, while methods to reconstruct “human loadings”, particularly atmospheric loadings, are well developed, methods to partition sediment chemistry among these landscape sources and provide appropriate constraints during interpretation of these records are not well developed.

The clarification of fluvial inputs is particularly relevant given the recent recognition of the importance of legacy sediment in geomorphic systems. Sediment chemostratigraphy has long been used to infer floodplain processes (Knox, 1987; Marron, 1992; Hudson-Edwards et al., 1997; Bain and Brush, 2005). We know that mobilization of metal contaminated legacy sediments can be devastating to in-stream biological systems (Moore and Luoma, 1990). However, the connection between trace metal legacy contamination and the delivery of metal contamination to receiving waters is only rarely recognized and considered in material budgets (Spliethoff and Hemond, 1996; Pizzuto, 2014). Addressing legacy sediment challenges requires tools to assess the risks they pose to downstream areas.

Mixing models are a fundamental approach for attribution of contaminants in complicated source mixes. These models range in complexity from linear mixing of components derived from factorial approaches (Hooper et al., 1990) to simple and direct mixing of distinct isotopic compositions in very specific chemical species (Bouchaou et al., 2008; Cole et al., 2011). To date, mixing approaches are less common in sedimentary analyses relative to water analyses. However, mixing model approaches are one potentially powerful means to partition the trace metal content observed in sediment records. Specifically, Monte Carlo Markov Chain (MCMC) approaches have emerged to interpret food webs (Parnell et al., 2010; Layman et al., 2012; Phillips et al., 2014) with substantial overlaps in source compositions and variability in source signatures. For example, these approaches have been adapted to urban stream chemistry to estimate loadings from poorly constrained sewer sources and denitrification processes (Divers et al., 2014; Xia et al., 2017). The further application of these MCMC approaches to sediment chemistries can allow portioning of metals among complicated and uncertain sources, in this case, atmospherically and fluvially delivered metal contaminants. Further, the MCMC approach allows for the potential to account for differences in operational sediment extraction methods when predicting source mixes.

This paper applies MCMC mixing model methods to lake metal sediment records from the Yunnan province in China and partitions observed metal content to relevant sources. The Yunnan is one of the only field locations where examination of a long (>500 yrs) history of legacy extraction and refining can be compared with abundant lake sediment records (Hillman et al., 2014, 2015, 2018). This paper partitions the trace metal histories recorded in three lakes, Erhai, Xingyun, and Dian based on literature geochemistry values to characterize the relative contributions of fluvially transported metals to these lake systems.

2. Study site and methods

Yunnan Province is located in southwestern China and home to numerous lakes formed by tectonic processes (i.e., development of fault basins) (Zhu et al., 1989). This study focuses on lake sediment records of metal content from three lakes: Erhai, Xingyun, and Dian (Fig. 1, Table 1). These lakes have long histories of metal accumulation, with accumulation of Pb and Hg apparent in Xingyun 1500 years before present (Hillman et al., 2014), the accumulation of Pb in Dian 2000 years before present (Hillman et al., 2018), and a substantial peak in Pb contamination in Erhai ~700 years before present (Hillman et al., 2015). In addition, all of the analyzed lakes are impacted by substantial increases in soil erosion and deposition associated with local forest clearance (Hillman et al., 2014, 2015, 2018). Therefore, more recent metal inputs could be associated with sediments stored in fluvial/colluvial environments before transport to the lake.

2.1. Core chronology

Core geochronologies were developed using identifiable terrestrial macrofossils including leaves and charcoal (Table S1). Samples were processed at the University of Pittsburgh (Abbott and Stafford, 1996) and analyzed at the W.M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California Irvine following standard pretreatment (Olsson, 1986). The INTCAL20 calibration curve (Reimer et al., 2020) was used to calibrate the measured ages. ^{210}Pb , ^{214}Pb , and ^{137}Cs activities were measured in the Xingyun and Erhai lake cores to constrain the ages of the upper 20 cm of sediment. The constant rate of supply ^{210}Pb age model (Appleby and Oldfield, 1983) was used to estimate ^{210}Pb stratigraphy. In the Dian sediment core the ^{210}Pb never reached supported concentrations estimated from ^{214}Pb activities. This study relies on previously published data and therefore reflects evolution in age-model development. Sediment ages were input into the BACON 2.2 code (Blaauw and Christen, 2011) (Xingyun and Dian) or the CLAM 2.2 code (Blaauw, 2010) (Erhai) to estimate most likely age models in the statistical software package R (R Core Team, 2013). We did not reassess the Erhai model as the differences between Clam 2.2 and BACON 2.2 lie in the assessment of uncertainties and resultant sedimentation rates are not distinct enough to justify reassessment (Trachsel and Telford, 2017), particularly as all of these age models have been evaluated in peer review. Age models are laid out in greater detail in the respective papers (Hillman et al., 2014, 2015, 2018).

Given the strongly contrasting time periods the cores represent, for this paper we focus on core sediments younger than 4000 years BP to simplify inter-core comparisons. This scope allows a deeper analysis of this inter-lake comparison than would be possible if changes across tens of thousands of years were considered. Though the earliest human activities in the region are of considerable interest (Yao, 2005; Yao and Zhilong, 2012; Yao et al., 2015), there are substantial activities to untangle in more recent human histories. The longer time scales are beyond the scope of this paper and will be analyzed separately.

2.2. Core sediment geochemistry

The chemostratigraphies of the cores were reconstructed by extracting metals from 0.5–1.0 cm core increments every 3–5 cm down-core for metal analysis. Increments were freeze-dried and homogenized. A ~ 0.1 g subsample from each increment was extracted with 1 M HNO_3 for ~24 h (Graney et al., 1995). This method is designed to extract anthropogenic metals and metaloids, in particular, both those associated with exchange sites and most of the other non-residual phases.

A subset of sediment samples were also extracted in aqua regia to evaluate the potential contribution of residual mineral matrix chemistry to ratio signals. Small subsamples of freeze-dried, pulverized sediment (0.03–0.04 g) were refluxed in aqua regia (3:1 vol:vol $\text{HCl}:\text{HNO}_3$) and dried down until detrital material was no longer observed in the digestion liquid. Once the material was digested the final aqua regia digestate was

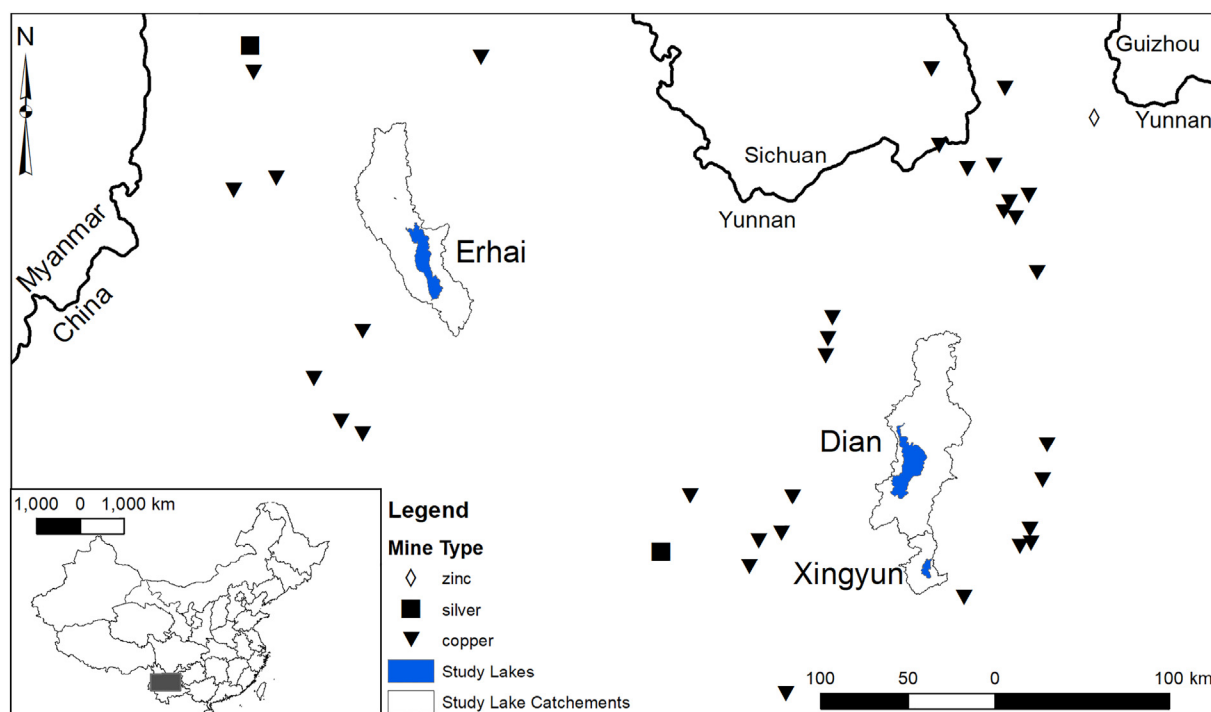


Fig. 1. Location of lakes, including lake catchment boundaries. Inset shows location of map in China (grey box is the extent of the larger map). Historical mine locations and type shown with symbols: diamonds (zinc), squares (silver), and copper (triangle) (Kim, 2011).

dried down and the digested materials dissolved in sub-boil distilled 2% nitric acid (the ICP matrix).

All extractants were diluted in 2% sub-boil distilled nitric acid for matrix consistency during measurement of metal concentration on a PerkinElmer Nexion 300x inductively coupled plasma mass spectrometer (ICP-MS) at the University of Pittsburgh. Every 10th sample was run in duplicate. In the metals presented here, duplicate concentrations were always within 10% of each other and within 5% the vast majority of the time. During measurement blanks were run every 10 samples to assess memory effects. In addition, drift checks were run every 10 samples to assess instrument drift.

2.3. Mixing space definitions

The mixing space was developed empirically. Element-element relationships were examined using scatter matrix plots of all core metal data to identify linear or multiple linear relationships (such relationships indicate consistent ratios between elemental compositions useful in end-member mixing analysis). Ratios identified in the scatter plot were compared in ratio-ratio plots to identify strong candidates for mixing analysis (e.g., the triangular cloud in Fig. 2). Finally, these clouds were compared with literature elemental ratios for appropriate endmembers to assess how these endmembers bracketed the data in ratio-ratio space. The Pb/Cd vs Cu/Zn mixing space emerged from this process, particularly given the ratio-ratio

composition of potential endmembers important in the differentiation among various legacy contaminated sediment sources:

- 1) "Background": Ideally, this endmember reflects the geochemistry of source rocks local to the geographic scope of the mixing analysis. In a complicated geologic environment such as the Yunnan, some sort of weighting is generally used in determining average values. For example, weighting based on the relative weathering rates of specific mineral components in the bedrock allows accurate estimates of endmember contributions (Bullen et al., 1997; White et al., 1999). However, in many cases geochemical data on all of the bedrocks encountered simply do not exist. In these cases broad aggregations such as upper continental crust (UCC) concentration are used. Here a systematic measurement of elemental content in rocks characteristic of the Yangtze craton (Gao et al., 1998) is used. While Erhai is located just outside of the Yangtze Craton, we assume that the trace metal information from the Yangtze Craton will be more representative than UCC estimates drawn from broader geographic regions.
- 2) "Smelter": This endmember should represent the chemistry of industrial emissions from metal refining operations. Reliance on modern measurements of actual stack emissions will be strongly biased by technological improvements in efficiency and emission controls. Therefore, for this endmember we rely on measurements of soil chemistry near smelters,

Table 1

Lake and core characteristics of cores discussed in this study.

Lake	Lake Surface Area (km ²)	Catchment Area (km ²)	Lake Max. Depth (m)	Year Core Collected	Core site coordinates	Water depth at core site (m)	Number of sediment samples analyzed	Drives and depths
Erhai	250	2300	21.5	2012	25°43'38"N 100°12'01"E	11	121	Composite depth 2.59 m
Dian	300	2800	5	2012	24°53'09"N 102°40'02"E	5	53	Composite depth 3.96 m
Xingyun	34	380	11	2008	24°21'57"N 102°47'29"E	11	79	D-1: 2.65 m D-2: 2.49 m D-3: 2.33 m D-4: 2.71 m D-5: 2.6 m No overlaps

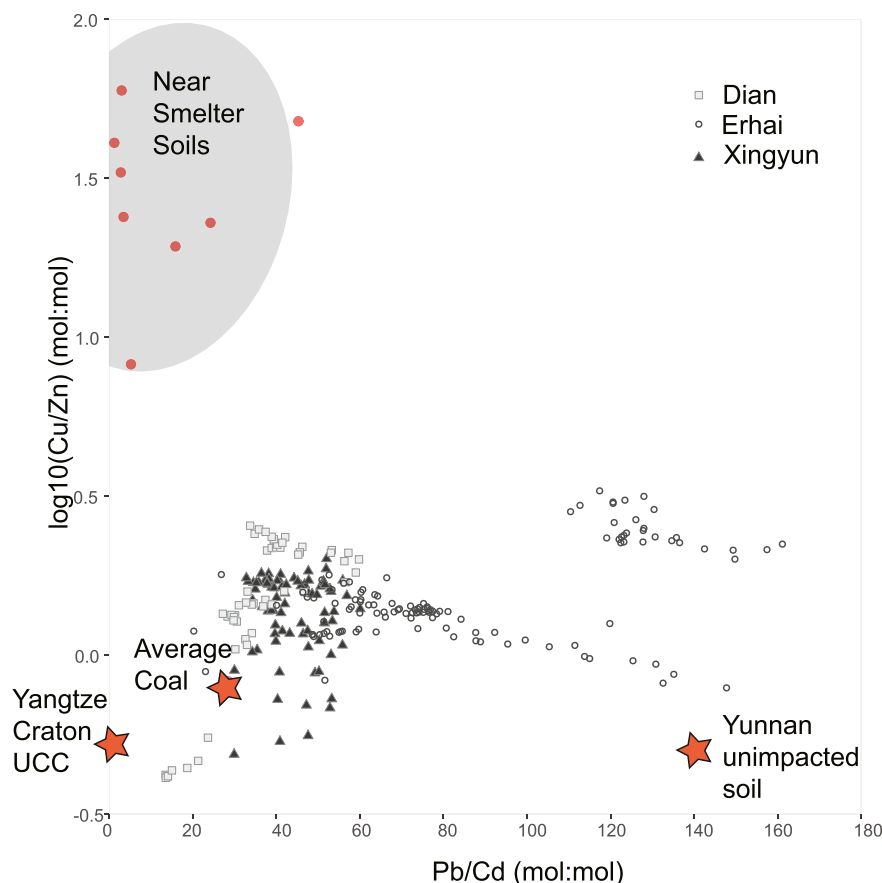


Fig. 2. Sediment increment chemistries plotted in trace metal ratio space (grey symbols) defined by relevant endmember chemistries, as labeled (large orange symbols). The near smelter soil samples are shown with orange dots encompassed by the grey area. Determination of the endmember is based on the average of the dots and the bounds of the grey area.

collected in the Yunnan (Lanping; Peng, 2009). In the near smelter environment, we assume that the magnitude of emissions will be sufficient to make the smelting emission chemistry dominant in the anthropogenic portion and that the emissions near site are reflective of emissions over wider spatial areas. This chemistry collected from the literature is consistent with spatially broader estimates of emissions chemistry (Pacyna and Pacyna, 2001).

- 3) “Soil”: This endmember is based on the metal content of local soils and is assumed to reflect the geochemistry of soils that have accumulated atmospheric deposition of metals over millennia of human occupation in the province. We rely on average data reported for the Yunnan as “background” soil content, i.e., these soils were sampled in areas not subject to contamination directly downwind of known point sources (China National Environmental Monitoring Center, 1990; Chen et al., 1991). This choice was intended to use values less impacted by human activities over the 4000 year period.
- 4) “Coal”: Coal is historically one of the primary fuels in China (Conti et al., 2016). The geochemical signature of coal combustion emissions is another potential endmember contribution to lake sediment geochemistry. We gathered a wide variety of coal chemistry measurements from Yunnan and western Guizhou coals (Dai et al., 2003, 2004, 2006, 2007, 2008a, 2008b, 2014; Wang et al., 2012). In addition, we relied on the review and aggregation presented by Tian et al. (2015).

2.4. Mixing models

We utilized the SIAR mixing model approach (Parnell et al., 2010) based on Monte Carlo-Markov Chain (MCMC) methods to reconstruct relative contributions of endmembers to the sediment chemistry observed in the cores.

This mixing model was developed for use with stable isotope ratios in food webs with substantial overlap in the isotopic compositions of food sources. Here we use elemental ratios derived from the sediment core chemistry and the potential endmembers. We have adapted this approach because both isotope ratios and elemental ratios are used to probe dynamics systems with wide variance in concentration. Isotopic approaches allow examination of dynamics within a single element. We assume the relatively low assimilation rate of most trace metals by most biotic and geophysical processes preserves ratios in trace metal content and allows examination of source mixing. Further, in many cases, once trace elements are associated with a mineral surface or organic matter, they remain associated unless they encounter relatively rarer chemical conditions (e.g., reducing zones). Therefore, even if these metals are stored for significant periods on the landscape, we expect ratios of metals to remain relatively consistent, preserving the terrestrial sediment signature. That said, if one element in a ratio pair is dramatically consumed by a particular process, this is equivalent to a fractionation processes in stable isotopic analysis and these processes can be simulated in the SIAR framework.

We utilized SIAR mixing models with all four endmembers described above and with smelter/soil/background endmembers (i.e., coal was omitted). Concentration dependencies were not used in SIAR models as interest is in estimates of proportional source contributions. Fractional corrections were not incorporated as we assumed minimal fractionation in the elemental ratios for this initial adaptation of the methodology. The SIAR defaults for prior probabilities of source proportions were used so initial proportions were Dirichlet distribution (Parnell et al., 2010). Models were run for 500,000 iterations, with a burn-in of 5000. Chains were thinned by 15 and convergence evaluated with the diagnostics built into the SIAR package.

Table 2

Endmember ratio values used in mixing models discussed in this study. Parenthetical values are standard deviations used to define uncertainty. End member values were developed as described in Section 2.3.

Scenario	Background		Smelter		Soil		Coal	
	Pb/Cd	Cu/Zn	Pb/Cd	Cu/Zn	Pb/Cd	Cu/Zn	Pb/Cd	Cu/Zn
Base	0.013(0.00853)	0.415(0.172)	12.7(15.4)	31.9(16.8)	140(18.0)	0.501(0.354)	28.2(21.6)	0.815(1.02)
Base, Smelter Sensitivity	0.013(0.00853)	0.415(0.172)	12.7(15.4)	15.0(16.8)	140(18.0)	0.501(0.354)	n.a.	

2.5. Sediment connectivity

Sediment connectivity between upland areas and the lakes was assessed using methods developed by Cavalli et al. (2013). These methods define sediment connectivity as the ratio between the upstream sediment production potential and the gradient of the downstream path.

3. Results & discussion

3.1. Endmembers

The endmember values (Table 2) determined from the literature generally bracket the metal chemistries measured in the cores (Fig. 2). In the case of the coal endmember, the variability in the measured coal chemistries was larger than the variability in observed core chemistries (Fig. S1). However, re-examination of these values revealed that many coal chemistries were measured as geological oddities (e.g., examination of a coal seam that had interacted with hydrothermal waters (Dai et al., 2004)) or were measured in coals that were not primary energy sources historically or at present (Dai et al., 2004). Available literature did not provide sufficient

data to create a weighted value, therefore, during subsequent analyses we have used the aggregated chemistry of coal from the Yunnan Province reported by Tian et al. (2015) as the representative coal endmember (Fig. 2).

3.2. Scenarios – base

The first mixing model scenario used all four basic endmembers (Table 2). Each lake was run separately and source contributions to metals observed in the cores estimated (Fig. 3). This scenario reveals limitations in the analysis methods. The metal ratio combination characteristic of coal is located essentially in the middle of the data cloud, resulting in a strong likelihood of the model predicting a substantial portion of the mix from coal to sediment metal concentrations. The coal endmember is predicted to contribute roughly a third of the mix consistently across cores and through time (Fig. 3). This contribution is predicted throughout the entire sediment record (including sediments older than 4000 bp), yet the earliest documented use of coal in China is ~4000 bp (Dodson et al., 2014). Further, this analysis assumes that the coal contribution reflects raw coal content despite the strong likelihood of fractionations in metal content during combustion and rain out processes. The widespread use of coal would suggest a

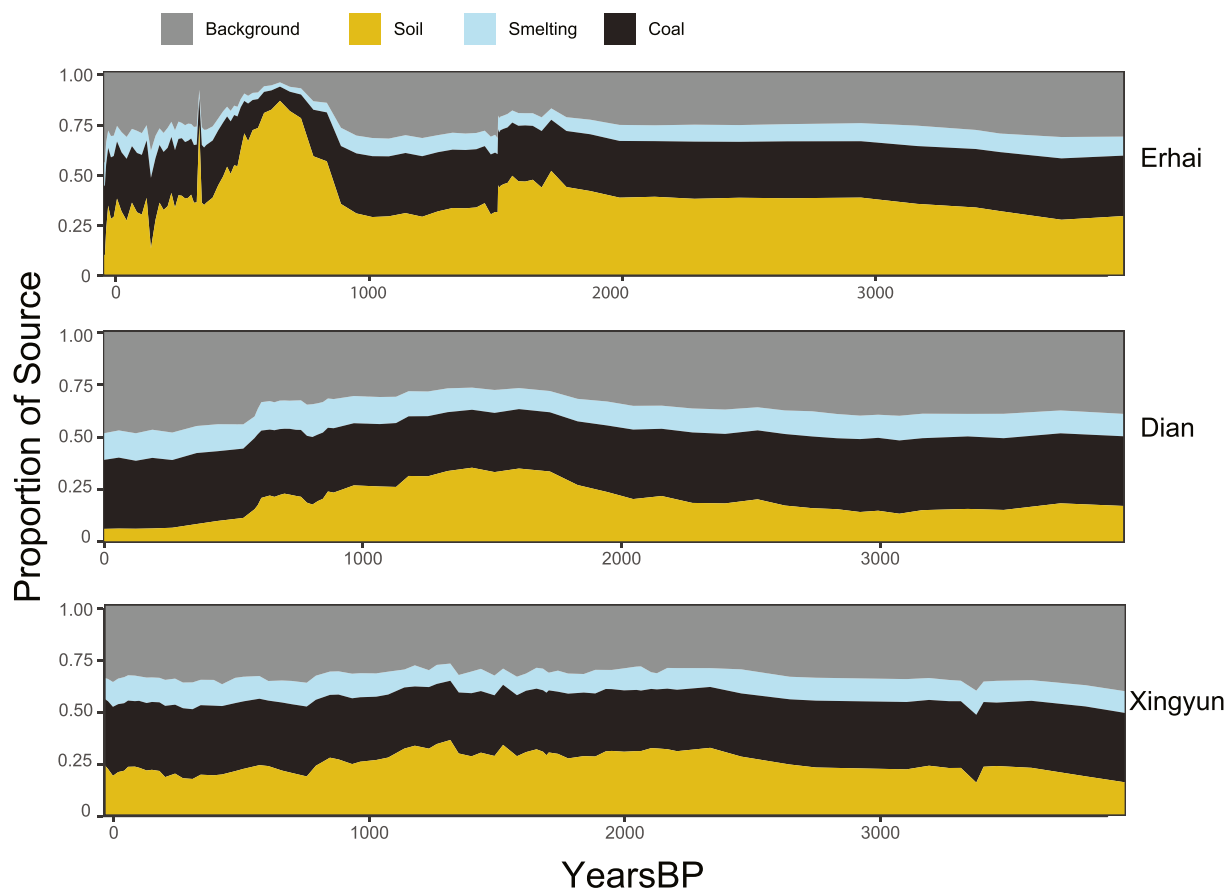


Fig. 3. The relative contributions of source endmembers to lake sediment chemistries through time. These results are from a mixing model that includes the coal endmember. Summary measures of each data series including uncertainties are presented in Figs. S2-S4.

relatively diffuse contribution across the landscape, a signature that is likely redundant with the soil signal. For these reasons, the mixing analysis was conducted without the coal endmember for all subsequent analysis.

3.3. Scenarios – base without coal

The second mixing model scenario considered only the background, soil, and smelter endmembers (Table 2) and was run for each of the lakes separately to partition metals to each source (Fig. 4). The mix of source contributions varies among the lakes. At ~4000 bp, all three lakes have similar endmember contributions, roughly 50–60% background, 20–30% soil, and 10–20% smelter. This proportion remains relatively consistent through 2000 bp.

In more recent periods (2000 bp to present) the source contributions are more variable and dynamic. Between 800 bp and 500 bp in Erhai is a period where the soil endmember dominates sediment chemistry. In contrast, the sediment records reconstructed from the other two lakes indicate metal source proportions are more consistent. Dian has a period where the importance of the soil endmember grows (1500 bp to 500 bp), but the shift to soil-like chemistry is not nearly as stark as Erhai. In more recent periods Dian has the highest contribution of background material, with roughly three quarters contributed by background sources. Finally, Xingyun has the most consistent mix of sources through time, with minimal deviations from the mix observed beginning around 4000 bp. Some this variability appears to result from basin geologic and topographic characteristics, discussed in detail below.

Available data and natural heterogeneity do not allow quantitative comparison among lakes. For example, variability in bedrock chemistry likely

contributes to the variability of the relative contributions of background and soil among the lakes (e.g., background contributions are more important in Dian than Erhai). Assigning an accurate, lithology-weighted chemistry to a single basin is a challenge in itself. Further, this lithology weighted estimate, if possible, does not account for wide variation in mineral weathering kinetics and the distribution of geochemical environments (e.g., wetlands or fracture zones) in a particular basin. Therefore, the variation in the background/soil mix from lake to lake likely results from local variations in geochemistry and geomorphology rather than differences in absolute background and soil contributions. Additional sampling of basin geologic materials may reduce this interbasin variability.

In addition, we fully expect the soil end member evolved through time. However, it is not at all clear this evolution was monotonically to more contaminated status. Soil erosion preferentially operates on shallow soils, zones with relatively greater amounts of organic material and iron oxyhydroxides, or areas where metals would accumulate. Therefore it is likely this endmember fluctuated through time as accumulations were eroded and new soil materials formed. The endmember is based on minimally impacted soils (China National Environmental Monitoring Center, 1990), which should minimize fluctuations to a more contaminated status. Beyond that, there seems no good way to characterize these changes through time. This evolution may explain the gradual increased “soil” contribution from 4000 to 2000 years BP in all lakes (Fig. 4). That said, these uncertainties are greatest in the early periods, periods that are relatively consistent in relative contributions (Fig. 4).

The consistent contribution of the smelter endmember does not necessarily agree with known human history in the region. There are potential, but unlikely, explanations for the contribution of this endmember such as



Fig. 4. The relative contributions of source endmembers to lake sediment chemistries with time in the Base without Coal scenario. Specific measures of each data series including uncertainties are presented in Figs. S5–S7.

wildfires mobilizing metals from vegetation or soil above local ore outcrops. However, it is much more likely that this consistency is a result of the relatively extreme smelter endmember value and the resultant insensitivity of the mixing space to the smelter endmember. In particular, mean values for smelter contributions seem to be driven by extreme values given the relationship between the mean and the median in individual source contributions (Figs. S5–S7). To examine this sensitivity, simulations were repeated using a mean smelter endmember with a Cu/Zn ratio half of that in the observed smelter endmembers (i.e., the ratio was decreased from 31.9 to 15, with variability identical to the observed values, Table 2. Note this value was arbitrary and meant to simplify interpretation of the sensitivity results.). In these simulations the mixing analysis predicted a 50% increase in the relative contributions of smelter sources (Fig. S8). Since near smelter sites are strongly enriched in copper, relative increases in copper concentrations in lake sediments must be substantial in order to move the predicted mixture toward smelter inputs. This sensitivity analysis demonstrates that if copper enrichment of near smelter soils were lower, then a larger portion of lake sediment chemistries would be predicted to be smelter inputs. Without additional precision in local geochemical conditions, particularly atmospheric deposition chemistry, this mixing space will remain at least in part qualitative.

Regardless of the limitations arising from imprecision in endmembers and challenges in the mixing space, the changes in relative contributions of smelter and sediment bound inputs match well with other reconstructions of environmental and human conditions based on cores in these lakes. In Erhai, there is a dramatic shift to dominance by soil endmember chemistry between 800 and 500 bp. This shift corresponds with the Yuan dynasty and subsequent periods, an interval of intense human activity (Hillman et al., 2015). Dian sediments also match with human histories documented elsewhere. The gradual increase in the contribution of soil endmember chemistries at ~1500 bp coincides with the intensification of terraced agriculture in the Yunnan Lakes region and physical changes in the sediment noted in the core (Hillman et al., 2018). Maximum contributions from the soil endmember occurs roughly 1200 years BP, and following this maximum, the contribution of the soil endmember gradually declines, replaced by the contributions attributed to the background. There is a secondary maximum in soil endmember contributions around 900 bp. This increase in soil contributions coincides with a period of lake level decline due to manipulation of the lake outflow (Hillman et al., 2018). In more recent core sediments (500 bp to present) the mix returns to proportions measured prior to substantial human impacts, though smelter endmembers are increased in these sediments relative to the older sediments. This signal may result from the proximity of Kunming, a rapidly growing urban center, adding an urbanization influence not as apparent in the other lakes.

3.4. Metal extraction methods and sediment chemistry signals

The metal extraction methods used in this study have been widely utilized in previous reconstructions of sediment chemistries (Abbott and Wolfe, 2003; Pompeani et al., 2013; Hillman et al., 2017; Rossi et al., 2017). However, as we begin to compare metal histories among lakes, it's important to clarify what signal the extraction captures. The 10% nitric extraction should effectively extract all exchangeable and carbonate bound metals, in addition to extracting a substantial, but not necessarily quantitative, portion of the Fe/Mn oxide and organic bound fractions (Tessier et al., 1979; Horowitz, 1984; Graney et al., 1995). Graney et al. (1995) consider this to reflect the “anthropogenic” fraction. Therefore, we expect the sediment chemistry to reflect metals accumulated during recent pedogenesis, transport to the lake, and scavenging of metals in the water column from atmospheric deposition to the lake surface during settling. In contrast, the measurements of the soils, background (i.e., UCC), etc. used to estimate endmembers are total measures (i.e., complete digestion of the sediments that may include use of hydrofluoric acid to digest the silicate matrix). While this discrepancy can influence this mixing analysis, the uncertainty framework allows examination of these discrepancies and accounting for the uncertainty.

To examine this source of uncertainty, a subset of thirty-two sediment samples from Dian and Erhai were digested using a more aggressive aqua regia total digestion described in the methods. As expected, the different digestion methods measure unique phases of the sediment chemistry, with relative enrichments in copper and lead in the nitric acid extracted metal ratios (Fig. S9, note this is a plot of ratios). These enrichments result from increased yields of Zn and Cd in the aqua regia extraction that lower the ratio. This is consistent with Graney et al.'s (1995) interpretation of the extraction, as the increased relative fluxes of Cu and Pb due to human activity are captured by the extraction.

This does present challenges in the interpretation of the mixing model, as direct comparison of the endmembers and sediment chemistries is not only uncertain due to normal environmental variance, it is also uncertain due to extraction biases. Use of the MCMC approach allows accounting for these differences in extraction. The additional uncertainty can simply be used to compensate in endmember definitions and match sediment chemistries. If more aggressive methods extract, on average, more Cd and Zn, the endmembers can be “adjusted” to reflect the expected results from a 10% nitric extraction. That is, given the relative enrichment in Cd and Zn in the nitric extracts, particularly at higher ratios, we can increase endmember values to reflect this systematic difference (Fig. S10, Table 2).

When endmembers are altered to account for the differences in extraction methods, background contributions to sediment chemistry is estimated to increase (Fig. S11). This change mutes the predicted contributions from the fluvial and smelter sources, though general trends remain the similar to those in Fig. 4. An enhanced measurement of soil geochemistries in these catchments would provide a more quantitative comparison across basins. Regardless, the qualitative differences remain. Further, the MCMC approach allows flexibility in matching contrasting geochemical data.

3.5. Geologic influences on lake sedimentation and core chemistry

Yunnan's geology influences the measured lake records. Three processes are identified and discussed here: 1) catchment bedrock and soils, 2) lake-upland sediment connectivity, and 3) tectonic activity. These processes are fundamental to the interpretation of the lake records. In these three lakes observed patterns are consistent with the expected geologic influence.

Bedrock in the Yunnan lake region is complicated and available mapping (Province Bureau of Geology and Mineral Resources of Yunnan, 1990) remains coarse (Fig. S12). There are five general geologic materials forming regional bedrock: granitoid/plutonic materials, carbonate dominated sedimentary/metasedimentary rocks, sandstone dominated sedimentary/metasedimentary rocks, metasedimentary (slate and leptynite), and near shore deposits. Xingyun only drains metasedimentary and carbonate bedrock (Fig. S12). Sediment production from both rock types can be small relative to other lithologies (Syvitski and Milliman, 2007). Carbonate weathering tends to be dominated by the dissolved load and slate weathers slowly due to mineralogy and rock morphology. This expected lower sediment production likely limits delivery and explains the importance of smelter endmembers to sediment chemistry in Xingyun compared to Erhai and Dian, which both contain substantial regions of granitoid and sandstone lithology. Likewise, comparison of the Erhai catchment with the Dian catchment reveals proportionally more plutonic/granitoid rock connection to the lake. In the Dian catchment, only a small southern portion of the lakeshore connects with the plutonic/granitoid materials compared to at least half of Erhai's western shore. The soils developing above the plutonic/granitoid lithology are mapped as luvisols (Fig. S13), a relatively fertile soil that does not occur widely in the other watersheds. These contrasts in soil (sediment) production likely contributes to the muted fluctuations in the soil chemistry endmember contributions observed in the Dian and Xingyun lake records.

In terms of sediment delivery, near lake soils are disproportionately important. Sediment mobilized near the lake has the most direct and shortest path to the lake. In general, the lakes are surrounded by cambisols, red soils that have not fully formed a clay-rich B horizon (inceptisols), and

anthrosols, soils dominated by human activities (Fig. S13). However, Erhai has significant areas of both lixisols and acrisols on its eastern shore. Both acrisols and lixisols are thick, highly weathered soils (oxisols). Lixisols are noted for their erodibility. Erhai is the only lake with substantial coverage by luvisols (alfisols), likely the soils most suitable for agriculture in the catchment that have not been converted to anthrosols. Given the relative productivity, these soils may have been preferentially converted to agriculture during expansion of production from the lake flats into the surrounding hills. Among these lake records, Erhai has the largest proportion of soil endmember inputs over the last 4000 years and the most dramatic increase in soil inputs during more recent (within 1000 yr) sedimentation (Fig. 4). Further, the more erosion prone (on one side) and fertile (on the other) soils are directly connected (Cavalli et al., 2013) to the lake (Fig. S14). This connectivity likely made Erhai relatively more susceptible to soil erosion during human disturbance, particularly when compared to the less connected Xingyun and Dian catchments.

Another fundamental difference in soil distribution is the occurrence of smaller subsidence depressions that tend to form gleysols. For example, in the Xingyun watershed, ~5% of basin area is mapped as gleysol (Fig. S15). Further, this is an underestimate, as mapped anthrosols cover areas that likely were gleysols (i.e., the near-lake regions of sediment fill). These soils are the wettest and most fertile, resulting in concentrated human activity. These smaller subsided areas are also depositional environments that create upland sediment sinks and reduce sediment connectivity (Figs. S15 and S16). This disconnection contributes to the insensitivity of soil endmember contributions to Xingyun core chemistry during recent (within the last 100 years) human disturbances (Fig. 4).

The tectonic activity in the Yunnan region formed the lake basins and continued tectonic activity impacts erosion and sedimentation in the basin. In terms of connectivity, faulting can enhance delivery of dissolved materials to the lake by connecting the upland and the lakes with preferential hydrologic flowpaths. Fault densities (km fault/km² catchment) in these lake catchments are consistent, ranging between 0.07 and 0.08 km/km² (Fig. S12). Further, there are no cases where mapped faults connect unexpected lithologies to the lakes. So, while faults are an important consideration in metal delivery, the effects are likely similar among these lakes.

More important than fault location is the seismic history of these faults. Earth movement, particularly in wet periods can trigger mass wasting and rapid delivery of sediments to the lakes and lake tributaries. The long history of earthquakes in the Yunnan has been reconstructed from recorded histories (Lee et al., 1976) (Fig. S17). There is limited correspondence with the sediment record (Fig. 4), but that may result from the contrast in temporal scales (discrete earthquakes vs. sediments accumulating over decades). Moreover, several of the major pulses of sediment bound metals to the lake occur well before (i.e., prior to 500 years bp) and therefore earlier than the period when most of the earthquakes have been reconstructed (Fig. S17). In particular, mapping of tectonic event locations (Fig. S18) suggest several earthquakes occurred near Erhai and relatively close to areas with high sediment connectivity to the lake (Fig. S18). Similar events earlier in history may have contributed to the observed spike in soil metal contributions to lake sediment chemistry.

3.6. Metal delivery mechanism and observed sediment chemistry

Metal transport pathway strongly influences observed metal concentrations in lake sediments. Erhai has strong sediment connectivity to its catchment and relatively more erosion prone soils in its catchment. This arrangement, along with tectonic history, create peaks in lead concentrations much higher than other lakes (Fig. 5). The highly elevated lead concentrations observed in Erhai between 900 and 500 years BP are ~four times higher than the highest concentrations observed in the other lakes. The mixing approach presented here removes considerable ambiguity in the interpretation of the differences among the lakes. The highest lead concentrations are associated with a period of dominance from the local soil

endmember to the Erhai sediment chemistries. Without the mixing analysis, comparisons among the lakes suggests Erhai was subject to considerably more metal contamination than the other lakes, and potentially suggests important holes in the mining historical records (e.g., Fig. 1). The mixing analysis indicates this period of high Pb deposition resulted from soil Pb inputs to the lake that have chemistries similar to the soil endmembers, suggesting a majority of the metal content was transported on fluvially transported sediments. Clarification of sediment source through mixing analysis improves our interpretation of historical processes on the landscape and reveals the importance of remobilized legacy contamination to lake metal loadings.

4. Conclusions

The contribution of legacy contamination to lake sediment metals can be clarified with Bayesian mixing approaches based on trace metal ratios in lake sediments and relevant endmembers. For example, the largest observed concentrations of lead in any of the lakes in this study are associated with a period where upland sediment sources are predicted to strongly dominate the lake sediment chemistry. While these results are promising, it's important to note that mixing approaches do not always work. For example, overlapping endmembers are hard to resolve as demonstrated by the coal limitations here. Regardless, the use of trace metal ratio mixing frameworks to interpret reconstructed metal histories has the potential to provide substantial insight.

Clarification of the relative contributions of fluvially transported metals is fundamentally important to the interpretation of the reconstructed core histories. When elevated lake sediment metal concentrations result from increased erosion, land disturbance is necessarily the fundamental mechanism driving lake sediment chemistry rather than contemporary changes in metallurgical activity. Mixing analysis clarifies the relative mix of contribution sources, and a Bayesian approach allows the substantial flexibility necessary to account for the large uncertainties that remain in these systems. In particular, here we are able to compare metal measurements obtained with distinct digestion approaches, a promising route for untangling the wide variety of available data.

Finally, these analyses reveal the geomorphology of the drainage networks, the distribution of soils and geologic substrates in the catchments, and tectonic histories are important controls on lake sensitivity to landscape disturbance. The specific arrangement of sources and sinks is a primary control on how lake sediments record land use dynamics. Clarification of sources and sinks using these methods is fundamental to accurate interpretation of lake sediment records and assessment of the risk of legacy contamination to downstream receiving waters.

CRedit authorship contribution statement

Daniel J. Bain: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Aubrey L. Hillman:** Conceptualization, Methodology, Investigation, Writing - review & editing. **Mark B. Abbott:** Conceptualization, Investigation, Writing - review & editing. **Rebecca A. Tisherman:** Conceptualization, Investigation, Writing - review & editing. **Duo Wu:** Conceptualization, Investigation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Science Foundation: NSF GLD 1648772. The manuscript was strengthened by feedback from four anonymous reviewers.

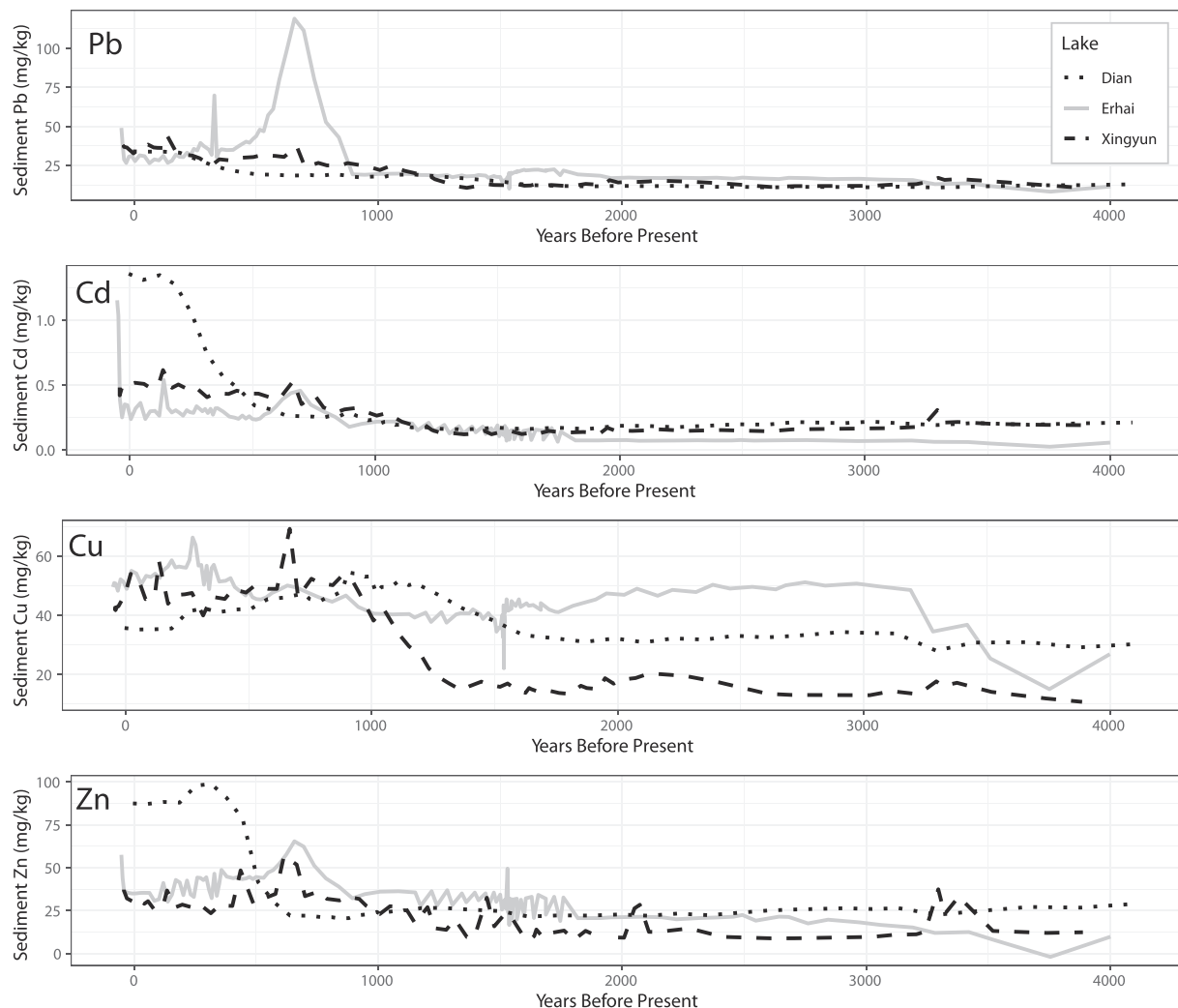


Fig. 5. Metal concentration histories reconstructed for the three lakes discussed in this study (Erhai is grey, solid, Dian is black, dotted, and Xingyun is black, dashed).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.153247>.

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