

**Report to Utah Division of Water Quality in response to request for extended Scope of Work regarding
source identification for metals in the San Juan River system**

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Summary

The goal of this project is to corroborate findings from a previous study concerning the delineation of mining versus non-mining sources of particulate metals in a sediment core taken from Lake Powell. Additional sediment cores sampled during the same time period at nearby sites in the San Juan River delta were analyzed and compared to the original core. Despite differences in the total depth of the three cores, sediment layers with elemental signatures of mining-impacted tributaries and snowmelt runoff conditions were observed in all three cores and showed correspondence with depth. Additionally, the 3.3 m distance between two distinct snowmelt-deposited layers in one of the cores corroborates the interpretation that the 3.4 m length of the previously analyzed core was deposited over a period of approximately one year.

Introduction

Delineation of mining versus non-mining sources of particulate metals (PM) in deposited sediment of Lake Powell (Frederick et al., 2019) was accomplished using sediment samples from one of three USGS cores collected in 2010 (Hornewer, 2011). Elemental and isotopic signatures were used to link deposited particles in Lake Powell sediment to their suspended counterparts in upstream source tributaries. Mining and non-mining sources corresponded to season, where particles from mining-impacted watersheds were predominantly conveyed by snowmelt runoff, and where particles from non-impacted watersheds were predominantly conveyed by rainfall runoff (Frederick et al., 2019). Characteristics of the examined Lake Powell sediment core (Core 2) indicate that its 3.3 m length represented approximately 1.5 years of sediment accumulation (Frederick et al., 2019). However, this apparent short duration represented by Core 2 highlights the need to determine whether Cores 1 and 3 corroborate the finding in Core 2.

The objectives of this study were therefore to determine whether the defining characteristics of Core 2 were consistently represented in Cores 1 and 3. These defining characteristics were variations with depth in sediment color, particle grain size, metal concentrations normalized to aluminum, and ratios of metal concentrations determined *via* cold hydrochloric acid leach versus complete digestion using hydrofluoric acid.

Methods

Field Sites

Sediment cores were collected from three sites in the San Juan River Delta of Lake Powell in August 2010 (Hornewer 2014) (Figure 1).

Sample Collection

Three sediment cores (Core 1, Core 2, and Core 3) collected in August, 2010 had individual thicknesses of 1.48 m, 3.37 m, and 4.6 m, respectively (Hornewer 2014). The complete sampling methodology and

coring procedure are given in Hornewer (2014) and Hart et al. (2005). Various strata were subsampled (20, 32, and 49 subsamples, for Cores 1, 2, and 3, respectively) dried, digested *via* total digestion (HCl, HNO₃, HClO₄, and HF at low temperature), and analyzed *via* inductively coupled plasma atomic emission spectrometry (ICP-AES) (Hornewer 2014). Additional sediment samples were sub-sectioned from the frozen cores in Fall 2017 at the USGS laboratory in Boulder, CO (6, 19, and 15 samples from Cores 1, 2, and 3, respectively).

Sediment Color

Sediment color was assigned based on Munsell Soil Color Charts (Munsell Colorx-rite 2009).

Trace Elements

Subsamples from Cores 1 and 3 were analyzed *via* methods developed in Frederick et al. (2019) for the analysis of Core 2. Cores were analyzed for elemental concentrations *via* ICP-MS with a 10% HCl digestion for 48 h at 22°C. Water content and bulk density of the sediment samples were determined by weighing a known volume of sample before and after drying. Sediment elemental concentrations were then corrected to represent the dry elemental concentration. A 10% HCl leaching was assumed to extract only the metal/metalloid coating on the mineral (e.g., elements that precipitate upon mixing acidic mine waste with circum-neutral river water) (extractable phase), rather than the entire mineral matrix (total digestion).

Particle Size

Grain size for Cores 1 and 3 was analyzed *via* Sympa Tec Lixell QICPIC. Grain size for Core 2 had been previously analyzed *via* Sympa Tec Lixell Helos/KF laser diffraction using two lenses, which captured particle sizes 0.25 to 87.5 µm and 0.5 to 350 µm, respectively. To compare the two methods employed for grain size analysis, additional Core 2 samples were analyzed *via* QICPIC (Figure 3). QICPIC analysis yielded consistently higher median particle size (an average of 36 µm greater). Therefore, a correction factor of 36 µm was added to Core 2 samples analyzed *via* laser diffraction to normalize results to QICPIC data.

Results

The defining characteristics of Cores 1-3 are described below in the following order: sediment color, particle grain size, metal concentrations normalized to aluminum, and ratios of metal concentrations determined *via* cold hydrochloric acid leach versus complete digestion using hydrofluoric acid. The gradual increase in lake depth across the three sites (9 m increase across a 1100 m distance) (Hornewer 2014) allowed Cores 1, 2, and 3 to be compared side by side as a function of depth from the sediment-water interface (Figures 2-5).

Color

The dominant sediment colors in Cores 1 and 3 corresponded to colors observed in Core 2, which were primarily brown and reddish brown (Munsell Color 4/3 and Munsell color 4/4) (Figure 2). Frederick et al. (2019) concluded that colors in Core 2 corresponded to those of particulate matter (PM) in upstream tributaries, and so by extension Cores 1 and 3 also correspond to PM in upstream tributaries by virtue of their color.

Post-depositional or post-sampling color changes caused by oxidation or reduction of certain elements (e.g. iron and manganese) may complicate the comparison of sediment colors between Cores 1, 2, and 3. Additionally, color variations are subtle, creating difficulty in identifying distinguishing color layers. Therefore, color alone is not a reliable metric for comparison between the cores.

Particle size

Average particle size was modestly coarser (approximately 55 μm) in Core 1 (Figure 3) relative to Cores 2 and 3 (approximately 40 μm). Notably, the lower-resolution optical particle size analysis utilized for all three cores inflated size by a factor of four for particles below approximately 60 μm (Figure 3), such that the smallest particle size was approximately 10 μm as determined by laser diffraction versus 40 μm as determined by optical analysis. While the apparent average grain sizes among Cores 1-3 are influenced by this optical artifact, the coarser nature of Core 1 is likely qualitatively accurate and is consistent with its upstream location (Figure 1). The optical artifact does not significantly affect determination of the coarsest particle sizes.

An apparent coarse particle layer was observed at similar depth across Cores 1, 2, and 3 at 1.2 m, 1.4 m, and 2.0 m, respectively (Figure 3). This apparent coarse layer consisted of fine sand, or fine sand and silt, in Cores 2 and 3, respectively. In contrast, in Core 1 it consisted of organic matter, which therefore did not represent sediment contribution from upstream tributaries. In Core 1, that organic-rich sample (1-05) exhibited increased metal:Al ratios for Cu, Cd, and Pb (Figure 4), suggesting correspondence with similarly elevated metal:Al ratios in sample 2-03 above the coarse layer in Core 2.

Metal:Al Ratios

Cores 1 and 2 showed co-occurring peaks for Cd:Al, Cu:Al, Pb:Al, and Zn:Al ratios at similar depths (sample 1-05 at 1.1 m in Core 1, and sample 2-03 at 0.7 m in Core 2) (Figure 4). Corresponding peaks were not observed in Core 3 above 2 m, likely due to low sampling frequency. Cores 2 and 3 showed peaks in Ni:Al ratios located at 2.3 m and 2.6 m, respectively (samples 2-11 and 3-06, respectively), beyond the maximum depth of Core 1 (Figure 4). Cu:Al and Zn:Al peaks were located at this depth in Core 3, but not in Core 2 (Figure 4). In Core 3, additional co-occurring peaks in Cu:Al, Pb:Al, and Zn:Al ratios were located between 3.6 and 3.8 m (samples 3-12 and 3-13), beyond the depth of Core 2 (Figure 4). Other than the above-described features, metal:Al ratios were relatively constant with depth in the

three cores, noting that variations may be obscured by the low sampling frequency in portions of the cores. Metal:Al ratios were suppressed in Cores 1 and 3 relative to those in Core 2 (Figure 4) due to higher extractable Al concentrations in Cores 1 and 3 (Figure 5).

Extractable Metal Concentrations

Extractable metal concentrations showed similar trends to metal:Al ratios in all three cores. Cores 1 and 2 showed co-occurring peaks for Cd, Cu, Pb, and Zn at similar depths, 1.1 m and 0.7 m, respectively (samples 1-05 and 2-03, respectively) (Figure 6). Corresponding peaks were not observed in Core 3 above 2 m, likely due to low sampling frequency, although modestly elevated values for Cd, Cu, Pb, and Zn were observed at 0.4 m (sample 3-01). In Core 3, co-occurring peaks for Cd, Cu, Ni, and Zn were observed at 2.6 m (sample 3-06), below the maximum depth of Core 1, and this was not observed in Core 2 despite sufficient sampling frequency (Figure 6). In Core 3, co-occurring peaks for Cd, Cu, Pb, and Zn were located between 3.6 and 3.8 m (samples 3-12 and 3-13), beyond the maximum depth of Core 2 (Figure 6). In Cores 2 and 3, decreased extractable metal concentrations coincided or overlapped with the coarse layer (Figure 6).

Extractable:digested Ratios

For Cores 1, 2, and 3, sediment elemental concentrations in the extractable phase were 1 to 1000 times lower than those determined by digestion of the matrix (Figure 7). In all three cores, extractable:digested ratios were lowest for Al and Cr and highest for Cd and Mn (Figure 7). Extractable:digested ratios over 100 percent indicate minor variability with subsamples and cases where the near entirety of elemental concentration was contained on the surface coating rather than in the sediment matrix.

Peaks in extractable:digested ratios for nearly all metals were observed in Core 2 (sample 2-08 at 1.8 m) and Core 3 (sample 3-06 at 2.6 m) (Figure 7). In both cores, these increases were preceded by low extractable:digested ratios (samples 2-07, 3-04, and 3-05) that coincided or overlapped with coarser particle size (Figures 3 and 7). No clear trends with depth for extractable:digested ratios were observed in Core 1, likely due to short core length (Figure 7).

Discussion

Frederick et al. (2019) linked elevated Cd, Cu, Zn, and Pb concentrations and their respective metal:Al ratios in Animas River PM to mining activities using Pb isotopes. Excursions of these elemental concentrations and ratios in the Lake Powell sediment record were concluded to reflect PM from mining impacted tributaries, conveyed primarily *via* snowmelt runoff from higher elevation mined watershed areas. The upper portion of Core 2 corresponded to snowmelt-derived mining-sourced PM underlain by

a coarse layer corresponding to rainfall-derived non-mining-sourced PM. The fact that no additional snowmelt-derived layer was observed led to the conclusion that Core 2 represented approximately one year of deposition. The relatively short length of Core 1 limits interpretation, but it appears to correspond to snowmelt-derived PM, based on its signature corresponding to mining impacted tributaries (Figures 4 and 6).

In contrast to Cores 1 and 2, Core 3 shows two periods (at 0.4 m and 3.7 m depth) of snowmelt-derived PM based on elevated elemental concentrations and ratios (Figures 4 and 6). The 3.4 m of Core 3 that lies between the midpoints of the two snowmelt periods likely represents approximately one year of sediment accumulation, in agreement with the interpretation by Frederick et al. (2019) that the 3.4 m length of Core 2 represented approximately one year of sediment accumulation.

The 0.5 m depth difference between the corresponding coarse grain layers in Cores 2 and 3 is insignificant relative to the large distance (1000 m) between coring sites (Figure 1), especially given that the zone of deposition shifts from year to year in the San Juan River delta, so exact correspondence of layers across these distances may not be expected.

Conclusions

- Elevated values of Cd, Cu, Pb, and Zn and their respective metal:Al ratios, reflecting PM conveyed *via* 2010 snowmelt runoff from higher elevation mined watershed areas, occurred at corresponding depths in all three Lake Powell sediment cores.
- In Core 3, a second layer reflecting PM from mining impacted tributaries was likely deposited during 2009 snowmelt runoff. This layer was observed below the total depth of Cores 1 and 2.
- The 3.3 m of Core 3 that lies between the midpoints of the two snowmelt periods likely represents approximately one year of sediment accumulation, corroborating the interpretation by Frederick et al. (2019) that the 3.4 m length of Core 2 represented approximately one year of sediment accumulation.

References

Frederick, L., and Johnson, W.P. (2019). Source Identification of Particulate Metals/Metalloids Deposited in the San Juan River Delta of Lake Powell, USA. *Water Air Soil Pollut*, 230:128.

Hart, R.J, Taylor, H.E., Antweiler, R.C., Graham, D. D., Fisk, G.G., Riggins, S.G., and Flynn, M.E. (2005). Sediment chemistry of the Colorado River delta of Lake Powell, Utah, 2001: U.S Geological Survey Open File Report 2005-1178, p. 33.

Hornewer, N.J. (2014). Sediment and water chemistry of the San Juan River and Escalante River Deltas of Lake Powell, Utah, 2010-2011. United States Geologic Survey. Open File Report 2014-1096.

Munsell Color x-rite. Munsell Soil Color Charts with Genuine Munsell Color Chips. (2009). Year Revised, 2009, Munsell Color 4300 44th Street, Grand Rapids, MI 49512, USA.

Figures

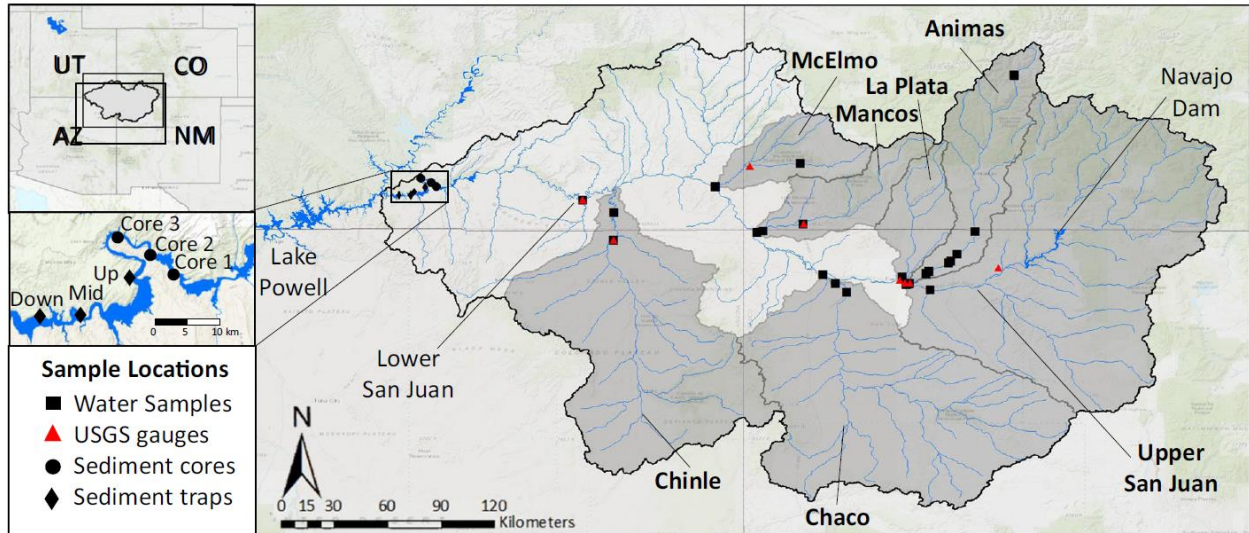


Figure 1: Map of the San Juan Watershed located in Four Corners, USA. Tributary watersheds are outlined and labeled in black. Locations for surface water samples (black squares), USGS stream gauges (red triangles), USGS sediment cores (black circles), and USGS sediment traps (black diamonds) are shown. USGS sediment cores were collected at USGS sites 0364200, 0382699, and 0410700, for Cores 1, 2, and 3, respectively. USGS sediment traps were collected downstream of Mexican Hat, UT at upstream, midstream, and downstream locations.

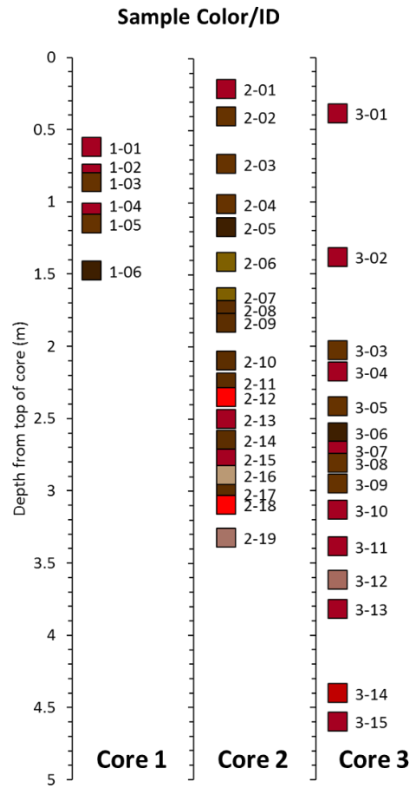


Figure 2: Dominant Munsell color of sediment (Munsell Color x-rite 2009) and sample ID as a function of depth from the top of the core for Cores 1, 2, and 3.

Sample Color/ID and Median Grain Size (μm)

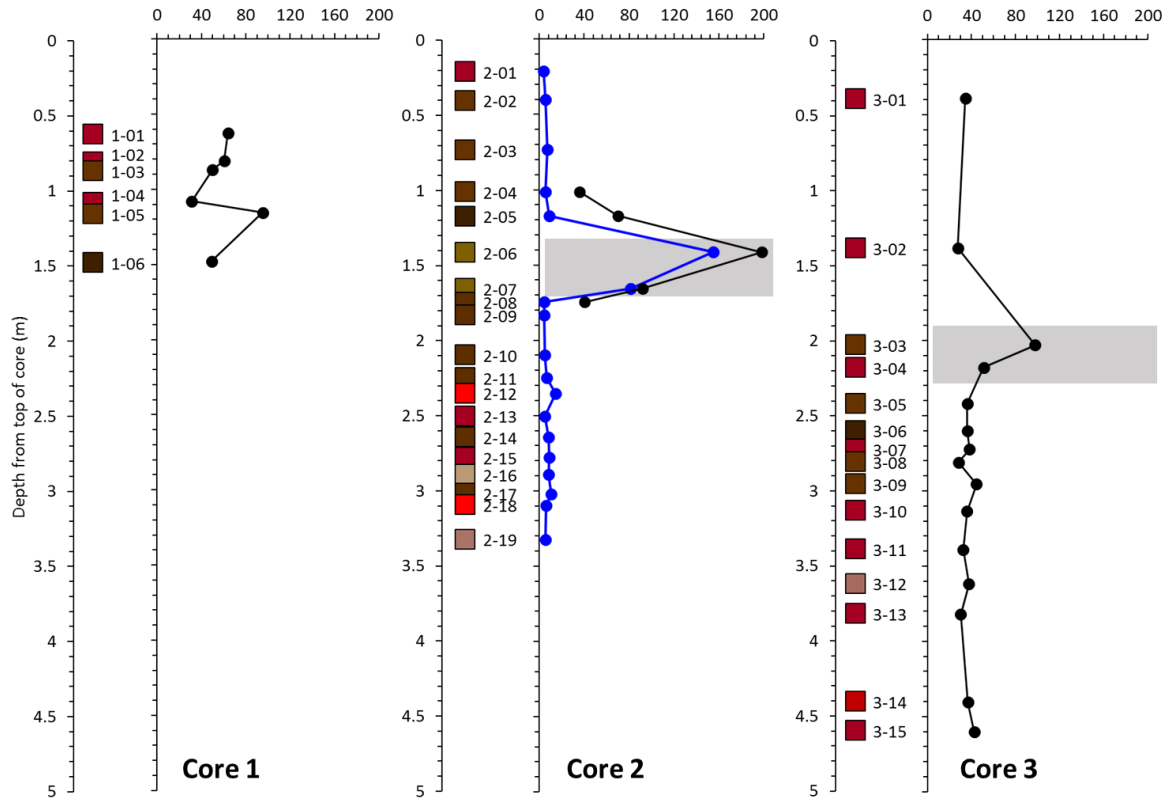


Figure 3: Sample color/ID and median grain size (μm) as a function of depth from the top of the core (m) for Cores 1, 2, and 3. Blue lines denote samples analyzed via Sympa Tec Lixell Helos/KF laser diffraction, while black lines represent Sympa Tec Lixell QICPIC. Shaded gray boxes represent the coarse particle size layer observed in Cores 2 and 3.

Sample Color/ID and Metal:Al Ratios

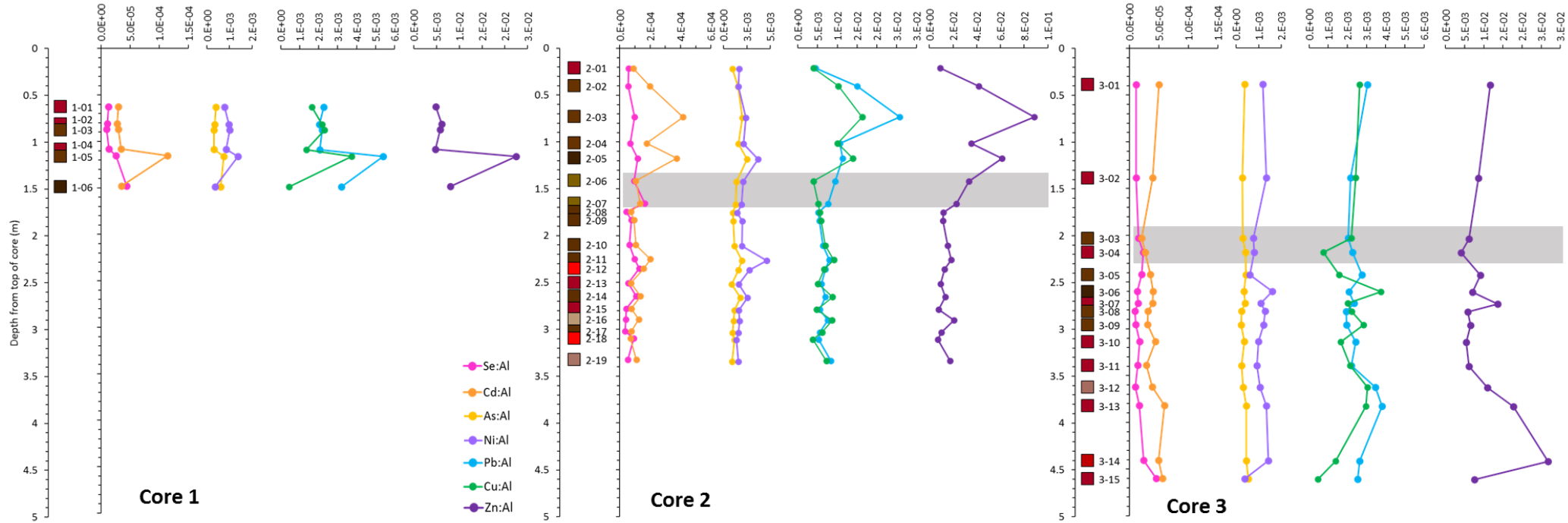


Figure 4: Sample color/ID and ratio of extractable As (gold), Cd (orange), Cu (green), Pb (light blue), Mo (dark blue), Ni (purple), Se (pink) and Zn (dark purple) to Al as a function of depth from the top of the core (m) for Cores 1, 2, and 3. Shaded gray boxes represent the coarse particle size layer observed in Cores 2 and 3.

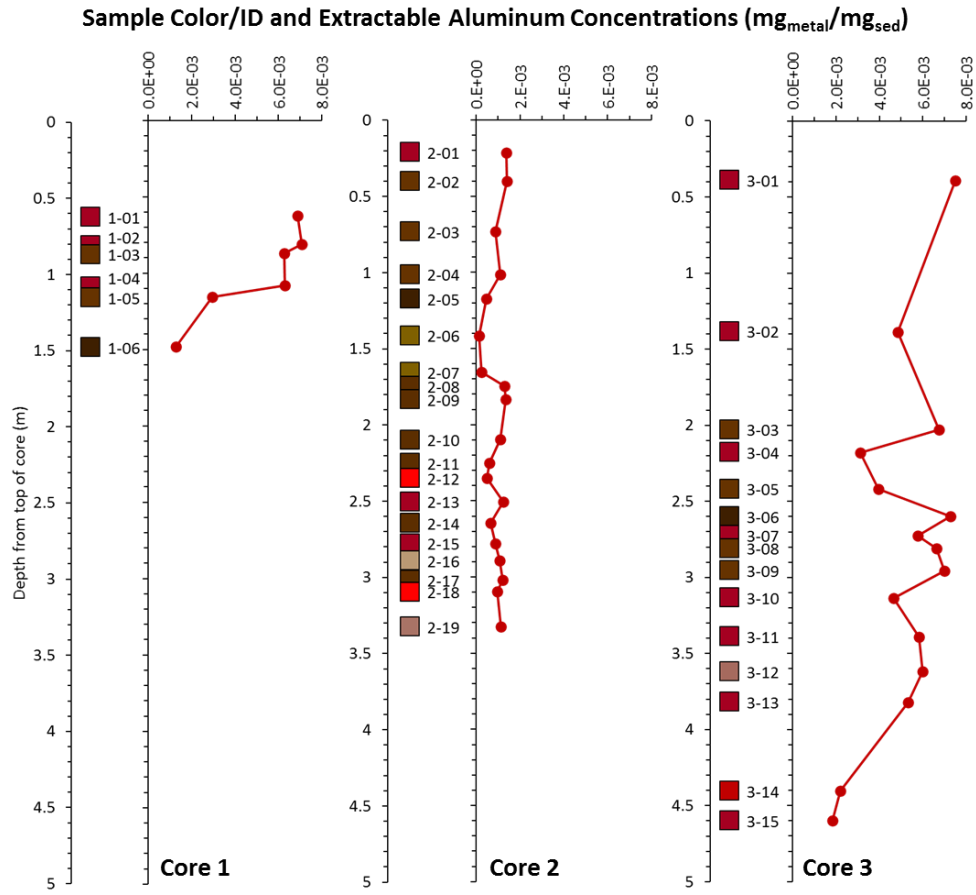


Figure 5: Sample color/ID and extractable concentration of Al (aluminum) as a function of depth from the top of the core (m) for Cores 1, 2, and 3.

Sample Color/ID and Extractable Metal Concentrations ($\text{mg}_{\text{metal}}/\text{mg}_{\text{sed}}$)

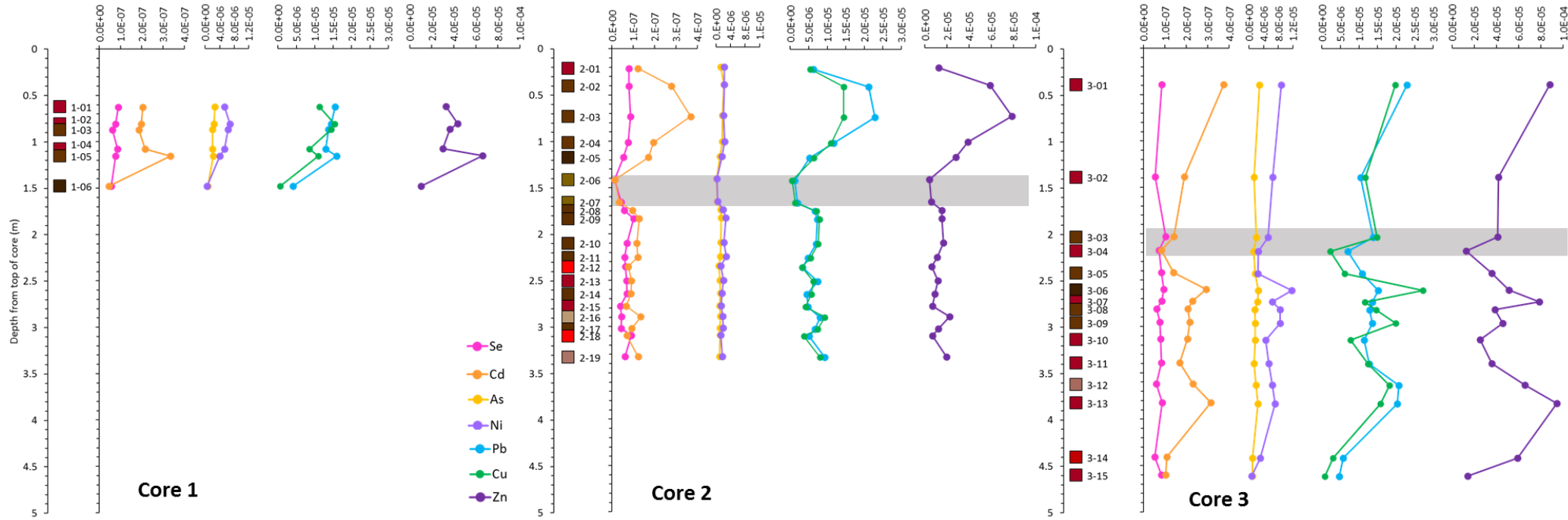


Figure 6: Sample color/ID and extractable concentration of As (gold), Cd (orange), Cu (green), Pb (light blue), Mo (dark blue), Ni (purple), Se (pink), and Zn (dark purple) as a function of depth from the top of the core (m) for Cores 1, 2, and 3. Shaded gray boxes represent the coarse particle size layer observed in Cores 2 and 3.

Sample Color/ID and Extractable:Digested Ratios

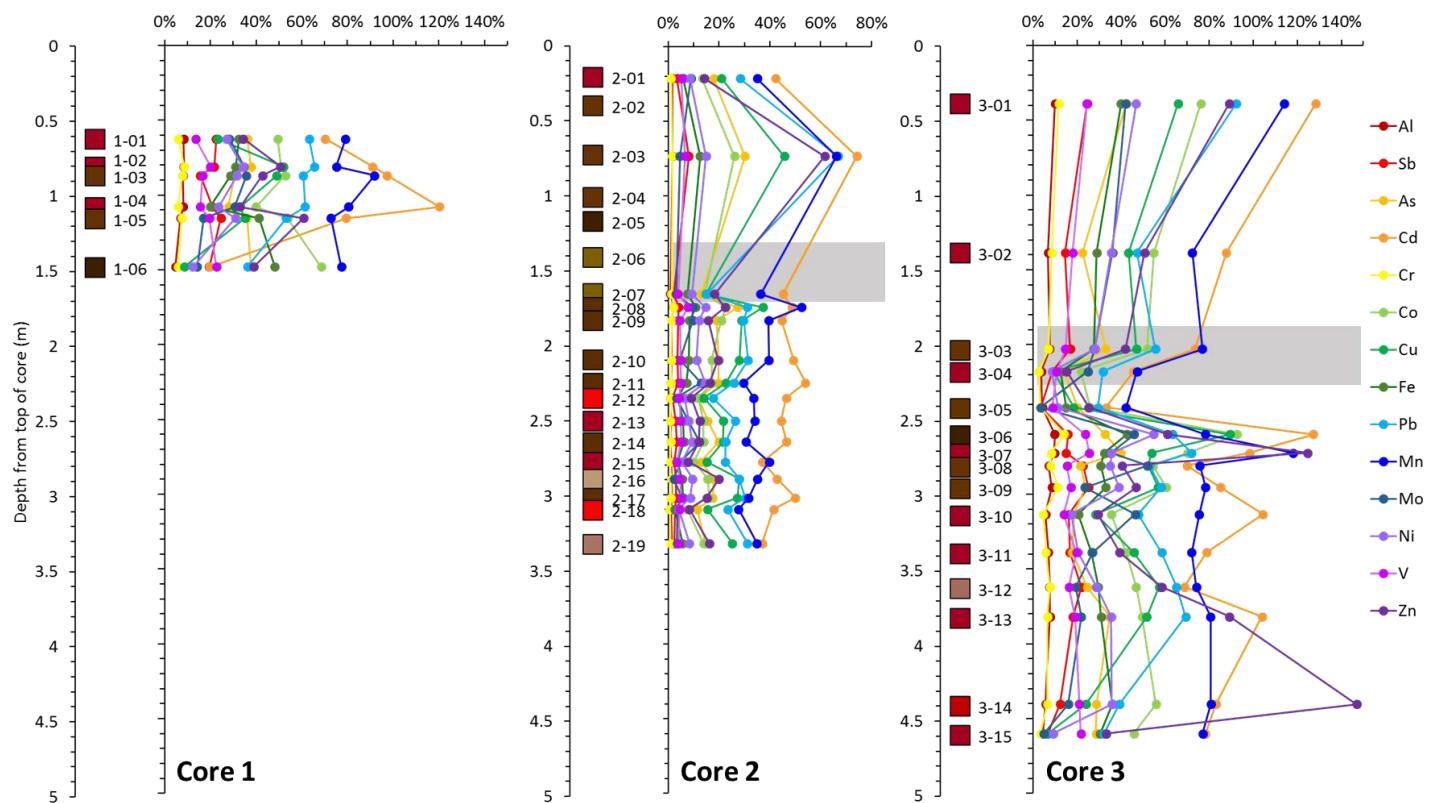


Figure 7: Sample color/ID and percent of metal in extractable phases relative to full digestion as a function of depth from the top of the core (m) for Cores 1, 2, and 3. Shaded gray boxes represent the coarse particle size layer observed in Cores 2 and 3.

Supporting Information

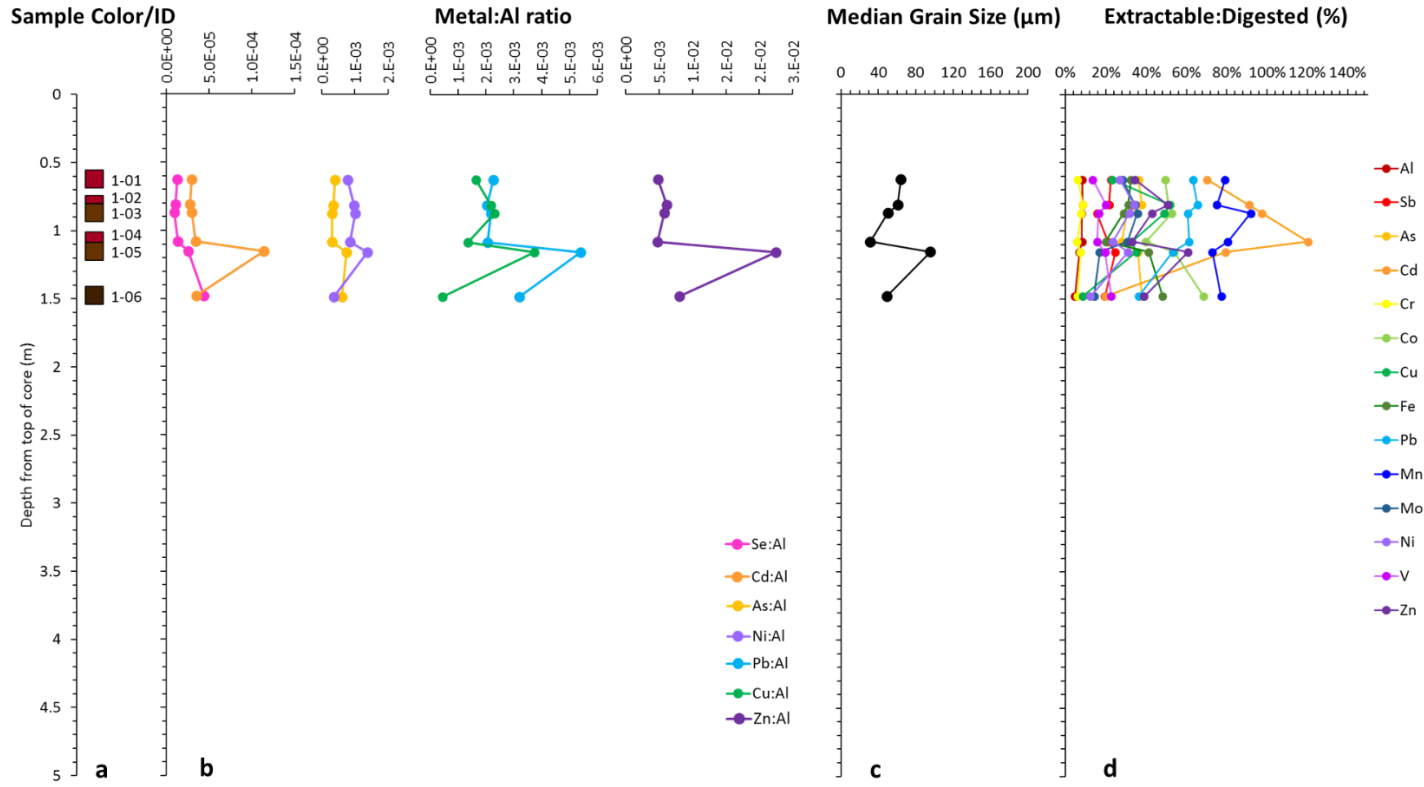


Figure SI 1: Core 1 profiles. **a** Dominant Munsell color of sediment (Munsell Color x-rite 2009) and sample ID as a function of depth from the tope of the core. **b** Ratio of extractable As (gold), Cd (orange), Cu (green), Pb (light blue), Mo (dark blue), Ni (purple), Se (pink), and Zn (dark purple) to Al as a function of depth from the top of the core (m); **c** Median grain size (μm) for samples (black line) as a function of depth from the top of the core (m); and **d** Percent of metal in extractable phases relative to full digestion as a function of depth from the top of the core (m).

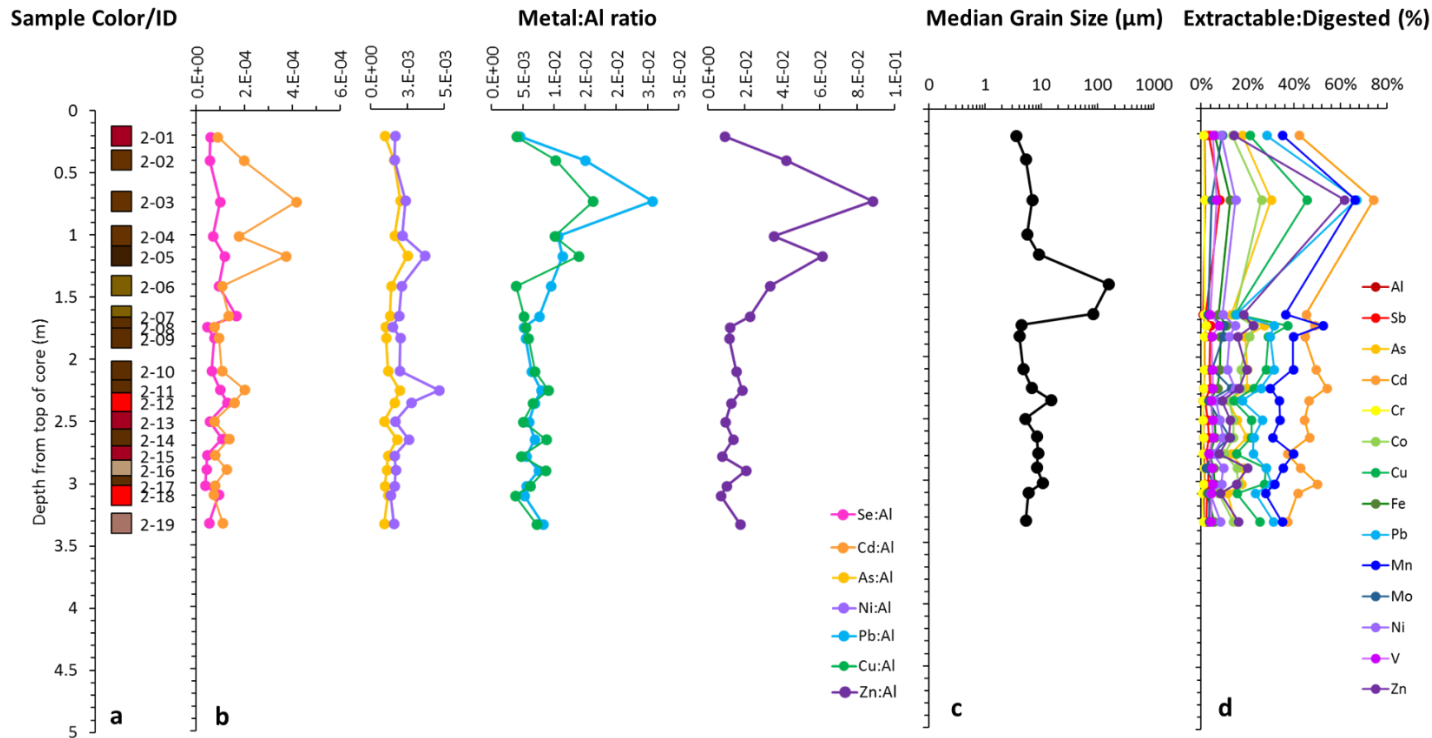


Figure SI 2: Core 2 profiles. **a** Dominant Munsell color of sediment (Munsell Color x-rite 2009) and sample ID as a function of depth from the top of the core. **b** Ratio of extractable As (gold), Cd (orange), Cu (green), Pb (light blue), Mo (dark blue), Ni (purple), Se (pink), and Zn (dark purple) to Al as a function of depth from the top of the core (m); **c** Median grain size (μm) for samples (black line) as a function of depth from the top of the core (m); and **d** Percent of metal in extractable phases relative to full digestion as a function of depth from the top of the core (m). The lesser number of samples in D reflects lesser samples fully digested (Hornewer 2014).

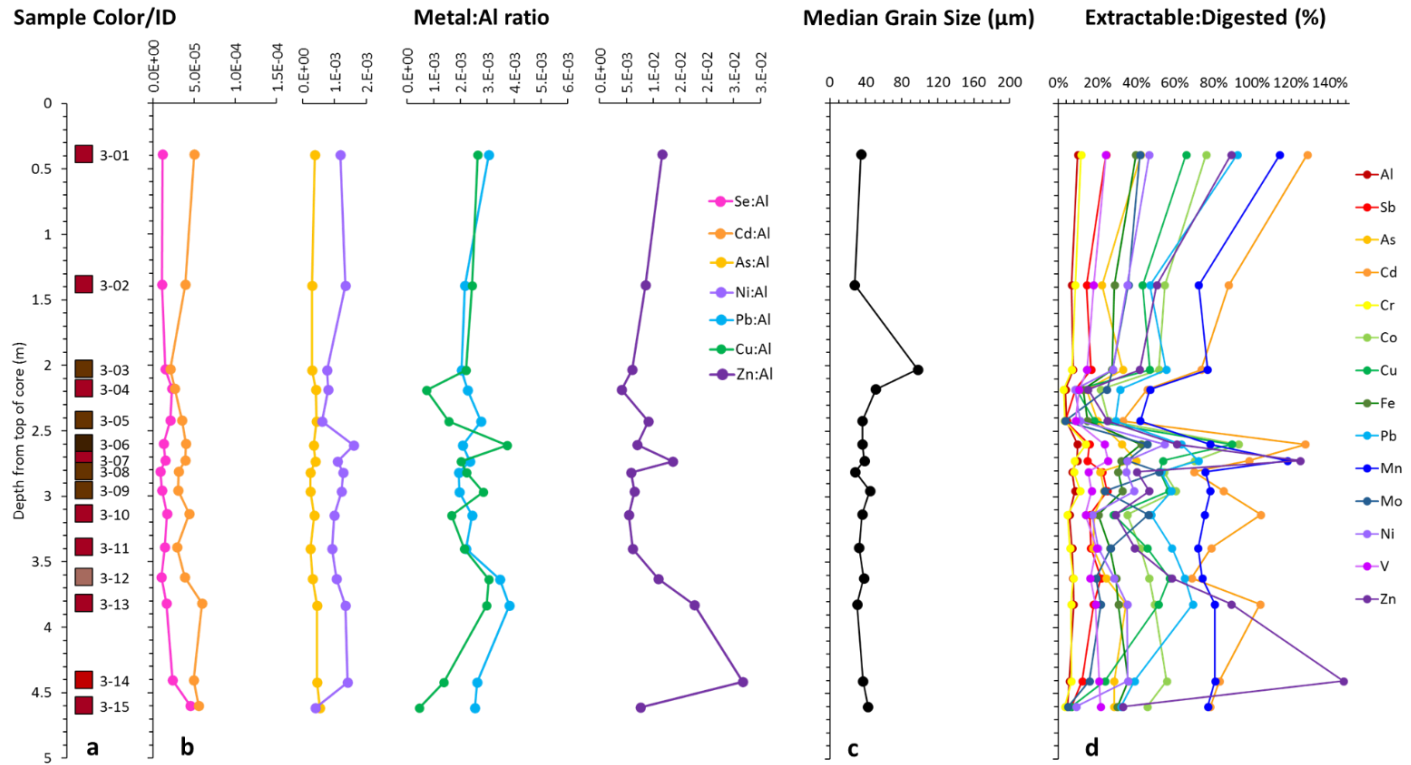


Figure SI 3: Core 3 profiles. **a** Dominant Munsell color of sediment (Munsell Color x-rite 2009) and sample ID as a function of depth from the top of the core. **b** Ratio of extractable As (gold), Cd (orange), Cu (green), Pb (light blue), Mo (dark blue), Ni (purple), Se (pink), and Zn (dark purple) to Al as a function of depth from the top of the core (m); **c** Median grain size (μm) for samples (black line) as a function of depth from the top of the core (m); and **d** Percent of metal in extractable phases relative to full digestion as a function of depth from the top of the core (m).