ABSTRACT

In this study, the sediment of the Dianshan Lake, one of the major freshwater sources for Shanghai, was analyzed at varying depths to determine its historical environmental toxicity profile. Six heavy metal elements (Cd, Cr, Pb, Zn, Hg, and As) were analyzed, using a three step Sequential Extraction Procedure to determine the speciation of each metal, which gives a more accurate profile on their mobility and bioavailability(toxicity). The order of mobility was found to be Cd > Pb > Zn > Cr > Hg > As. Levels of mobile species of Cr, Zn, Hg, and As were found to increase in the past decade, while Cd and Pb have remained constant. Peaks in mobile or total species concentration for Cr, Pb, and As are observable at 9-13 cm depth, corresponding to China's rapid industrialization in the 1980's.

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OBJECTIVES

The objective for this project was to analyze sediment samples from the Dianshan Lake for heavy metals across multiple depths to gauge the historical and present-day trends of each metal. I also aim to use Sequential Extraction Procedure to get a more accurate speciation analysis of each heavy metal, which will be used to predict the sources of contamination, as well as the potential hazard each metal poses to the environment.

3. BACKGROUND

3a. Speciation and Sequential Extraction

Simply knowing the total concentration of heavy metals in a particular sediment sample indicates little about the actual properties and hazard posed by the contaminated sediment. In sediments and soils, heavy metals of the same element do not all have the same environmental properties due to differences in oxidation state and ligation. While some heavy metals are found in their elemental state in sediment, most notably Hg(0), the vast majority of heavy metals in sediment become oxidized and bind to various species in solution, which causes them to precipitate into the sediment as heavy metal salts. The environmental hazard posed by heavy metal salts is directly correlated to the binding strength between each heavy metal ion and its corresponding ligating species, and can be determined based on the conditions required to break this bond and release the heavy metal ions back into solution. For example, carbonate-bound heavy metal ions are weakly bound, as protonation of the carbonate group (a weak base) is all that is required to free the bound metal ion. As a result, carbonate-bound heavy metal ions are released from the sediment if there is a drop in water pH, making them a significant environmental hazard. At the other extreme, silicate-bound heavy metal ions generally are buried deep within the silica matrix, and are very difficult to extract. Extraction of silicate-bound heavy metal ions is only possible by reacting the sediment with boiling hydrofluoric acid, to create volatile fluorosilicates and releasing the bound heavy metal ions. Because of this, silicate-bound heavy metal ions are almost completely environmentally inert, and are generally only measured to gather geochemical data. The composition of the various species of heavy metals present in a sediment sample is referred to as its speciation. Determining the speciation of each heavy metal present in sediment provides information about the potential environmental hazard the sediment poses, as well as the degree of anthropogenic influence – recent human activity usually results in significantly larger quantities of mobile species (1).

Because there are so many different inorganic and organic species that are bound to the heavy metals in the sediment, it would be a daunting task to quantify each individual species' concentration and determine its environmental hazard. Instead, the species are grouped into categories corresponding to the environmental conditions required to disassociate the bound heavy metal from the species. Then, they are quantified by inducing those environmental conditions in the sediment, and measuring how much heavy metal is released. This approach is done using a series of increasingly harsh environmental conditions in which the reagents used necessarily become increasingly caustic to dissolve more tightly bound heavy metal species at each step. This process, which is called Sequential Extraction Procedure (SEP), can involve anywhere from two to twenty steps, depending on the desired specificity.

Sequential Extraction is not a very precise analytical technique. There are many different species that can dissociate in any of multiple steps, depending on the experimental conditions and the reagents used. Additionally, it requires exact conditions, as changing the temperature, pH, amount of solvent used, concentration of reactants, or time spent reacting can affect the amount of heavy metal extracted. Therefore, speciation analysis performed with one SEP cannot be compared to speciation analysis performed with another SEP. To remedy this problem, the Community Bureau of Reference (BCR – now Standards, Measurements, and Testing Program of the EU) recommended the adoption of a standardized 3-step SEP (2), based on the procedure devised by Tessier (3). The scheme for the sequence is below.

Scheme 1. 4-step Sequential Extraction Procedure

Step	Reactants/Conc/Conditions	Targeted species
1	0.11M acetic acid, 10ml	Free ions, Water-soluble, Exchangeable, Carbonates
2	0.5M NH2OH.HCl, pH 2-3, 10ml	Reducible: Iron and Manganese Oxides
3	8.8M H2O2 pH 2, 2.5ml x2, then 1M NH4OAc pH 2, 12.5 ml	Oxidizable: Organics, Sulfides
4*	10ml *aqua regia*(3:1 HCl:HNO3)	Residual: All non-silicate-bound species

*Residual species analysis is not part of the BCR standard.

The first step of this sequence, reaction with dilute acetic acid, will extract all of the most mobile and hazardous species. The most prominent species in this group are carbonates, ionic compounds such as chlorides and hydroxides, neutral species, and cation-exchangeable species (1). These species may be mobilized if there is a change in the ionic concentrations in the lakewater, or if there is a change in pH.

The second step of this sequence, reaction with acidic hydroxylammonium, is designed to reduce any iron and manganese oxides or hydroxides that bind to the heavy metal ions. This species is found in high concentrations in very oxygenated environments. These oxides and hydroxides are good heavy metal sinks because the heavy metal ions can easily displace iron or manganese ions (4). A drop in the oxygen levels or the redox potential of the lakewater has the potential to dissociate the oxides and free the bound heavy metal ions.

The third step of this sequence, reaction with hydrogen peroxide followed by ammonium acetate, is designed to extract all oxidizable species. These include all organically-bound species, as well as sulfides. These species are found primarily when there is a high concentration of organic matter in solution, or if there is an anaerobic environment. If there is a sudden increase in oxygen levels, for example, via dredging, these species will be released into solution (5).

This sequence is very useful, as it corresponds to three major environmental changes that could occur in a lakebed environment(pH change, reduction, and oxidation, respectively) and each reactant does not extract any species that would be extracted in other steps, nor are they strong enough to interact with the strongly-bound residual portion of heavy metals. The fourth solvent used, *aqua regia*, dissolves all residual components except for silicates. Since silicate-bound metals are biologically inert, and because of the conditions required to extract metals from within the silicate matrix, it is common to end the residual step of the sequential extraction procedure with *aqua regia*. Doing this is referred to as taking the *pseudototal* of a sediment sample.

3b. Heavy metal-specific speciation characteristics

As would be expected, each of the different metals studied vary in their binding affinity to various species found in the soil phase. Environmental effects to the soil and lake water will also affect the adsorption and dissolution of each heavy metal differently. Significant amounts of metals bound to unusual species is a useful indicator of human interference in the environment.

Mercury binds very strongly to sulfides, primarily forming the well-known compound HgS, or cinnabar, along with many other sulfur-based compounds. These sulfides are the primary species of mercury found in sediment, and bind strongly enough to be extracted by *aqua regia* (6). Biological activity, at the top layer of sediment, in the presence of excess sulfides, is capable of methylating these complexes and creating methylmercuries, one of the more toxic forms of mercury, though typically these species only comprise about 1% of the total mercury content (7). Methylmercuries bind to organic matter strongly. These methylmercury-organic complexes, however, can be bound by Fe and Mn Oxides depending on the redox conditions of the sediment and lake. Under aerobic conditions, Fe and Mn oxides provide a strong sink for organically-bound Hg; however under anaerobic conditions, the Fe and Mn oxides will decompose and release the bound mercury (7). Mercury is also found in chlorides and hydroxides, both of which are highly mobile species and would be extracted in step 1 (6). Elementary mercury is stable in its neutral form, and is usually found in sediments in some concentration. Elementary mercury is an atmospheric pollutant, and is usually deposited in the sediment through adsorption from the air, though once found in sediment, it is relatively immobile (6).

Arsenic, similar to mercury, has a primary binding form in tightly-bound sulfides, which are only dissociated under strong acids. This usually consists of 50-90% of the total arsenic content. Within its mobile phases, arsenic preferentially binds to iron oxides. Due to this, the redox conditions of the sediment and lake influence the release and containment of arsenic. Under aerobic conditions, complexed Fe(III) can be reduced to Fe(II), resulting in the release of arsenic. A sizeable portion of arsenic also exists as ionically bound and exchangeable species (8).

Cadmium preferentially binds to carbonates (5). Due to this, cadmium is often mobilized after a pH change in the environment. Cadmium also has a moderate affinity for iron and manganese oxides, sulfides, and organic matter, particularly when pH changes or other environmental effects make carbonates less available. Cadmium is especially sensitive to changes in oxygen levels, oxygenation rapidly converts sulfides into iron and manganese oxides, and raises its mobility (9). Cadmium is usually one of the more mobile heavy metal elements in sediment phase.

Chromium has two stable oxidation states: Cr(III) and Cr(VI). Of these two, Cr(VI) is highly toxic, and much more water-soluble, while Cr(III) is a essential micronutrient, and usually precipitates into sediment (10). The iron and manganese oxide phase (though mostly iron) is primarily responsible for the adsorption of free chromium ions, usually after Cr(VI) has been reduced to Cr(III). Chromium is mostly found in sediments in a low-oxygen environment, though it is not uncommon to find both oxidation states bound to sulfides or organic material (11).

Lead preferentially binds to iron and manganese oxides and hydroxides (5), although it also shows some affinity for moderately soluble carbonates and hydroxides, depending on several different factors. Higher pH as well as greater carbon content, for example, leads to greater adsorption. The total amount of lead deposition in the sediment is also dependent on the rate of water flow, greater flow lead to less tightly bound species being formed (12).

Zinc speciation is mainly determined by the redox potential of its environment. Under aerobic conditions, carbonates and iron and manganese (hydr)oxides are favored, while under anaerobic conditions, sulfides are favored (13).

3c. Sediment Dating

It is possible, by radioactive dating, to determine the age of a sediment sample. While this technology was not available to us to determine the age of each sediment sample analyzed, previous studies on the Dianshan Lake have found the rate of sediment accumulation to be fairly stable compared to the rest of China, averaging 0.6cm/year (14). This gives an approximate sense of the year corresponding to the depth of each sediment sample, as indicated in table 1.

Table 1. Depth of sediment in Dianshan Lake by year

Depth of Sediment	Approximate Year
0-3cm	2002-2006
4-6	1997-2002

7-9	1992-1997
10-12	1987-1992
13-15	1982-1987
16-18	1977-1982
19-21	1972-1977
22-23	1968-1972

There are two key periods of sedimentation of concern in this study. The first comes from depths 9-16cm, which corresponds to the 1980's, when China was undergoing rapid industrialization and opening its borders to foreign commerce. During this period, China's environmental protections were weak or nonexistent. Accordingly, we wanted to look for higher pollution levels, indicating unmanaged heavy metal waste disposal, either by dumping into the lake or by burning. The second is the first 5 cm, which corresponds to the past few years, and correlates to both the effectiveness of China's environmental practices, but also to the immediate hazard posed to the greater Shanghai area by these heavy metals.

3d. Toxicity Standards

Currently, there are no rigid standards for maximum permissible concentration of mobile or total species for lake sediment. The adsorption and release of heavy metals to sediment does so based not only on the species binding each metal, but also on the size of each sediment particle (15), the size of the water pores between each particle (5), total organic carbon content (16), and the environmental conditions surrounding the sediment layer (12). Several attempts have been made to standardize the maximum permissible concentrations, but because of the vast difference speciation makes on environmental impact, progress in this field has been very difficult (17). The most commonly used assays to determine environmental toxicity are a very mild extraction with ion-rich water, to extract the most mobile and dangerous species of heavy metals, or by exposing sediment samples to benchmark organisms, and observing their behavior. A more recently-developed but useful technique is determining community-based sediment quality, by assessing the background levels of pollution for a certain area (which should come off in the residual fraction), as well as certain other variables (e.g. TOC, pH), and then looking for heightened levels of pollution and unusual speciation compared to the background levels in various key locations (18). There is even less consensus on the maximum permissible concentrations for each fraction of the BCR extraction sequence.

3e. Lakebed environment characteristics

Much can be learned about the environment at the lakebed by analyzing the results of heavy metal speciation. Reducing environments, i.e. anaerobic, are caused by putrefaction, sewer waste, or contamination, and tends to have lots of free sulfides. Sulfides, when bound to metals, will show up in either steps 3 or 4, as well as having implications for the biological activity found there (e.g. Hg-methylating bacteria is only found near high concentrations of sulfides) (7). Likewise, aerobic environments promote formation of Fe/Mn oxides and hydroxides. Acidic conditions promote the formation of chlorides and sulfides, while neutral or alkaline conditions favor carbonates (19).

3f. Site-specific background

The Dianshan Lake is a critical source of fresh water to Shanghai and its surrounding area, being responsible for supplying 30% of Shanghai with fresh water. Unfortunately, Dianshan Lake and its downstream subsidiaries suffer from high pollution levels, mainly as a result of coal power plants, industrial waste and a lack of proper sewage disposal (20). Until a recent initiative to clean up the water systems of Shanghai, water from the Dianshan Lake had been classified as undrinkable (21). Currently, the major pollutants of concern in the lake are nitrogen and phosphorus, from sewage and agricultural runoff, which have caused severe eutrophication in the past. Since China has embarked on a more environmentally-friendly campaign, identifying potential environmental hazards, as well as evaluating the merits of China’s environmental policies has become a chief concern for both government officials and the general populace, which is taught from an early age to never drink any faucet water without boiling it first. Another serious environmental issue for China is heavy metal contamination, which arises mainly due to improper industrial disposal techniques. This issue affects both the air quality of China as well as the water quality, and in many ways is a lot more serious a concern for China’s citizens, as unlike organic pollutants, heavy metals will accumulate in the body. As China takes steps to reduce its emissions, it is important to analyze the effects of its actions to judge their effectiveness. By analyzing the sediment of Dianshan Lake for heavy metals at various depths, we can determine the historical human influence on the environment, as well as the present-day hazard they pose.

4. EXPERIMENTAL

4a. Experimental Sequence

A modified BCR procedure was followed. .25g of sediment was ground by mortar and pestle and subjected to a 4-step Sequential Extraction Procedure. All samples were diluted to 25mL with 1:10 conc. HNO3:water solution. Samples were analyzed by Atomic Absorption Spectrometer (Thermo by Electron Corporation, model S4AA) for elements Cd, Cr, Pb, and Zn, as well as Atomic Fluorescence Spectrometer(AFS-930, Chinese model) for elements As and Hg. Blanks were taken at every step.

Exchangeable and Acid-Soluble Fraction

10mL of 0.11M acetic acid was added to the sediment sample in a test tube. The mixture was shaken for 16 hours at room temperature then centrifuged at 3000 rpm for 20 minutes. The liquid phase was removed and stored at 4C, and the remaining sediment was washed with 20mL ultrapure water. The mixture was shaken for several minutes, then centrifuged at 3000 rpm for 15 minutes. The liquid phase was discarded, and the sediment residue was stored at 4C for further analysis.

Reducible Fraction

10mL of 0.5M NH2OH.HCl adjusted to pH 2 with 1:10 concentrated HNO3:water solution was added to the remaining sediment. The mixture was shaken for 16 hours at room temperature then centrifuged at 3000 rpm for 20 minutes. The liquid phase was removed and stored at 4C, and the remaining sediment was washed with 20mL ultrapure water. The mixture was shaken for several minutes, then centrifuged at 3000 rpm for 15 minutes. The liquid phase was discarded, and the sediment residue was stored at 4C for further analysis.

Oxidisable Fraction

5 mL of 8.8M H2O2 adjusted to pH 2 with conc. HNO3 was added to the remaining sediment in two parts, the first 2.5mL was added at room temperature and allowed to react for an hour, then the second 2.5mL was added and allowed to react for an hour at 85C. Then, 12.5mL of 1M ammonium acetate adjusted to pH 2 with conc. HNO3 was added. The mixture was shaken for 16 hours at 85C then centrifuged at 3000 rpm for 20 minutes. The liquid phase was removed and stored at 4C, and the remaining sediment was washed with 20mL ultrapure water. The mixture was shaken for several minutes, then centrifuged at 3000 rpm for 15 minutes. The liquid phase was discarded, and the sediment residue was stored at 4C for further analysis.

Residual Fraction

10 mL *aqua regia* (3:1 HCl:HNO3) was added to the remaining sediment and boiled for an hour. The mixture was centrifuged at 3000 rpm for 20 minutes. The liquid phase was removed and stored at 4C, and the remaining sediment was washed with 20mL ultrapure water. The mixture was shaken for several minutes, then centrifuged at 3000 rpm for 15 minutes. The liquid phase was discarded, and the sediment residue was stored at 4C for further analysis.

4b. Samples Analyzed

Figure 1: Sampling sites on the Dianshan Lake

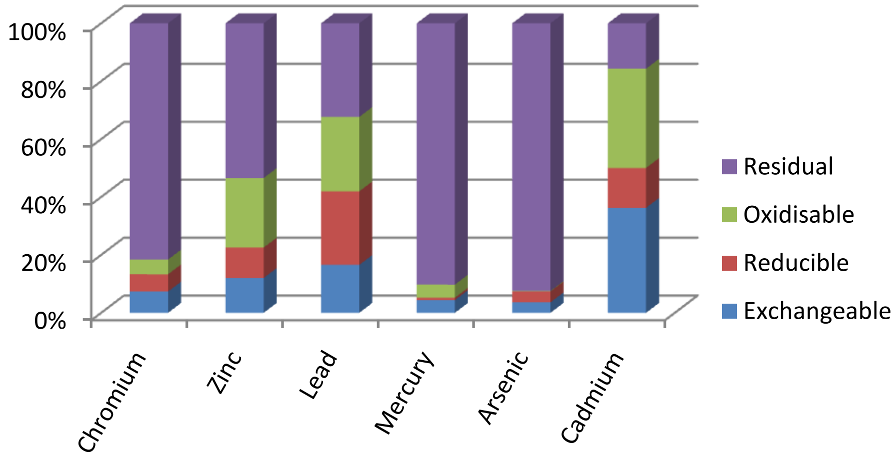
Samples were analyzed from sites 1, 4, and 5 of the Dianshan Lake, as shown in Fig. 1. All samples were taken in September 2006. Each core sample taken was 23 cm deep, and divided out into 23 1cm samples. Four different datasets were taken, one for sites 1 and 4, and two for site 5. The dataset for site 1 consisted of 12 data points, at 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22 cm. The dataset for site 4 consisted of 5 data points, at 4, 8, 12, 16, and 19 cm. The first dataset for site 5 consisted of 6 data points, at 1, 5, 9, 13, 17, and 21 cm. The second dataset for site 5 consisted of 17 data points, at 2, 3, 4, 6, 7, 8, 10, 11, 12, 14, 15, 16, 18, 19, 20, 22, and 23 cm.

5. RESULTS AND DISCUSSION

5a. Total Element Mobility

The greatest advantage of Sequential Extraction Procedure is its ability to discern a substrate's ecological hazard in a way that has immediate, practical application. The species of heavy metal extracted in the first fraction are the most mobile and bioavailable, as well as the most indicative of anthropogenic activity, so this fraction is the most useful to examine. As expected, Cadmium has the highest relative concentration of exchangeable and acid-soluble species, followed by lead and zinc(Fig.3a). Iron and Manganese oxides, found in fraction 2, are important geological sinks for heavy metals, but can dissociate inside a reductive environment. Lead had the highest relative concentration of reducible species, followed by Cadmium and Zinc(Fig.3b). Fraction 3, which contains heavy metals bound to sulfides and organic material, also extracted a significant amount of Cadmium, Lead, and Zinc(Fig.3c). The overall series of element mobility is (in order of decreasing mobility) Cd > Pb > Zn > Cr > Hg > As. The low residual values for lead and zinc indicate their sources are anthropogenic, whereas the relatively high residual values for As and Hg indicate low human activity(Fig.3d). Total speciation results for each element are summed up in Fig.2.

Figure 2. Total speciation of all metals studied



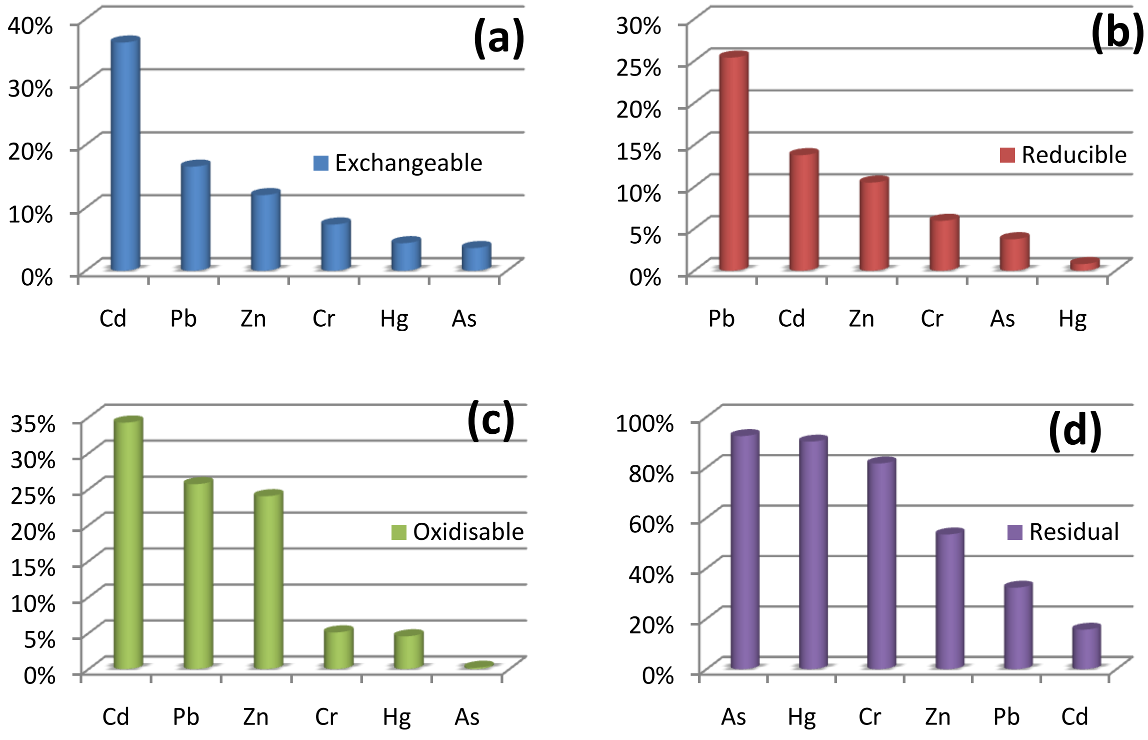


Figure 3(a-d). Element affinity to each of the 4 steps of the modified Sequential Extraction Procedure

5b. Speciation of Lead

The distribution of lead species over time shows several interesting characteristics. Lead is predominantly bound to manganese oxide species, occurring in at least 30% of all lead tested except in site 5-2, which has a high concentration of residual and oxidizable species(Fig.6). This, along with the significantly higher total concentration of lead in site 5-2 seems to imply that sample 5-2 is contaminated. The data indicates that there is a fairly even distribution of lead over time, though there is a measurable increase (200-600 mg/kg) in total lead concentration in all samples from cm 13 to cm 9(Fig.4b). In samples 1 and 4, this increase is seen in the reducible fraction, while it is seen in the oxidizable fraction in sample 5-2 and the acid-soluble fraction in sample 5-1(Fig.5). This depth corresponds to the 1980s, where China was beginning to industrialize, so we should expect to see increases in pollution around this area. Acid-soluble species of lead are the second-most common species, though the recent drop in this lead species from cm 8 to cm 1 may indicate improved lead disposal practices. Lead is the second most mobile species, and its low residual content indicates a primarily anthropogenic origin, though the constant levels of lead throughout time most likely indicates that the lead is primarily deposited by airborne contaminants being absorbed into the lake and then the sediment, rather than by illegal dumping into the lake. The exception is from cm 13 to cm 9, where a significant increase in both total and reducible lead content most likely indicates some amount of illegal dumping occurred of a particular type of industrial waste during that timeframe. Total mobile content varies from between 1500mg/kg to 2500mg/kg(Fig.4a), which is a dangerously large amount of lead, exceeding most maximum permissible concentration standards by at least tenfold (17).

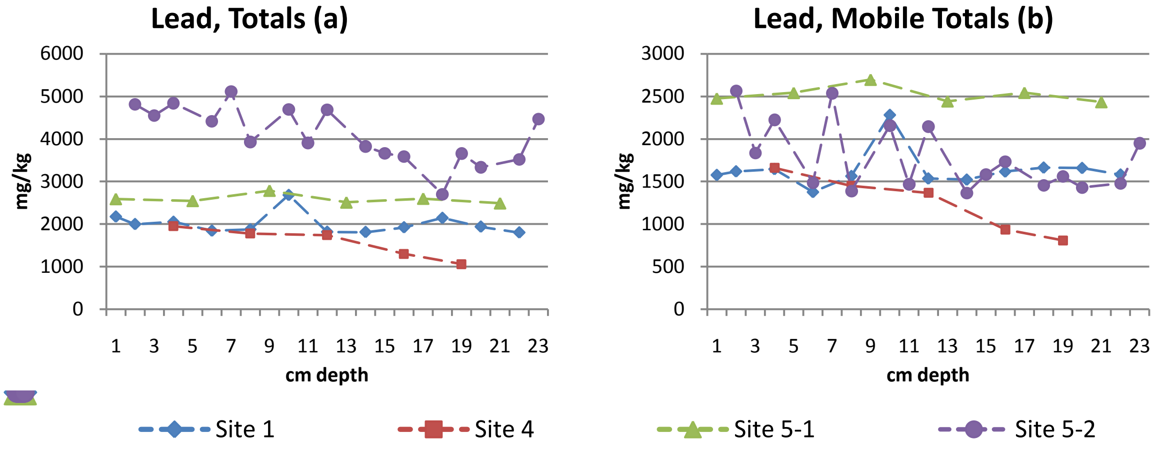


Figure 4. Total concentration values for lead, (a) including residual fraction, (b) only including the first 3 mobile fractions

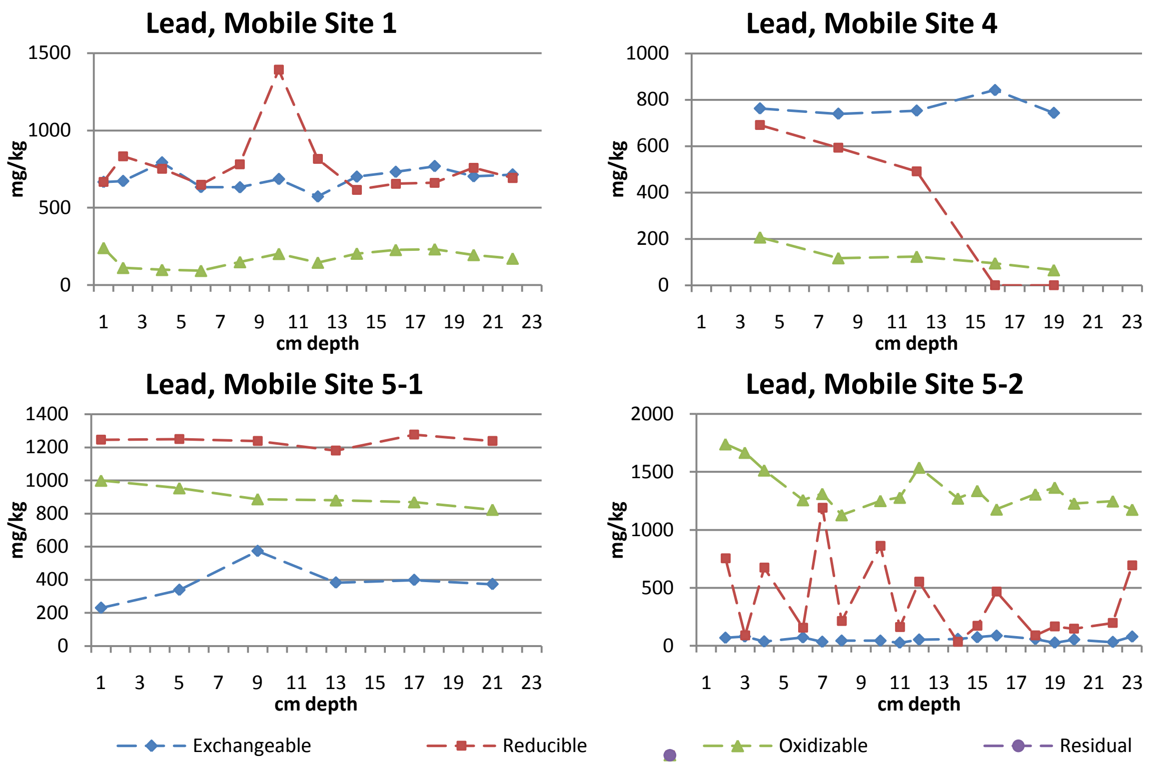


Figure 5. Concentration values for each mobile species of lead over time, separated by sample site

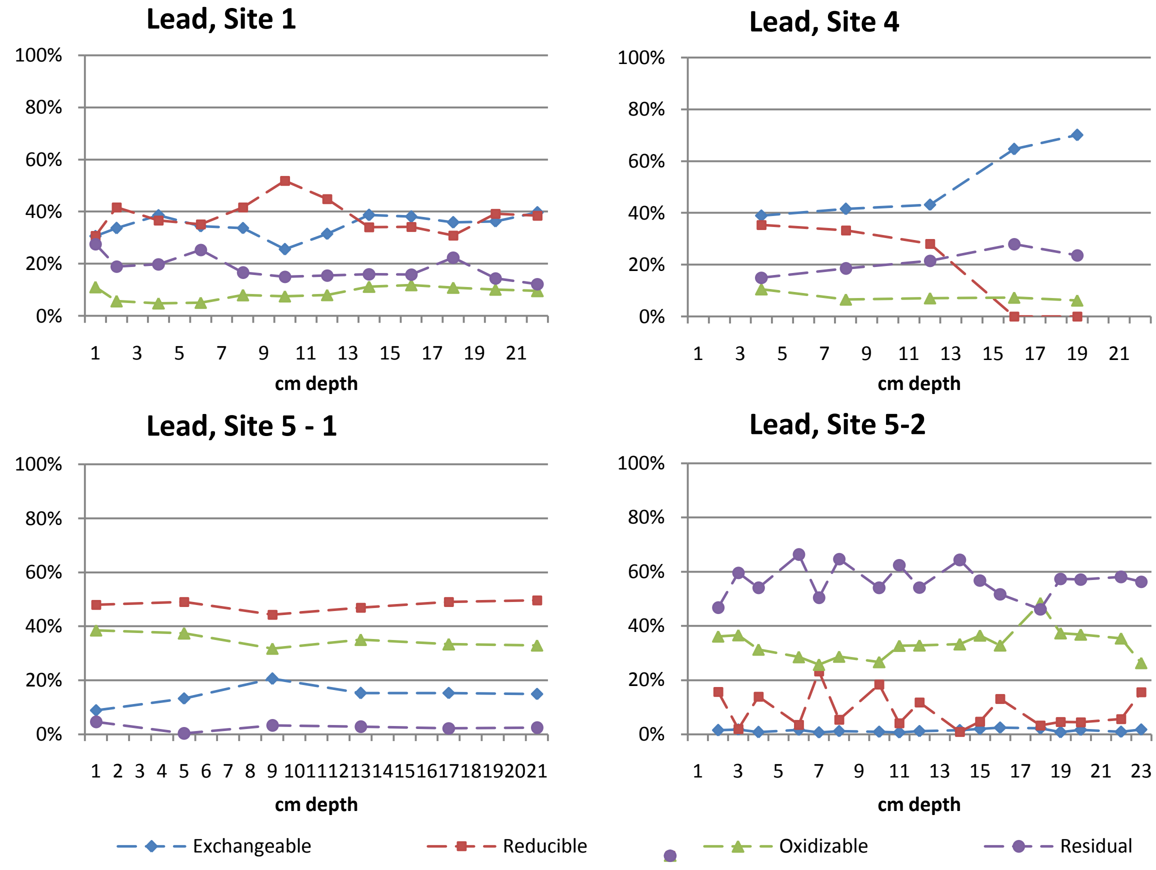


Figure 6: Speciation percentages of lead over time, separated by sample site

5c. Speciation of Chromium

Chromium is present in the lake sediment primarily in residual form, consisting of 65-90% of the total chromium species(Fig.9). In all 4 samples, the residual chromium content slightly declines towards the most recent sediment samples, indicating increased activity in the past several years. This could also be caused by capillary action, which moves the highly water-soluble Cr(VI) species toward the sediment surface (10). Although Chromium most preferentially binds to Iron and Manganese oxides, there is a significant portion of the sample found in the exchangeable phase. This implies a significant environmental hazard, since usually this fraction corresponds to Cr(VI) complexes. Oxidizable Chromium complexes were not found in sites 1 and 4, but were found in both samples of site 5(Fig.8). A small bump in mobile chromium levels is observed in sites 1 and 4 around 10-13 cm depth, possibly correlating to China's increase in industrialization. Total Chromium levels, and total mobile chromium levels slightly rise over time, from 45-90 mg/kg to 75-105mg/kg and from 6-12mg/kg to 10-14mg/kg, respectively(Fig.7).

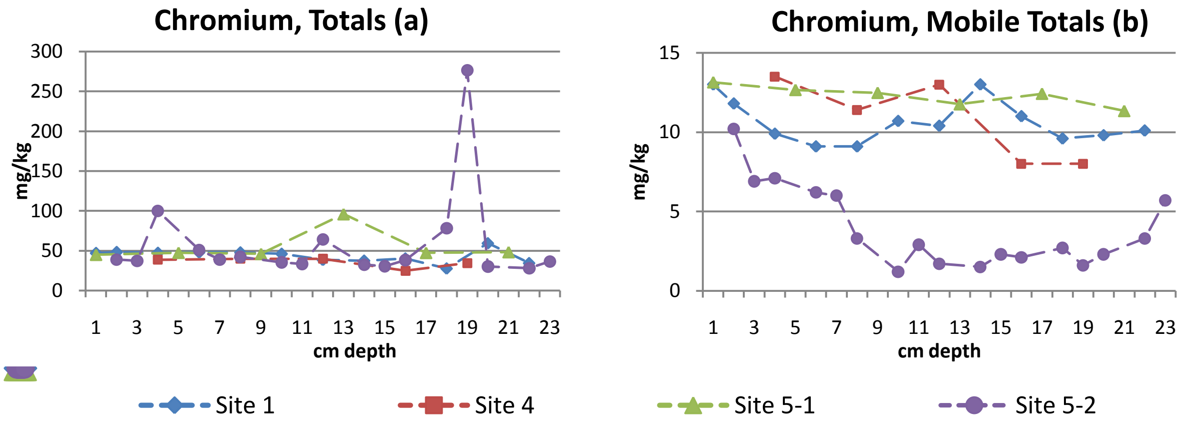


Figure 7.Total concentration values for chromium, (a) including residual fraction, (b) only including the first 3 mobile fractions

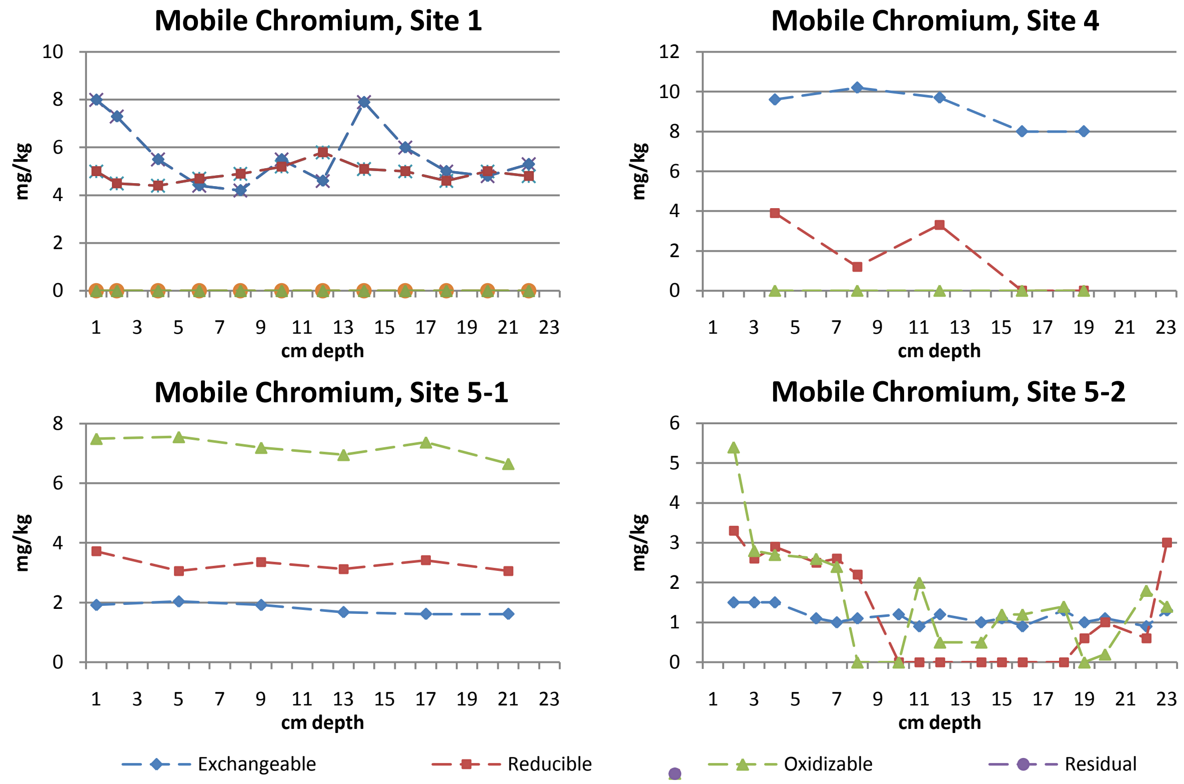


Figure 8. Concentration values for each mobile species of chromium over time, separated by sample site

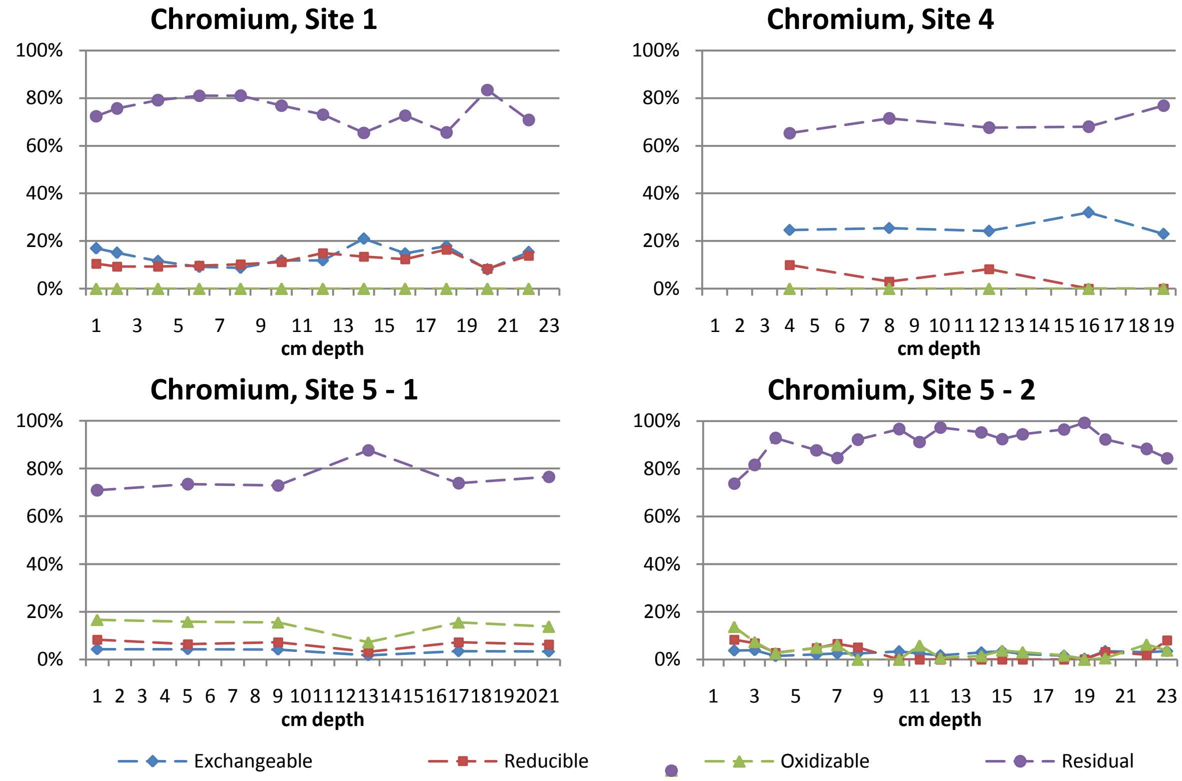


Figure 9. Speciation percentages of chromium over time, separated by sample site

5d. Speciation of Zinc

Zinc is the third most mobile element. Most of the metal is extracted in the residual fraction (40-70%), but the remainder is split between the other three mobile fractions, depending on the sample site(Fig.12). Sulfide complex formation was favored in Site 5, while exchangeable species were favored in Sites 1 and 4(Fig.11). This demonstrates the lake's geochemistry is not homogenous. But, since zinc is a redox-active element, the dominance in species formation between carbonates and sulfides clearly indicates an anaerobic environment across the entire lake. The split between carbonates and sulfides most likely indicates pH differences between sampling sites, as lower pH should lead to increased sulfide formation. Sites 1 and 4 may possibly have higher pH than site 5. Over time, there can be seen a steady decline in the residual species of zinc in all the sample sets, complemented by a steady increase in both the total level of zinc as well as each individual mobile phase(Fig.12). The total mobile phase levels have increased from 20-40mg/kg in cms 19-23 to 45-65mg/kg in cms 1-4(Fig.10b). This is strong evidence of human interference, which has continued unabated up until the time when the samples were taken. It may also demonstrate the slow, spontaneous changes in zinc's speciation from mobile species to less mobile species.

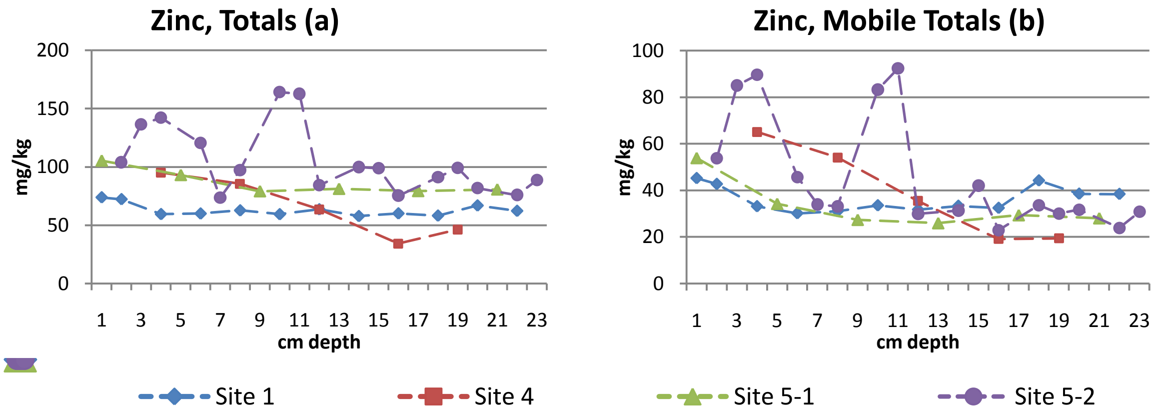


Figure 10. Total concentration values for zinc, (a) including residual fraction, (b) only including the first 3 mobile fractions

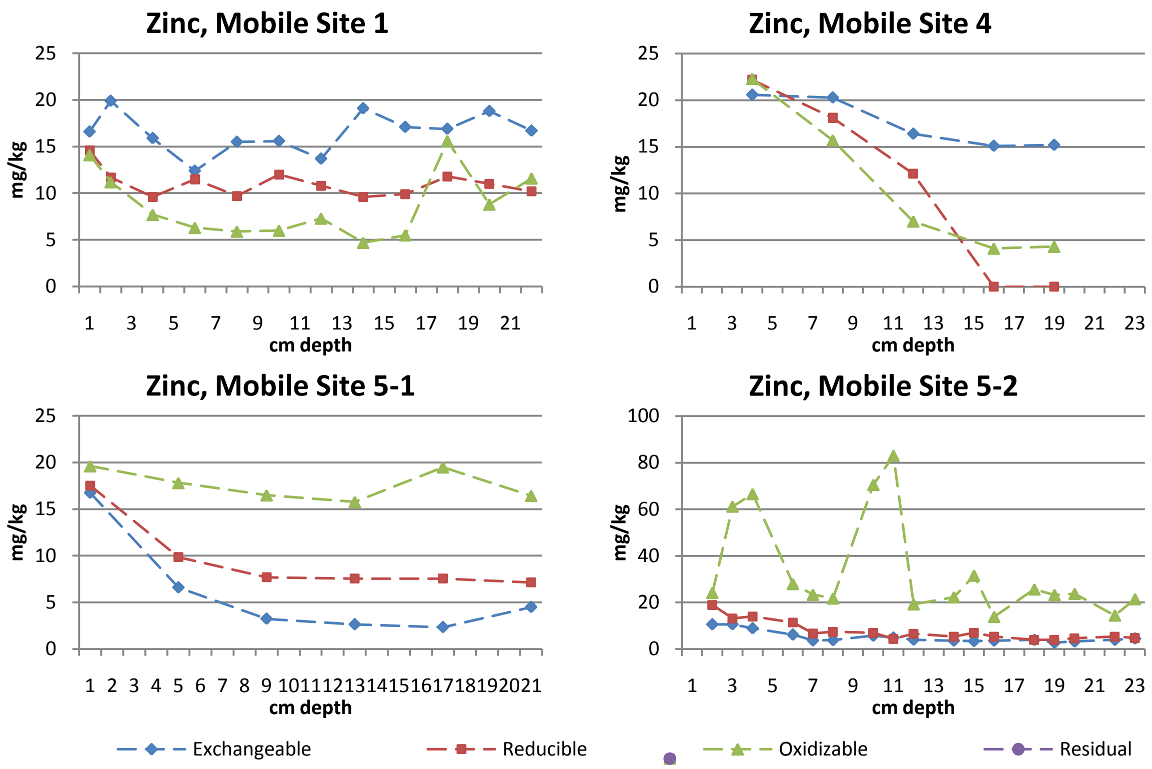


Figure 11. Concentration values for each mobile species of zinc over time, separated by sample site

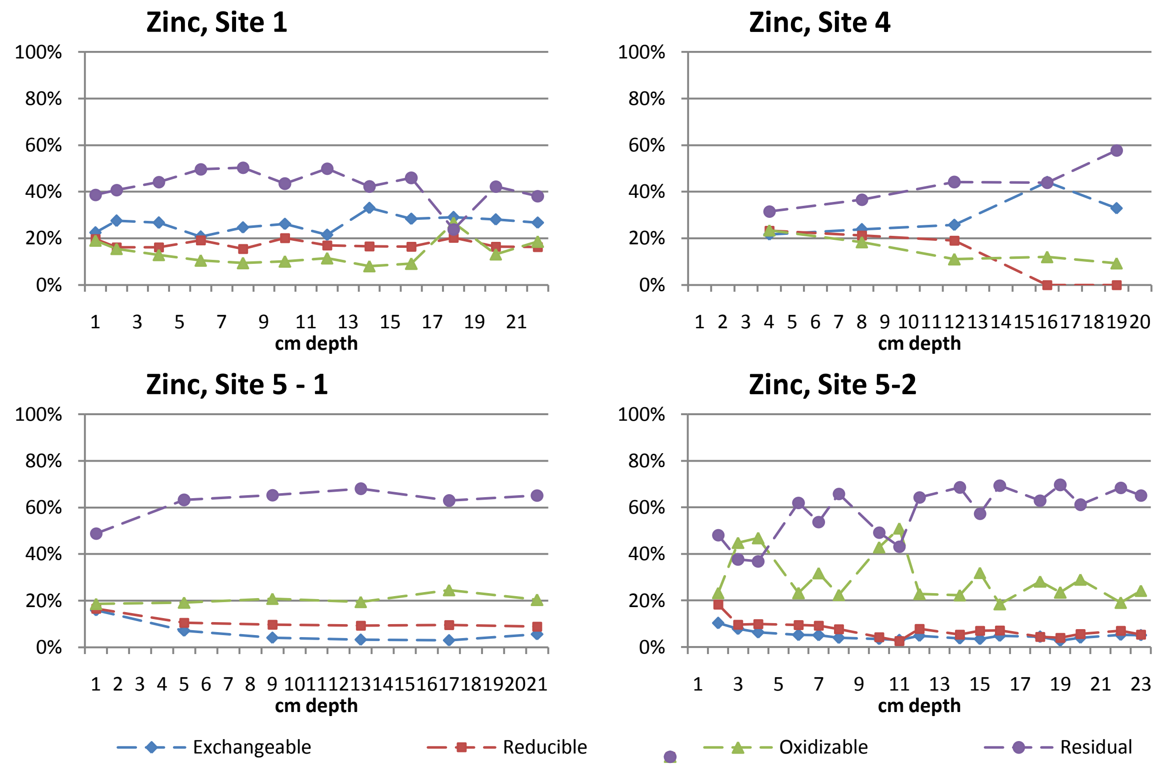


Figure 12. Speciation percentages of zinc over time, separated by sample site

5e. Speciation of Cadmium

Cadmium is the most mobile heavy metal of all those studied, with the residual fraction only comprising 20-40% of the total(Fig.15). Cadmium is stable in all three mobile phases studied, which accounts for the wildly differing results between sites and even between the two separate runs of site 5. It can be theorized from this that Cadmium is in constant equilibrium between binding species, even after the sediment has been isolated. The dominant species of Cadmium are exchangeable/carbonates for site 5, and oxidizable species in sites 1 and 4(Fig.14). Iron and Manganese oxides are much less common, only consistently being above 20% in sample 5-1(Fig.15). Cadmium, like zinc, is a redox-sensitive element, which means its binding preferences are determined by the relative level of oxygen in the environment. Cadmium binding sulfides and organics more than Fe/Mn oxides across all 3 sites indicates an anaerobic environment. However, unlike zinc, the split between different sites of sulfides and carbonates implies that site 5 has a lower pH than sites 1 and 4. The totals for Cadmium stay relatively constant at 100-600 mg/kg, except for site 4, which has a constant, sharp slope upwards. In the first three cm of sediment, though, there is a significant drop in the total mobile phases, for all the samples except site 4(Fig.13). This indicates improved cadmium disposal practices in recent years.

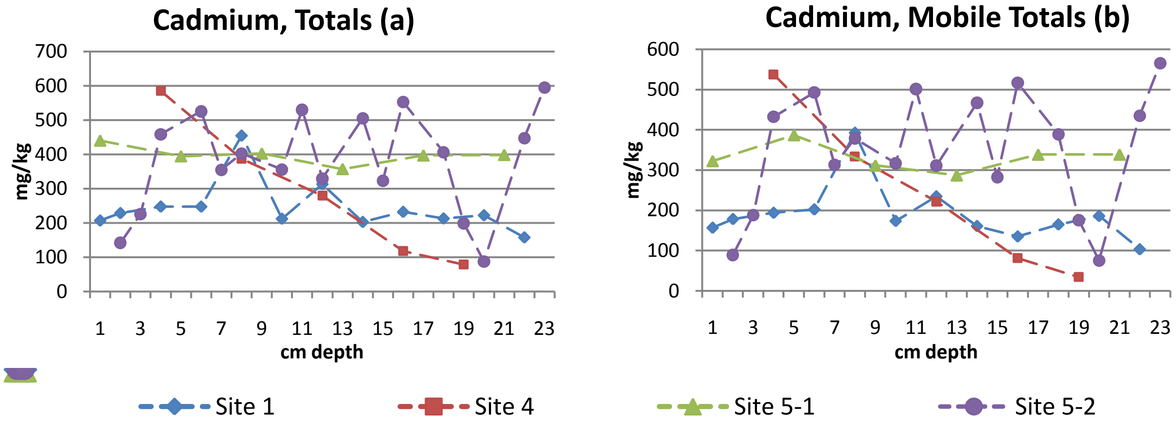


Figure 13. Total concentration values for cadmium, (a) including residual fraction, (b) only including the first 3 mobile fractions

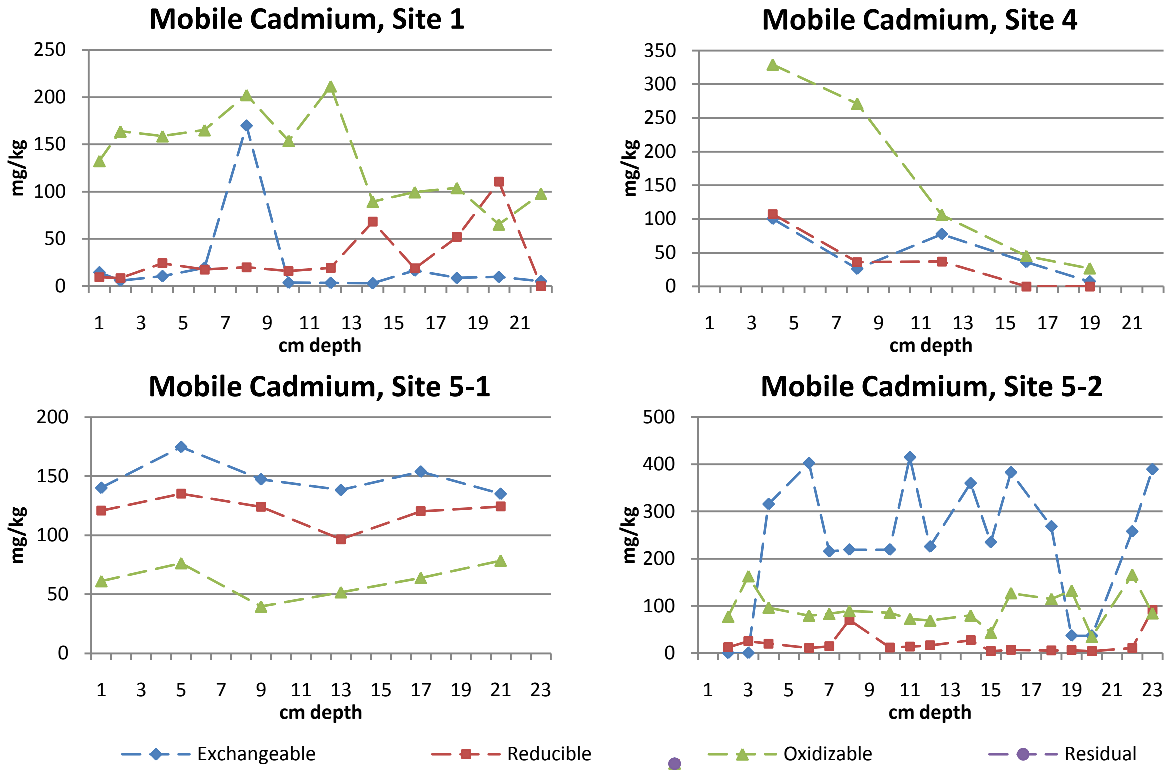


Figure 14. Concentration values for each mobile species of cadmium over time, separated by sample site

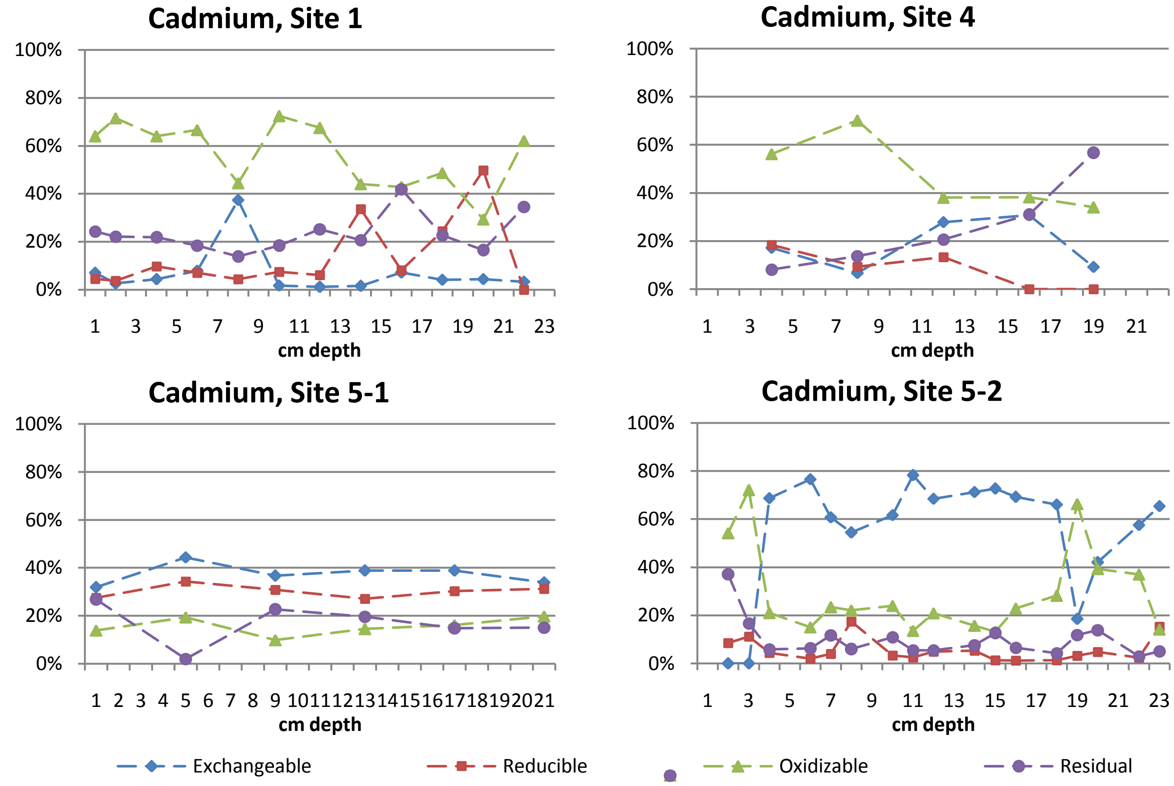


Figure 15. Speciation percentages of cadmium over time, separated by sample site

5f. Speciation of Mercury

Mercury is the second most immobile element. With the exception of site 4, which is believed to be contaminated in step 1, mercury has a residual component of 90-99%(Fig.18). Mercury is most often present in sediment as tightly-bound sulfides, which are environmentally safe, and come off in the residual phase. Other forms of mercury are much more environmentally toxic, for example, methylmercury, which is one of the most hazardous heavy metal-based neurotoxins, binds to organic compounds, and would come off in step 3, while Hg(0), an atmospheric pollutant, would come off in the exchangeable fraction. There are small amounts of each of the mobile mercury species. The oxidizable and reducible mercury species each have a constant value around 10 mg/kg, with values varying for the exchangeable species(Fig.17). It is also noticeable that each sample, except for site 4, records a significant jump in the total mobile content of mercury within the first three cm depth(Fig.17). This could correspond to one of two explanations: there is either some human activity in the past few years, or more likely, this is the natural behavior of mercury at this depth, where lightly-bound mercury species are converted over several years into residually-bound sulfides. Site 5 shows some interesting behavior – there is practically no exchangeable mercury, while the oxidizable fraction dominates the mobile species(Fig.17). This is presumed to be due to mercury-methylating bacteria, which thrives in high sulfide, low oxygen environments. Total mobile mercury content is found to be around 20-40 mg/kg(Fig.16b).

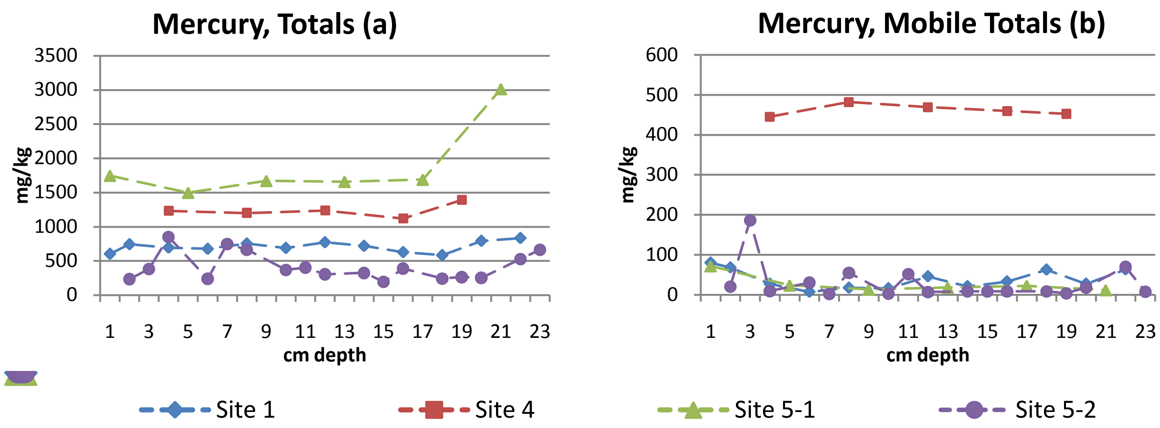


Figure 16. Total concentration values for mercury, (a) including residual fraction, (b) only including the first 3 mobile fractions

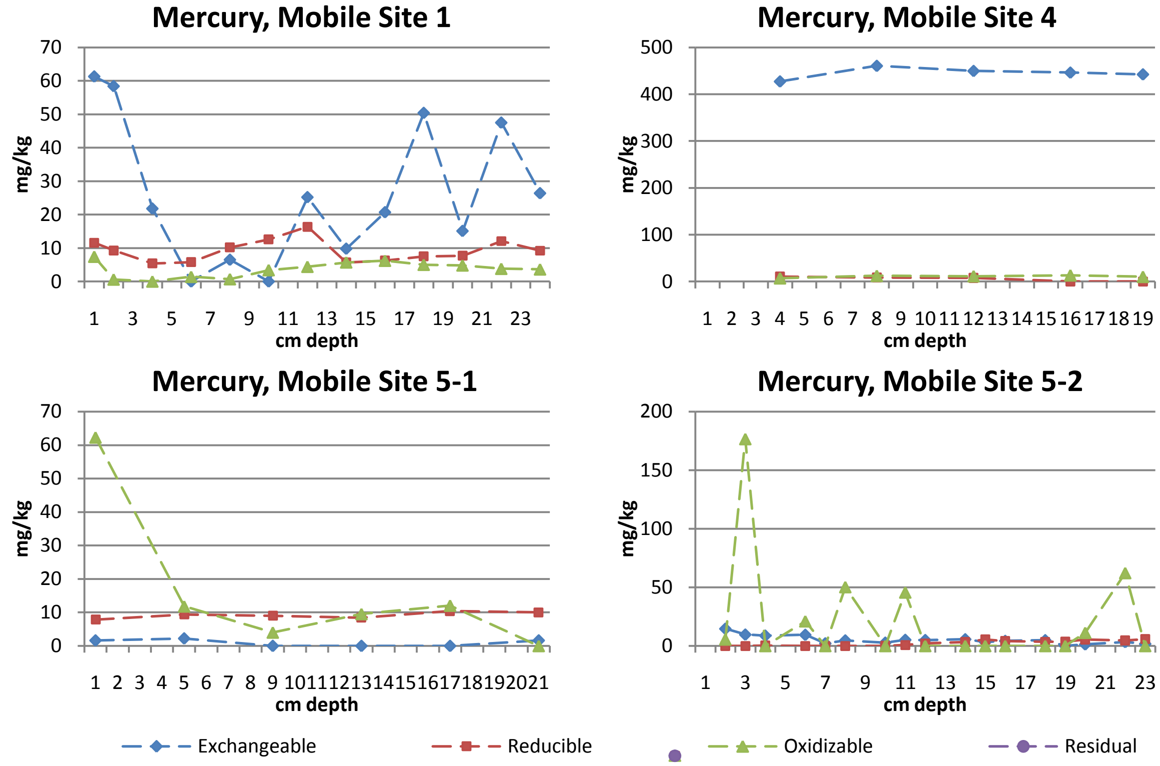


Figure 17. Concentration values for each mobile species of mercury over time, separated by sample site

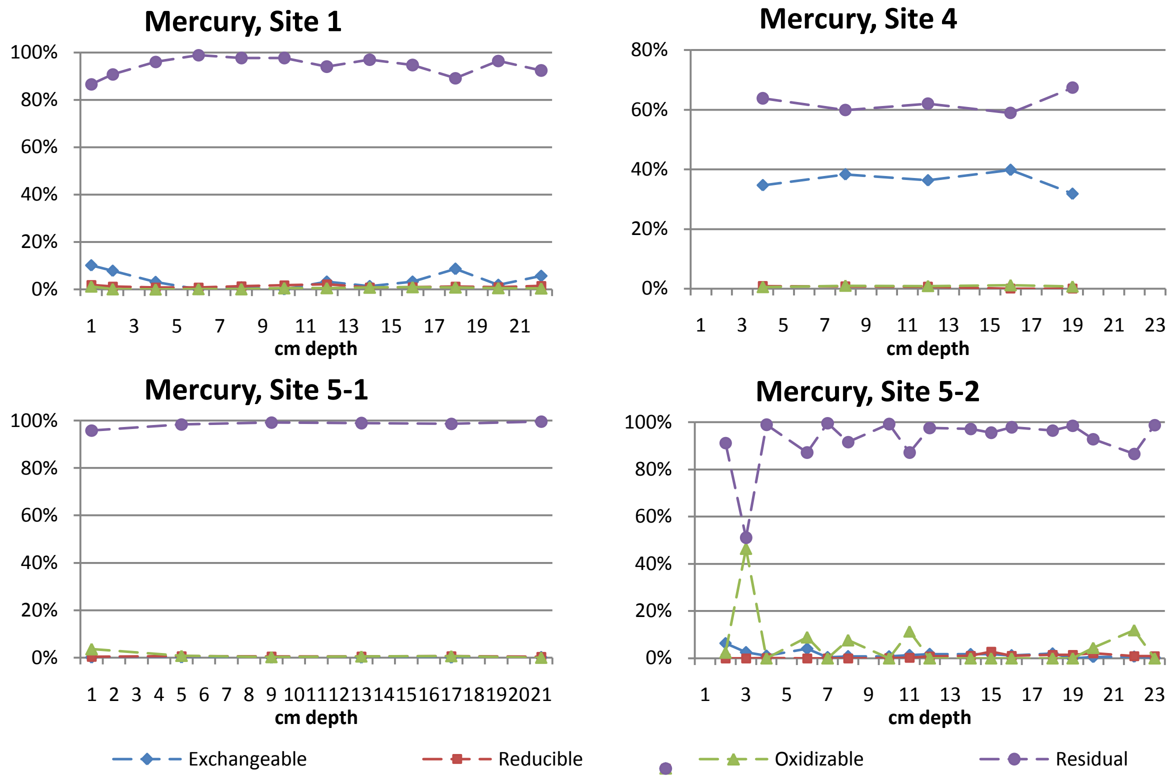


Figure 18. Speciation percentages of mercury over time, separated by sample site

5g. Speciation of Arsenic

Arsenic is also primarily found in the residual phase, consisting of 60-100% of the total. The remainder is split evenly between the exchangeable phase and the reducible phase(Fig.21). The oxidizable phase is barely seen, except for a distinguishable peak of 40-60 mg/kg that occurs at 14 cm in site 1, 12 cm at site 4, and 10 cm at site 5-2(Fig.20). This sediment depth corresponds to the time period when China was beginning to industrialize, and almost certainly corresponds to a specific type of industrial waste that was dumped there around the early 80's, with the effects of this contamination lingering for at least a decade. This is a very unusual species, and is rarely found in the literature, which makes this finding significantly more interesting. Although total arsenic content and total mobile arsenic content has remained relatively stable(Fig.19), the mobile arsenic content, in the form of exchangeable and reducible species, has consistently grown in all the samples except 5-2, where the oxidizable species is favored(Fig.20). Total mobile arsenic content is found to be around 100-300 mg/kg.

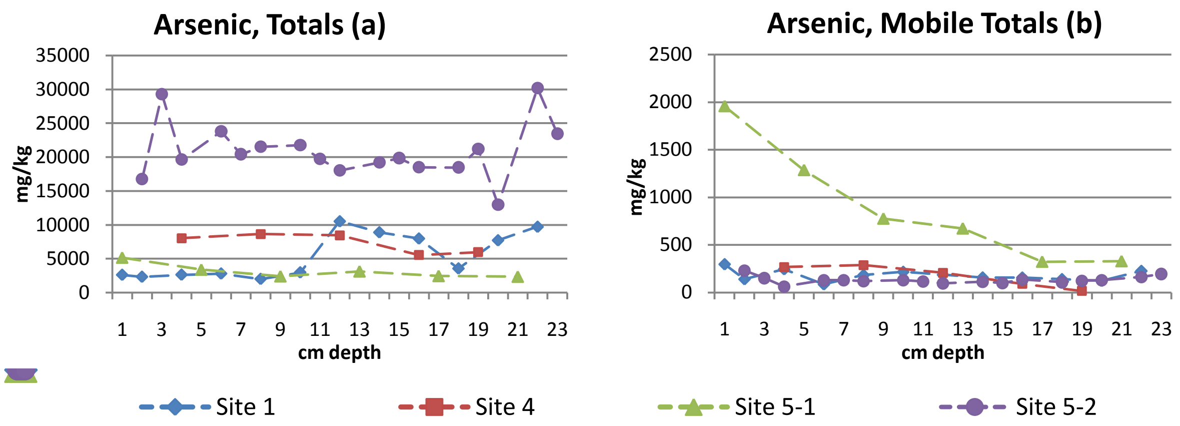


Figure 19. Total concentration values for arsenic, (a) including residual fraction, (b) only including the first 3 mobile fractions

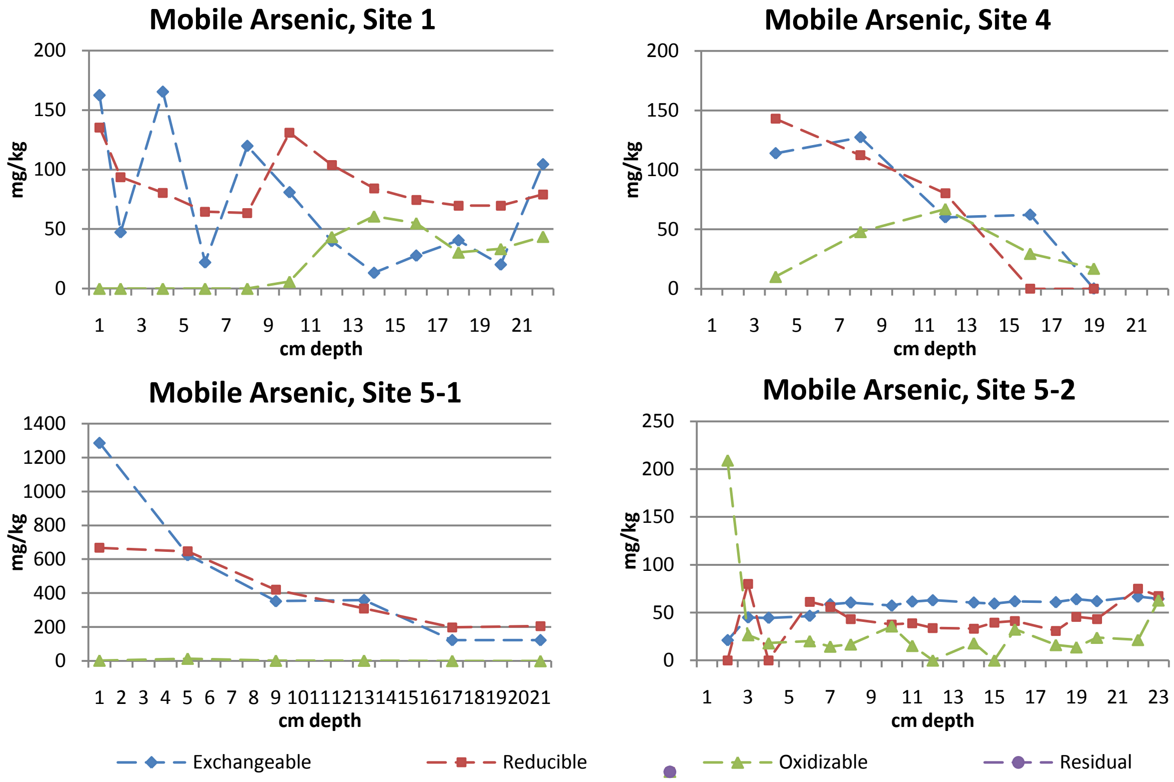


Figure 20. Concentration values for each mobile species of arsenic over time, separated by sample site

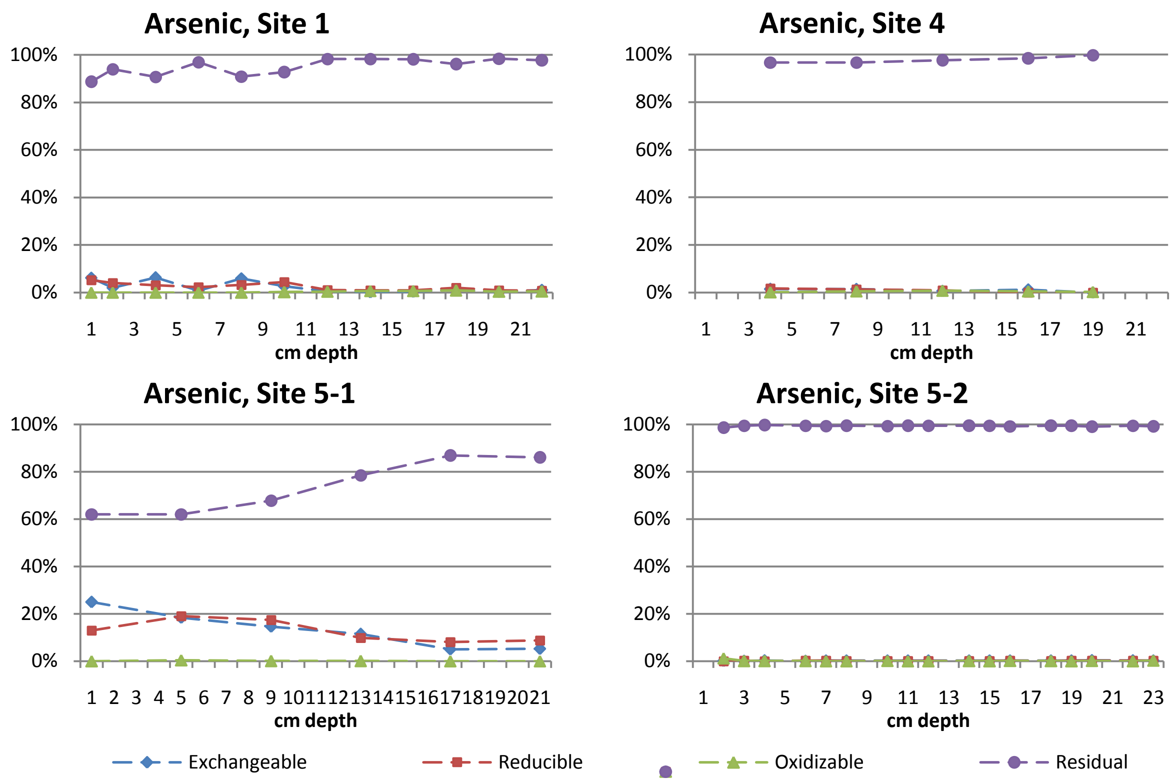


Figure 21. Speciation percentages of arsenic over time, separated by sample site

6. CONCLUSIONS

The Dianshan Lake sediment is a key source for information on the environmental practices of the Shanghai area, and all of China. Heavy metals were successfully extracted with sequential extraction procedure at varying depths and correlated to various parts of China's history. Lead, Chromium, and Arsenic all showed unusual rises in concentrations of mobile species at 9-17 cm deep, correlating to the rapid industrialization of China in the 1980's. The order of mobility was found to be Cd > Pb > Zn > Cr > Hg > As. The speciation of cadmium and zinc across all 3 sites strongly implies the lakebed environment is anaerobic and reducing, though there is inconclusive information about its acidity. Additionally, the speciation of mercury strongly indicates the presence of Hg-methylating bacteria at site 5, but not at sites 1 or 4. This is also evidence of anaerobic conditions, which correlates to Dianshan Lake's largest current and historical pollution source, sewage waste. Zinc, Chromium, Mercury, and Arsenic all show increases in mobile concentration in the past 5 years, though it is unclear whether this is evidence of current pollution practices or slow conversion of more mobile species into less mobile species.

7. ACKNOWLEDGEMENTS

I would like to sincerely thank Shanghai Jiao Tong University for hosting me during my stay in China. I would also like to thank their Dept. of Environmental Engineering, Prof. Zhang Hui, my advisor, and Du Xiaowei, my lab partner, for accommodating me and for help obtaining the data on sites 1 and 4.

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