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# A paleolimnological perspective on industrial-era metal pollution in the central Andes, Peru

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## ABSTRACT

To date, few studies have investigated the environmental legacy associated with industrialization in the South American Andes. Here, we present an environmental archive of industrial pollution from  $^{210}\text{Pb}$ -dated lake cores recovered from Laguna Chipian, located near the Cerro de Pasco metallurgical region and Laguna Pirhuacocha, located near the Morococha mining region and the La Oroya smelting complex. At Laguna Chipian, trace metal concentrations increase beginning ~1900 AD, coincident with the construction of the central Peruvian railway, and the rapid industrial development of the Cerro de Pasco region. Trace metal concentrations and fluxes peak during the 1950s before subsequently declining up-core (though remaining well above background levels). While Colonial mining and smelting operations are known to have occurred at Cerro de Pasco since at least 1630 AD, our sediment record preserves no associated metal deposition. Based on our  $^{14}\text{C}$  and  $^{210}\text{Pb}$  data, we suggest that this is due to a depositional hiatus, rather than a lack of regional Colonial pollution. At Laguna Pirhuacocha, industrial trace metal deposition first begins ~1925 AD, rapidly increasing after ~1950 AD and peaking during either the 1970s or 1990s. Trace metal concentrations from these lakes are comparable to some of the most polluted lakes in North America and Europe. There appears to be little diagenetic alteration of the trace metal record at either lake, the exception being arsenic (As) accumulation at Laguna Pirhuacocha. There, a correlation between As and the redox-sensitive element manganese (Mn) suggests that the sedimentary As burden is undergoing diagenetic migration towards the sediment–water interface. This mobility has contributed to surface sediment As concentrations in excess of  $1100 \mu\text{g g}^{-1}$ . The results presented here chronicle a rapidly changing Andean environment, and highlight a need for future research in the rate and magnitude of atmospheric metal pollution.

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## 1. Introduction

During the 20th century, the central Andes of Peru have experienced rapid industrialization. This development has inevitably led to an increase in heavy metal emissions and

their subsequent deposition to seemingly pristine mountain environments. The deposition of heavy metals has the potential to negatively impact lake-water quality surrounding regional mining and smelting centers. Determining the rate and extent of heavy metal deposition to Andean lakes is of critical

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importance, considering recent trends of a rapidly warming Andean climate and attendant cryospheric losses as sources of freshwater (Bradley et al., 2006). However, to date there have been few studies investigating the temporal evolution of heavy metal accumulation in lakes of the Peruvian Andes (Abbott and Wolfe, 2003; Cooke et al., in press, 2007).

The preservation of trace metals in lake sediment has allowed for the historical reconstruction of atmospheric metal deposition in both the Northern and Southern Hemispheres. This technique offers a retrospective approach in the absence of long-term monitoring data. While the Andes have a long history of pre-Colonial, Colonial, and industrial metallurgical activity (Cooke et al., in press), there have been almost no high-resolution lake-sediment studies from the Peruvian Andes that have focused explicitly on recent industrial growth and its environmental legacy.

Here, our focus is on the industrial era. To that end, we present two lake-sediment records of atmospheric metal deposition from lakes located in the central Peruvian Andes. The sediment cores presented here document heavy metal pollution associated with industrial emissions, and highlight a need for future research into metal deposition to Andean lake systems.

## 2. Study sites

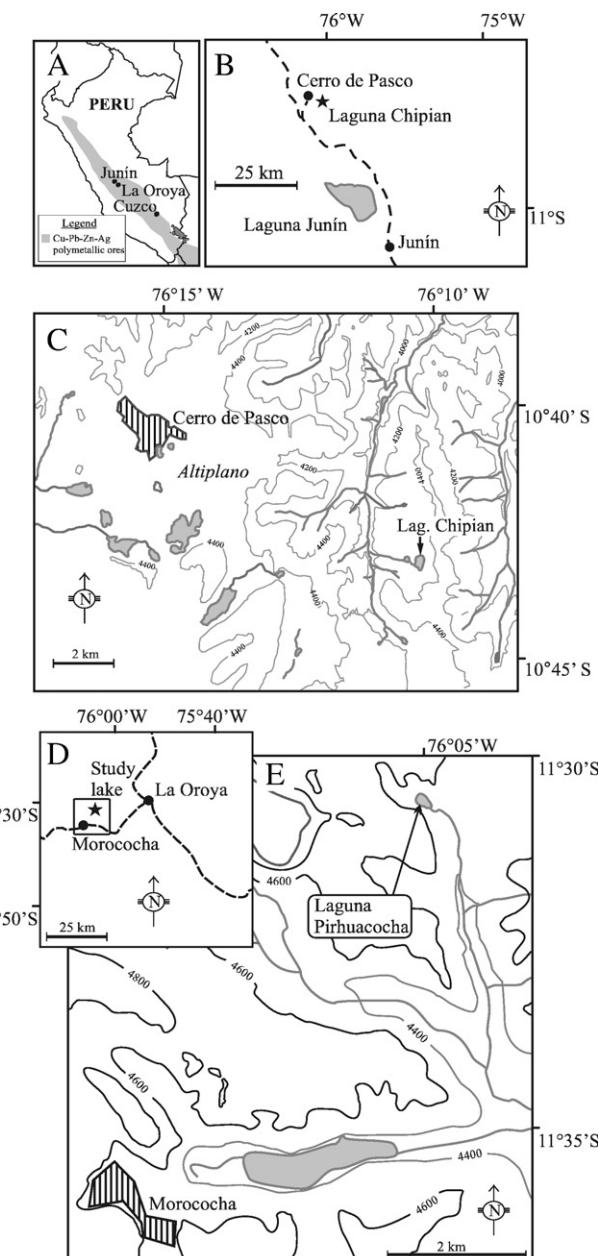
The city of Cerro de Pasco is located on the Altiplano (high plateau) of central Peru (Fig. 1B). With the onset of Spanish mining activities in 1630 AD, the region became one of the world's foremost producers of silver (Fisher, 1977). The primary mineral mined at Cerro de Pasco has been enargite ( $\text{Cu}_3\text{AsS}_4$ ), but principle ores also contain combinations of arsenopyrite ( $\text{FeAsS}$ ), aramayoite [ $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$ ], chalcopyrite ( $\text{CuFeS}_2$ ), argentiferous galena [ $(\text{Ag}, \text{Pb})\text{S}$ ], tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ), grantonite ( $\text{Pb}_9\text{As}_4\text{S}_{15}$ ), and sphalerite [ $(\text{Zn}, \text{Fe})\text{S}$ ] (Einaudi, 1977; Purser, 1971; Ward, 1961). The original Cerro (hill) is long since removed, and today Cerro de Pasco is an open pit mine, noted mostly for copper production, but also for gold, lead, bismuth, and zinc (Benavides, 1990). The mine is estimated to have contained one thousand tons of silver, four million tons of zinc, two million tons of lead, and lesser amounts of gold and bismuth prior to Colonial exploitation (Einaudi, 1977; Peterson, 1965).

Laguna Chipian ( $10^{\circ} 43' \text{ S}$ ,  $76^{\circ} 10' \text{ W}$ ; 4325 m a.s.l.) rests on carbonates terrain of Jurassic age, ~9 km southeast of Cerro de Pasco (Fig. 1C). Laguna Chipian is a small ( $0.12 \text{ km}^2$ ), shallow (3 m), alkaline ( $\text{pH}=10.6$ ) lake occupying a catchment of  $2.8 \text{ km}^2$ . Surface winds are variable, but blow predominantly from the west. A large collection of Colonial smelters and grinding wheels — presumably used during Hg amalgamation and processing and the smelting of Ag-bearing ores — is located in the valley bottom below Laguna Chipian (Cooke, 2006).

The Morococha mining region is located in the Junín district of the western Cordillera of central Peru (Fig. 1D). Colonial exploitation of Morococha first occurred during the 17th century (Purser, 1971). However, metallurgical activities have been continuous at Morococha since ~1000 AD (Cooke et al., 2007). The current mine is situated over hydrothermal replacement bodies, such as mantos, chimneys, and skarns (Gunnensch et al., 1990). In addition to native silver, the ores

contain combinations of bournonite ( $\text{CuPbSbS}_3$ ), arsenopyrite ( $\text{FeAsS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), emplectite ( $\text{CuBiS}_2$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ), argentiferous galena [ $(\text{Pb}, \text{Ag})\text{S}$ ], matildite ( $\text{AgBiS}_2$ ), proustite ( $\text{Ag}_3\text{As}_3\text{S}_3$ ), sphalerite [ $(\text{Zn}, \text{Fe})\text{S}$ ], stromeyerite ( $\text{AgCuS}$ ), and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) (Einaudi, 1977; Ward, 1961). During the 1990s, over 2.8 million tons of ore were mined at Morococha (M. Steinmann, personal communication).

Located 11 km northeast of modern silver mining operations at Morococha, Laguna Pirhuacocha ( $11^{\circ} 31' \text{ S}$ ,  $76^{\circ} 04' \text{ W}$ ; 4520 m a.s.l.; Fig. 1C) occupies Cretaceous terrain composed of



**Fig. 1—(A)** Map of Peru showing study region. **(B)** Map of Laguna Chipian in relation to nearby population centers, and **(C)** base map of the area around Laguna Chipian and Cerro de Pasco. **(D)** Map of Laguna Pirhuacocha in relation to the Morococha mining region and the La Oroya smelter, the largest and oldest smelting and refining center in Peru. **(E)** Base map for Laguna Pirhuacocha and surrounding area.

igneous, metamorphic, and carbonate sedimentary rocks. There is no hydrological connection between the lake and mining activity. The lake is small ( $0.05 \text{ km}^2$ ), occupies a non-glacial, undisturbed catchment of  $3.14 \text{ km}^2$ , is 18 m deep, and has a pH of 8.4. Laguna Pirhuacocha drains to the east through a small creek, and a shallow littoral bench sits at the mouth of this creek. Located well away from all modern day mining activities, both study sites are ideally suited to record atmospheric fallout of smelting emissions, both past and present.

### 3. Methods

#### 3.1. Core collection and chronology

During May and June of 2005, sediment cores were collected from the deepest points of Lagunas Chipian and Pirhuacocha using a slide hammer corer fitted with a 7-cm diameter polycarbonate tube (Blomqvist, 1991). Both cores contained an intact sediment–water interface, with no visible disturbance to the sediment column. The entire core from Laguna Chipian and the upper 15 cm of the Laguna Pirhuacocha core were extruded at 0.5-cm intervals to eliminate potential disturbance. The upper sediments of each core were dated using  $^{210}\text{Pb}$  activities ( $t_{1/2}=22.3$  years), measured by -spectroscopy, which measures  $^{210}\text{Pb}$  activity via  $^{210}\text{Po}$ , the granddaughter of  $^{210}\text{Pb}$ , assuming radioactive equilibrium between the two isotopes (Appleby, 2001).

#### 3.2. Sediment geochemistry and organic matter

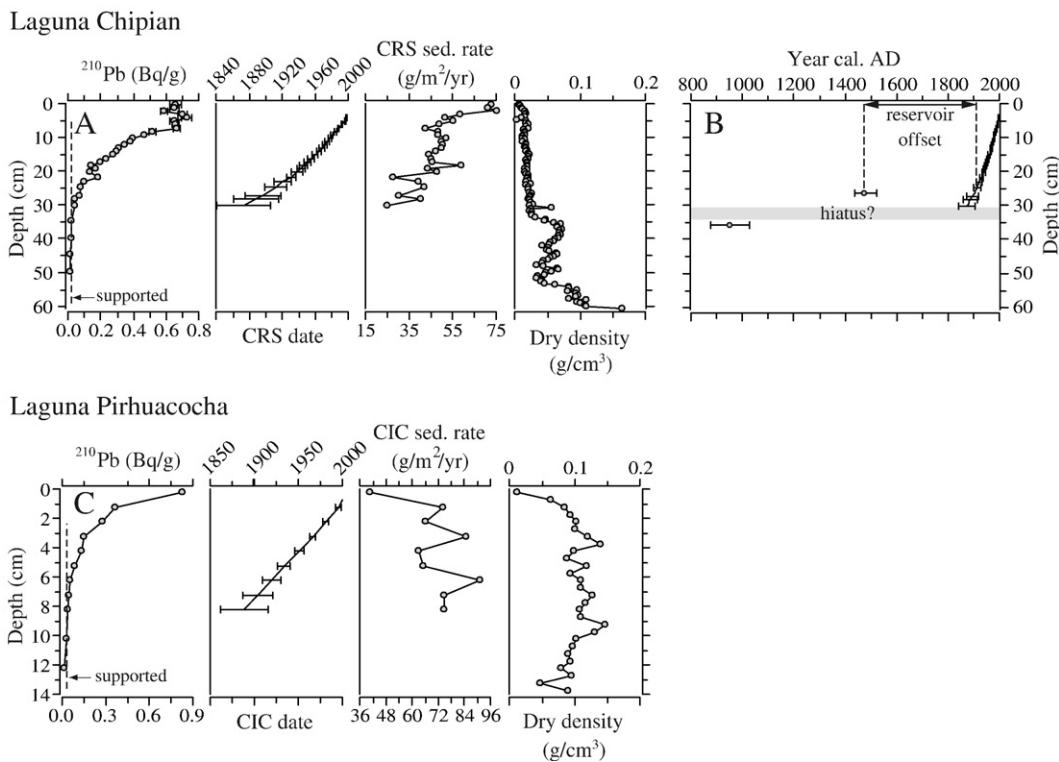
Elements were extracted from both cores using dilute acid extraction techniques. At Laguna Chipian, every 2-cm was sampled and analyzed, except for the interval 32.5–33 cm, for which insufficient sediment remained from other analyses. At

Laguna Pirhuacocha, every 0.5-cm interval was analyzed. All samples were freeze-dried and homogenized. Digestion and dilution vessels were acid cleaned and triple rinsed using 18 M ultrapure water. Between 0.1 (Laguna Chipian) and 0.5 g (Laguna Pirhuacocha) of precisely weighed sediment was extracted using 10 ml of 1.6 M Optima grade  $\text{HNO}_3$  at room temperature for 24 h. Subsequent 1 ml aliquots of supernatant were then diluted to 10 ml using 2% Optima grade  $\text{HNO}_3$ . This weak extraction procedure targets weakly-bound elements adsorbed to organic and inorganic surfaces and not those elements hosted in the lattice sites of detrital silicate minerals (Hamelin et al., 1990; Kober et al., 1999; Ng and Patterson, 1982; Shirahata et al., 1980). Graney et al. (1995) reported that the strength and type of acid (e.g.  $\text{HNO}_3$  vs.  $\text{HCl}$ ) has little impact on either the concentration of the Pb leached or its isotopic signature. Furthermore, Graney et al. (1995) showed that the weakly-bound Pb is isotopically distinct from that contained within mineral lattices after total digestion with HF. This extraction therefore, targets most, if not all, of the anthropogenic atmospheric input to the sediment.

Both inductively coupled plasma-atomic emission spectroscopy (ICP-AES Spectroflame-EOP at the University of Pittsburgh) and a Finnigan MAT double focusing magnetic sector ICP-Mass Spectrometer (ICP-MS ELEMENT at Penn State University) were used to measure elemental abundances. The elements analyzed by each instrument and the associated method detection limits (MDL) are shown in Table 1. Concentrations were verified against the certified multi-element standard, SPEX ICP-MS-2. Analytical error was  $\pm 10\%$  for every element run. Duplicates were run every 10th sample and were always within 8%. A minimum of 6 blanks or 10% the number of samples (whichever was greater) was carried through the entire procedure with each batch of samples (Boyle, 2001). Blanks were consistently below the MDL for each element. Elemental concentrations are reported as  $\mu\text{g g}^{-1}$  or  $\text{mg g}^{-1}$  dry sediment mass, as noted.

**Table 1 – Table of elements analyzed by each instrument and the associated method detection limits**

	Laguna Chipian			Laguna Pirhuacocha			ICP-AES
	Element	IDL	$\pm(1\%)$	Element	IDL	$\pm(1\%)$	
ICP-AES	K	39	9	K	20.0	0.7	ICP-AES
	Mn	6	1	Mn	2.4	0.1	
	Zn	2.6	0.6	Zn	0.7	0.1	
	Al	92	20	Al	47	6	
	S	46	10	S	24	3	
	Na	28	6	Na	14	2	
	Fe	23	5	Fe	12	1	
	Pb	5	2	Pb	4.8	0.6	
	Ni	3.0	0.6	Ni	8	1	
	Ca	28	6	Ca	15	2	
ICP-MS	Sr	2.6	0.6	Sr	1.0	0.2	ICP-MS
	Ti			Ti	2.2	0.3	
	Ag	0.003	0.001	Co	1.5	0.2	
	Cd	0.004	0.001	Cu	5.4	0.7	
	Sn	0.003	0.001	V	5.0	0.6	
	Sb	0.0009	0.0002				
	Bi	0.0003	0.0001	Ag	0.00023	0.00003	
	Ti	0.07	0.01	Cd	0.0010	0.0001	
	V	0.020	0.004	Sn	0.00049	0.00006	
	Co	0.011	0.002	Sb	0.00009	0.00001	
	Cu	0.06	0.01	Bi	0.00009	0.00001	
	As	0.12	0.03	As	0.019	0.002	



**Fig. 2** – Down-core sediment  $^{210}\text{Pb}$  activities, CRS age-depth models, CRS sedimentation rate, and dry density profiles. (B) Composite age-depth model for Laguna Chipian. Note the reservoir effect on charcoal AMS  $^{14}\text{C}$  samples of ~400 years (filled circles). Error bars on  $^{210}\text{Pb}$  dates are the 1 range and 2 on  $^{14}\text{C}$  dates. An apparent hiatus occurs at 30–35 cm depth and is coincident with a shift in core dry density and core geochemistry (see Fig. 3). (C) Laguna Pirhuacocha  $^{10}\text{Pb}$  activities, CIC age-depth model, CIC sedimentation rate, and dry density profiles.

At Laguna Pirhuacocha, total sediment organic matter was estimated by loss on ignition (LOI) at 550 °C for 3 h and carbonate content was estimated by weight loss at 950 °C for 2 h; both are expressed as a percentage of total pre-burn dry mass (Dean, 1974). Insufficient sediment remained for the uppermost sample, and no comparable data are available for the Laguna Chipian core for the same reason.

### 3.3. Calculations

To compensate for changing sediment mineralogy, and to provide a more complete picture of atmospheric deposition, concentrations were converted to fluxes [accumulation rate ( $\mu\text{g cm}^{-2} \text{ yr}^{-1}$ )], calculated as the product of trace metal concentration ( $\mu\text{g g}^{-1}$ ) and the CRS (Laguna Chipian) and CIC (Laguna Pirhuacocha) sedimentation rates ( $\text{g cm}^{-2} \text{ yr}^{-1}$ ).

## 4. Results and discussion

### 4.1. Core chronology

#### 4.1.1. Laguna Chipian

Total  $^{210}\text{Pb}$  activity in Laguna Chipian sediment displays a conspicuous non-monotonic behavior in the uppermost 8 cm, superimposed on an otherwise exponential decline down-core (Fig. 2A). Unsupported  $^{210}\text{Pb}$  activity was calculated by

subtraction of the supported activity, estimated by the average activity of the lowermost four samples. The non-monotonic behavior of  $^{210}\text{Pb}$  observed in the uppermost sediment implies that either sedimentation rates have increased during the 20th century, effectively diluting the  $^{210}\text{Pb}$  activity, or that sediment mixing has occurred in the uppermost ~8 cm. Whichever the case, a mixed surface layer is permissible in the constant rate of supply (CRS) dating model (Appleby, 2001), which assumes a constant rate of  $^{210}\text{Pb}$  supply to the study lake. Based on the cumulative unsupported  $^{210}\text{Pb}$  inventory, the flux of  $^{210}\text{Pb}$  to Laguna Chipian sediment is estimated to be 47  $\text{Bq m}^{-2} \text{ yr}^{-1}$ . Sediment CRS dates were calculated following Appleby (2001), thereby allowing for the construction of an age-depth relationship profile for the past ~120 years.

To estimate sediment ages beyond the limit of  $^{210}\text{Pb}$ -dating, accelerator mass spectrometer (AMS)  $^{14}\text{C}$  dates were obtained on charcoal. All dates were converted to calendar years AD using the IntCal04 dataset (Reimer et al., 2004), and are presented in Table 2 and Fig. 2B. The uppermost charcoal sample is located within the range of unsupported  $^{210}\text{Pb}$  activity however, it has a 2 calibrated age range between 1430 and 1520 AD, ~400 years older than the 1900 AD  $^{210}\text{Pb}$ -derived date. The discrepancy between the  $^{210}\text{Pb}$  and  $^{14}\text{C}$  dates can be explained as being due to either: (i) a gross error in the  $^{210}\text{Pb}$ -derived dates, or (ii) a reservoir effect on the charcoal samples dated. While the uppermost surface sediment appears to have been mixed, the  $^{210}\text{Pb}$  profile below 8-cm

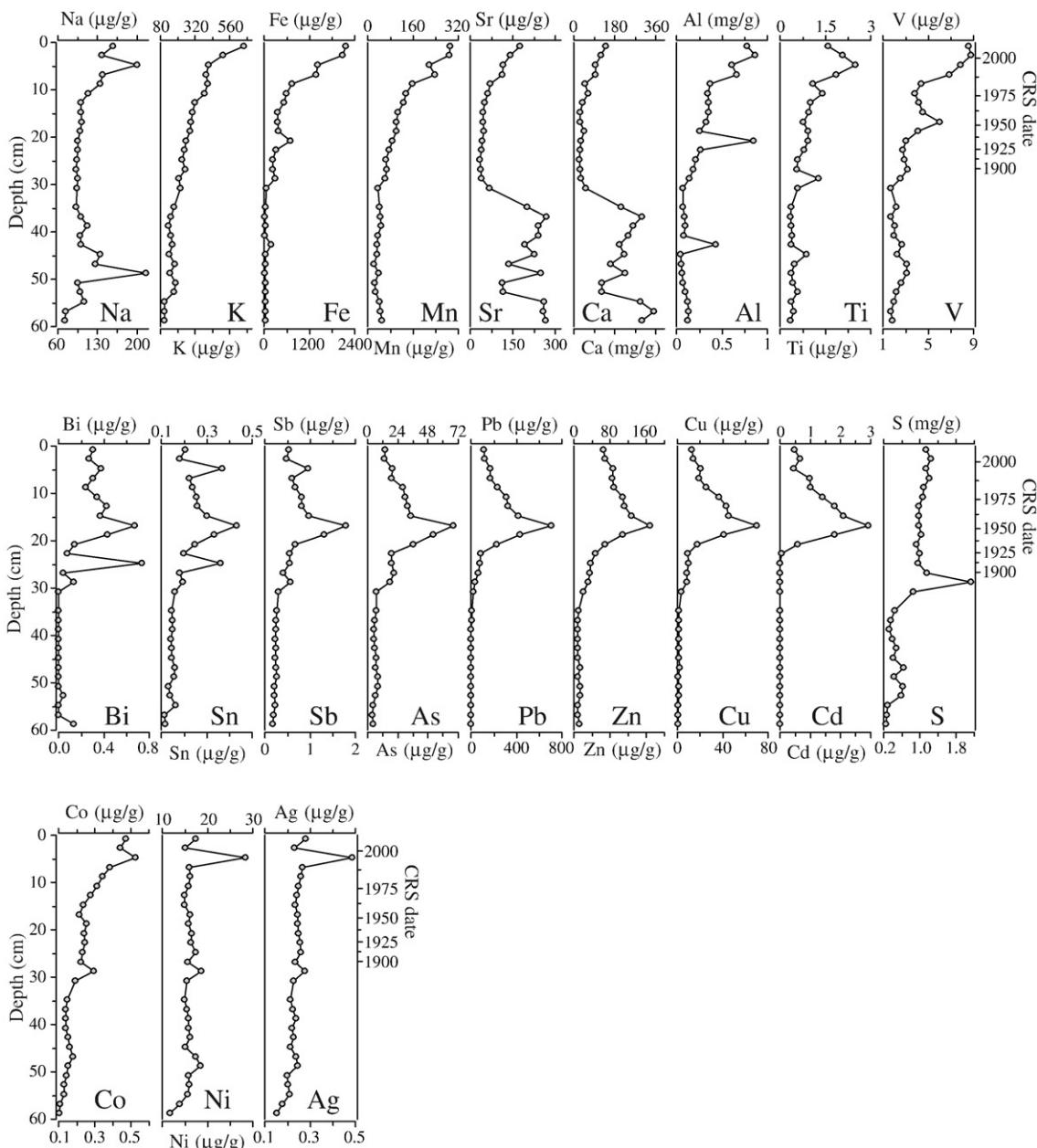
**Table 2 – Table of AMS  $^{14}\text{C}$  results from Laguna Chipian**

UCI sample #	Depth interval (cm)	Material	$^{13}\text{C}$ (‰)	$^{14}\text{C}$ age (yrs BP)	Size (mg C)	AD range (2 )		Median date (yr AD)	Relative probability
						Lower	Upper		
22771	26–28	Charcoal	-12	400	0.067	1430	1520	1480	0.9
22771	35–37	Charcoal	-12	1095	0.038	880	1020	950	1

depth preserves a monotonic decline of unsupported  $^{210}\text{Pb}$  captured by several successive samples. Therefore, it appears that the uppermost AMS  $^{14}\text{C}$  sample suffers from a hard-water reservoir effect, as observed elsewhere in the Andes (Cooke et al., 2007). Charcoal samples may be from aquatic taxa that

inhabit the littoral zone, which periodically burned when aerially exposed during periods of pronounced aridity. Lake-level in the Andes has fluctuated significantly in the past (e.g. Abbott et al., 1997), and both study lakes contain large littoral benches with abundant macrophytic growth. In light of this,

### Laguna Chipian



**Fig. 3 – Geochemical concentration stratigraphies and CRS dates for Laguna Chipian. All elemental concentrations are reported as  $\mu\text{g g}^{-1}$  dry sediment mass except for Ca and Al which are in  $\text{mg g}^{-1}$ . Analytical error bars are smaller than the data points shown.**

the assumption that most charcoal originates from equilibrated terrestrial origins (e.g. grasses) needs to be reexamined for the Andes.

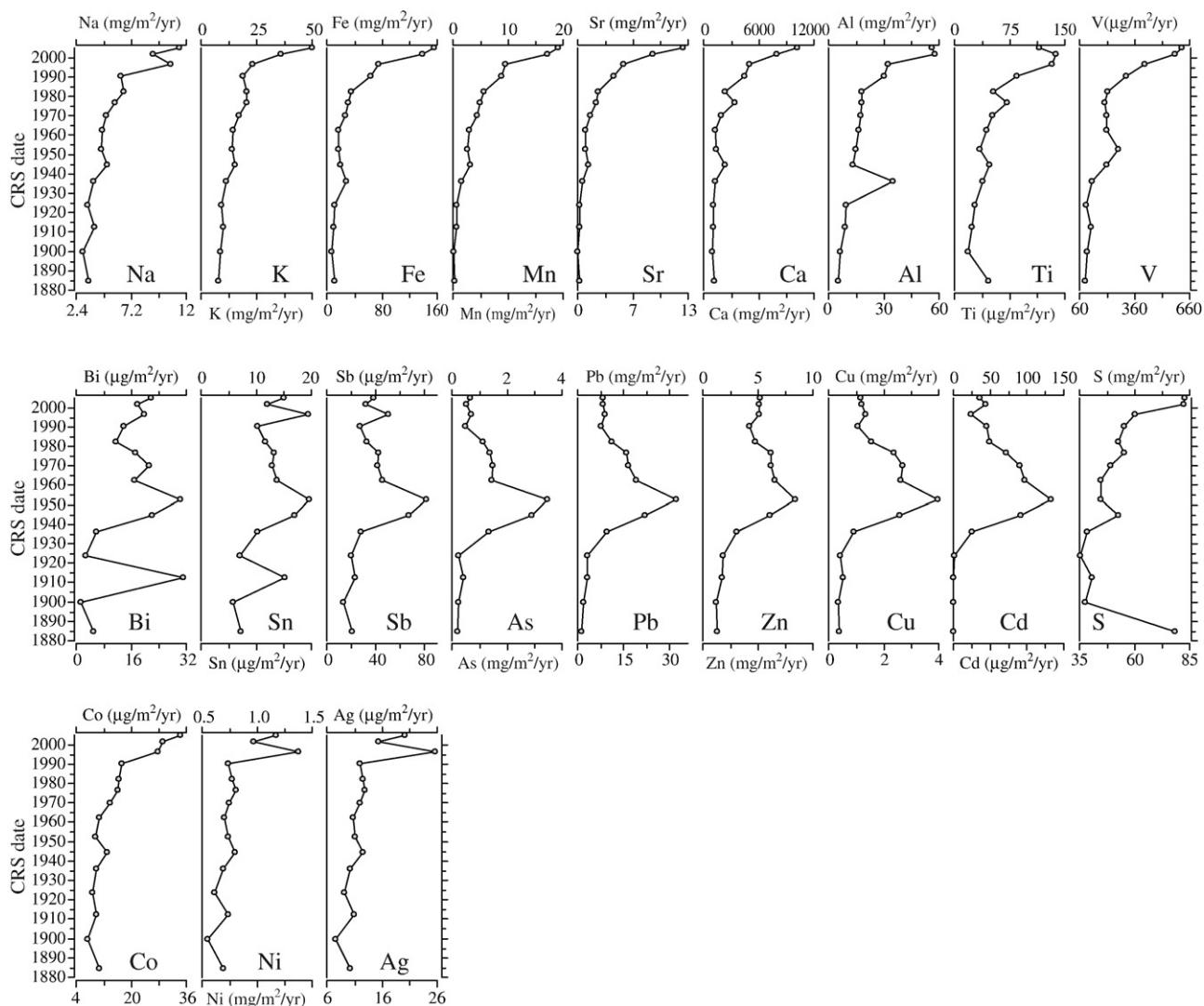
The second AMS  $^{14}\text{C}$  sample dates to ~950 AD (2 range 880–1020 AD), significantly older than the sediments that immediately overlie it. Even assuming a hard-water offset of ~400 years, the second  $^{14}\text{C}$  date appears too old (Fig. 2B). Therefore, either the reservoir effect has fluctuated with time, or a sedimentary hiatus occurs at ~30–35 cm depth. The exhaustion of unsupported  $^{210}\text{Pb}$  activity and the lower AMS  $^{14}\text{C}$  date also coincide with a significant increase in sediment dry density (Fig. 2A). Sediment at this depth was visibly compacted and notably darker than the predominantly lighter, tan colored sediment immediately above (Cooke, 2006). This shift also coincides with an order of magnitude decrease in both Ca and Sr concentrations (from ~300 to 30  $\mu\text{g g}^{-1}$ ). Given the significant sedimentological and geochemical shifts that occur at ~35 cm depth, and assuming a constant reservoir effect of ~400 years we suggest that a roughly 400-year hiatus

occurred at ~35 cm depth, though we recognize that this interpretation remains highly speculative given the limitations of AMS  $^{14}\text{C}$  dating in this setting. Nonetheless, the upper portion of the core appears to contain a continuous record, and our interpretations rest entirely on the  $^{210}\text{Pb}$  chronology.

#### 4.1.2. Laguna Pirhuacocha

As with Laguna Chipian, our discussion here focuses on the industrial era, and therefore only the  $^{210}\text{Pb}$  results are shown; a full discussion of the longer core chronology is given elsewhere (Cooke et al., 2007). Total  $^{210}\text{Pb}$  activity declines without reversal from a surface value of  $0.80 \text{ Bq g}^{-1}$  to a relatively steady supported background of  $0.03 \text{ Bq g}^{-1}$  at depths below 8.5 cm (Fig. 2C). The  $^{210}\text{Pb}$  results therefore indicate constant sedimentation downcore and the undisturbed nature of the Laguna Pirhuacocha core. Because sedimentation rates are nearly constant (Fig. 2C), the constant initial concentration (CIC) dating model was applied to calculate sediment ages (Appleby, 2001). The estimated flux of  $^{210}\text{Pb}$  to Laguna Pirhuacocha sediment ( $30 \text{ Bq m}^{-2} \text{ yr}^{-1}$ ) was lower

Laguna Chipian



**Fig. 4—Reconstructions of atmospheric deposition from Laguna Chipian plotted against CRS dates. Accumulation rates for Na, K, Fe, Mn, Sr, Ca, As, Pb, Zn, Cu, S, and Ni are in  $\text{mg m}^{-2} \text{ yr}^{-1}$ , while the remainder are in  $\mu\text{g m}^{-2} \text{ yr}^{-1}$ .**

than for Laguna Chipian, however, the flux of  $^{210}\text{Pb}$  to both lakes is comparable to other study sites from Chile, which range from ~23 to 50 Bq m $^{-2}$  yr $^{-1}$  (Chirinos et al., 2006).

#### 4.2. Sediment geochemistry and organic matter

##### 4.2.1. Laguna Chipian

In general, Na, K, Fe, Mn, Al, Ti, V, and Co within Laguna Chipian sediment increase up-core, reaching maximum concentrations (Fig. 3) and depositional fluxes (Fig. 4) at the sediment surface. Increases in Na and K in lake-sediment cores are primarily attributed to periods of enhanced soil weathering, while Al, Ti, and V largely reflect more refractory sources (Boyle, 2001; Engstrom and Wright, 1984; Norton et al., 1992). The largely parallel trend observed in Co suggests an erosional source for this element as well. In contrast, surface enrichments of Fe and Mn are more commonly interpreted as post-burial diagenetic artifacts resulting from the migration of soluble reduced Fe and Mn species towards oxidized surface waters where precipitation occurs (Hamilton-Taylor and Davison, 1995). However, Fe and Mn are highly correlated to K, Al, and Ti, with correlation coefficients ( $r^2$ ) ranging from 0.72 to 0.96. This high degree of correlation suggests that an erosional source, rather than a diagenetic signal, dominates the Fe and Mn profiles.

Unlike the aforementioned lithophilic elements, subsurface peaks characterize many of the trace metal profiles (Figs. 3 and 4). Strong increases occur earliest in Sn and Bi, followed by Pb, Zn, Cu, Cd, As, Sb, and finally Ni and Ag which are characterized by a single peak at 5 cm depth and a slight surface enrichment in flux. Sulfur values can roughly be divided into two populations of low (0.2–0.6 mg g $^{-1}$ ) and high (0.9–1.3 mg g $^{-1}$ ) concentrations, which are separated by a large spike at ~30 cm depth. These trace metal profiles (including S) do not correlate with any of the previously mentioned allochthonous elements, and reach concentrations and flux rates well above stable background values. For example, at 20 cm depth (~1955 AD) Pb concentration exceeds 800  $\mu\text{g g}^{-1}$ , more than two orders of magnitude above background ~5  $\mu\text{g g}^{-1}$ . Similar increases are noted in Bi, Sn, Sb, As, Zn, Cu, and Cd. Given the industrial history of the area, and because we know of no natural mechanism capable of inducing this level of trace metal enrichment, we attribute the observed rise in metal deposition to regional metallurgical activities and attendant atmospheric pollution. The Laguna Chipian lake-sediment record therefore appears to chronicle local- to regional-scale metal deposition associated with the mineral exploitation of the Cerro de Pasco region.

Cerro de Pasco was discovered by Colonial metallurgists in 1630 AD and was rapidly developed (Fisher, 1977). After Cerro Rico de Potosí, Cerro de Pasco was the second most important silver mine in Colonial Peru, eventually becoming the largest producer of silver in the New World (Purser, 1971; Fisher, 1977). As surface ores were quickly depleted, the ground beneath the mine became honeycombed with underground workings, and mercury amalgamation took over as the predominant silver extractive process (Fisher, 1977). Colonial smelters were highly polluting, and their geochemical signatures have been well documented at other lake sites in the Andes (Cooke et al., in press). Given the large amount of Colonial activity at Cerro de Pasco, and the abundance of Colonial smelters and amalgamation facilities down valley from Laguna Chipian, the apparent

lack of a Colonial (or earlier) smelting signal in Laguna Chipian sediment is likely due to the proposed depositional hiatus, rather than a lack of atmospheric metal pollution. Additional lake cores from the region will be needed to confirm our results and to investigate the possibility for Colonial and possibly pre-Colonial pollution associated with metallurgical activities.

The building of the central Andean railway marks the onset of large-scale mining in Peru. The railroad from Lima to Cerro de Pasco (through La Oroya) was completed in 1904 AD, which, in combination with the increased demand for copper by Europe and the United States, rapidly accelerated the growth of Cerro de Pasco. During the Colonial era (1630–1900 AD), mining activity at Cerro de Pasco had primarily been concerned with silver extraction; substantial copper deposits were well known, but had been ignored because of the long haul by horse or mule cart made the trip to the coast uneconomical (Waszkis, 1993). With the development of the railway, these previously unexploited deposits could be developed. During the early 20th century, there were at least eight active mines and two smelters in operation in the Cerro de Pasco region (Purser, 1971). Extractions activities were primarily aimed at Cu, Ag, and Bi recovery. All three metals display strong increases in the Laguna Chipian sediment record beginning ~1900 AD. However, this mining activity appears to have led to emissions of Bi, Sn, Sb, As, Pb, Zn, and Cd as well. These metals are intrinsically tied to the local mineralogy (see study sites above), and were likely released as by-products during smelting. Since the 1950s, the accumulation of As, and to a lesser extent Sb, Pb, and Cd at Laguna Chipian has declined to near background levels, while Bi, Sn, Zn, Cu, S, Ni, and Ag remain above background levels. These differences may reflect changing ore exploitation, or the evolution of mining technologies with time.

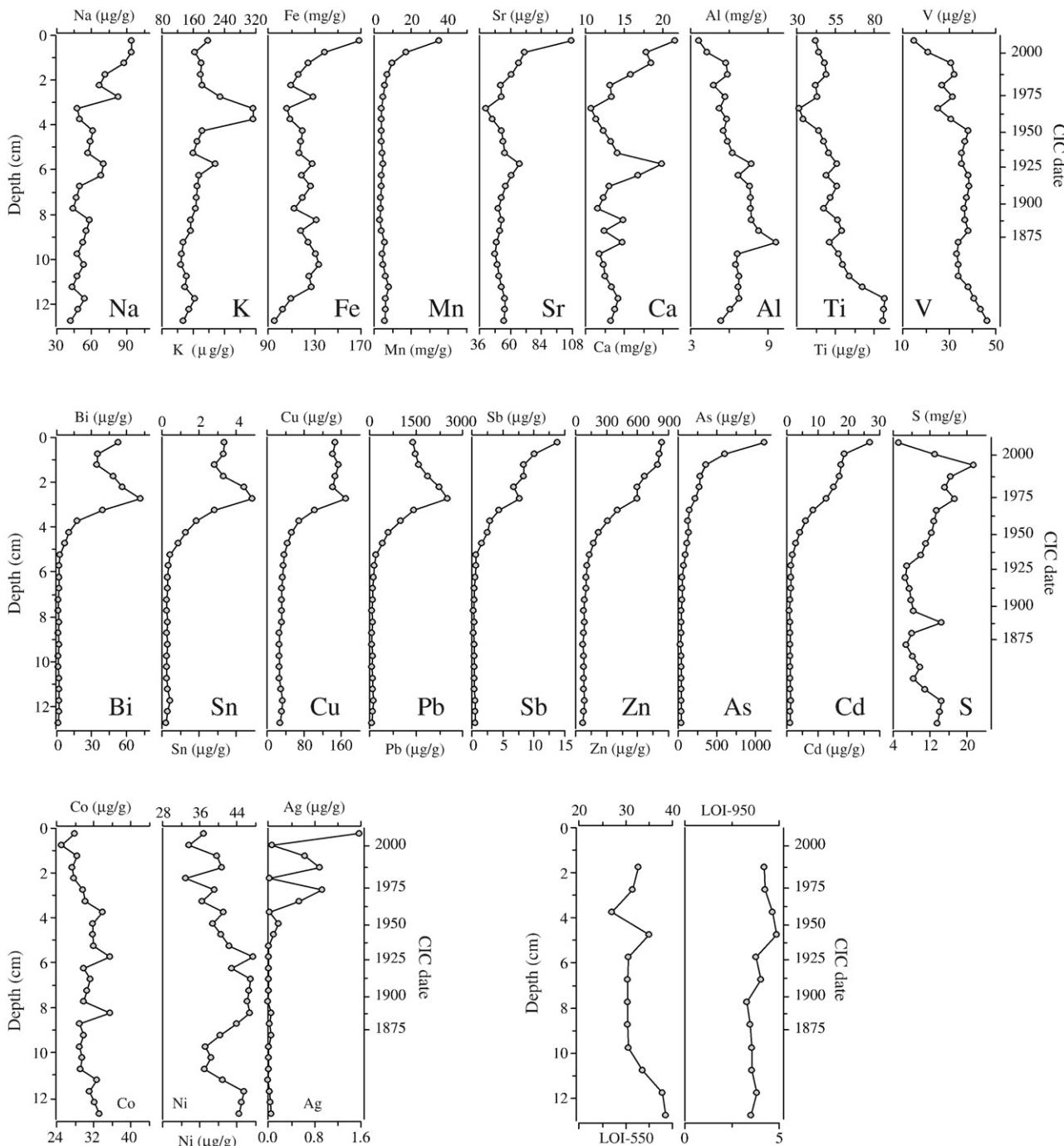
##### 4.2.2. Laguna Pirhuacocha

The geochemical stratigraphy from Laguna Pirhuacocha displays a somewhat different trend in the timing and magnitude of elemental increases, but follows the same general trend of increasing metal concentrations and flux through the 20th century. Our focus here is on the most recent portion of the lake-sediment record, but it is highly relevant to note that metal concentrations and fluxes are elevated prior to 20th century industrial activity (Cooke et al., 2007). Indeed, the geochemical and Pb-isotopic records at Laguna Pirhuacocha testify to a millennium of metal pollution from pre-Incan, Incan, and Colonial metallurgical activities at Morococha and the surrounding area. Nevertheless, 20th century trace metal concentrations (Fig. 5) and depositional fluxes (Fig. 6) clearly rise above previous levels, attaining a new level of enrichment.

The concentrations (Fig. 5) and flux (Fig. 6) of Na, K, Sr, Ca, Al, Ti, and V remain relatively constant during the period of the record, suggesting that catchment soil input has remained relatively constant with time. The deposition of Co and Ni also appears to have remained relatively constant, as they do not increase above background levels during the period of the record. In contrast, Fe and Mn display surface enrichments which are entirely consistent with the post-depositional release of reduced species of Fe and Mn, followed by vertical migration toward the oxidized sediment–water interface and precipitation in the oxidized sediments (Hamilton-Taylor and Davison, 1995).

Trends in trace metal concentration (Fig. 5) and flux (Fig. 6) are quite similar at Laguna Pirhuacocha, and with the

## Laguna Pirhuacocha



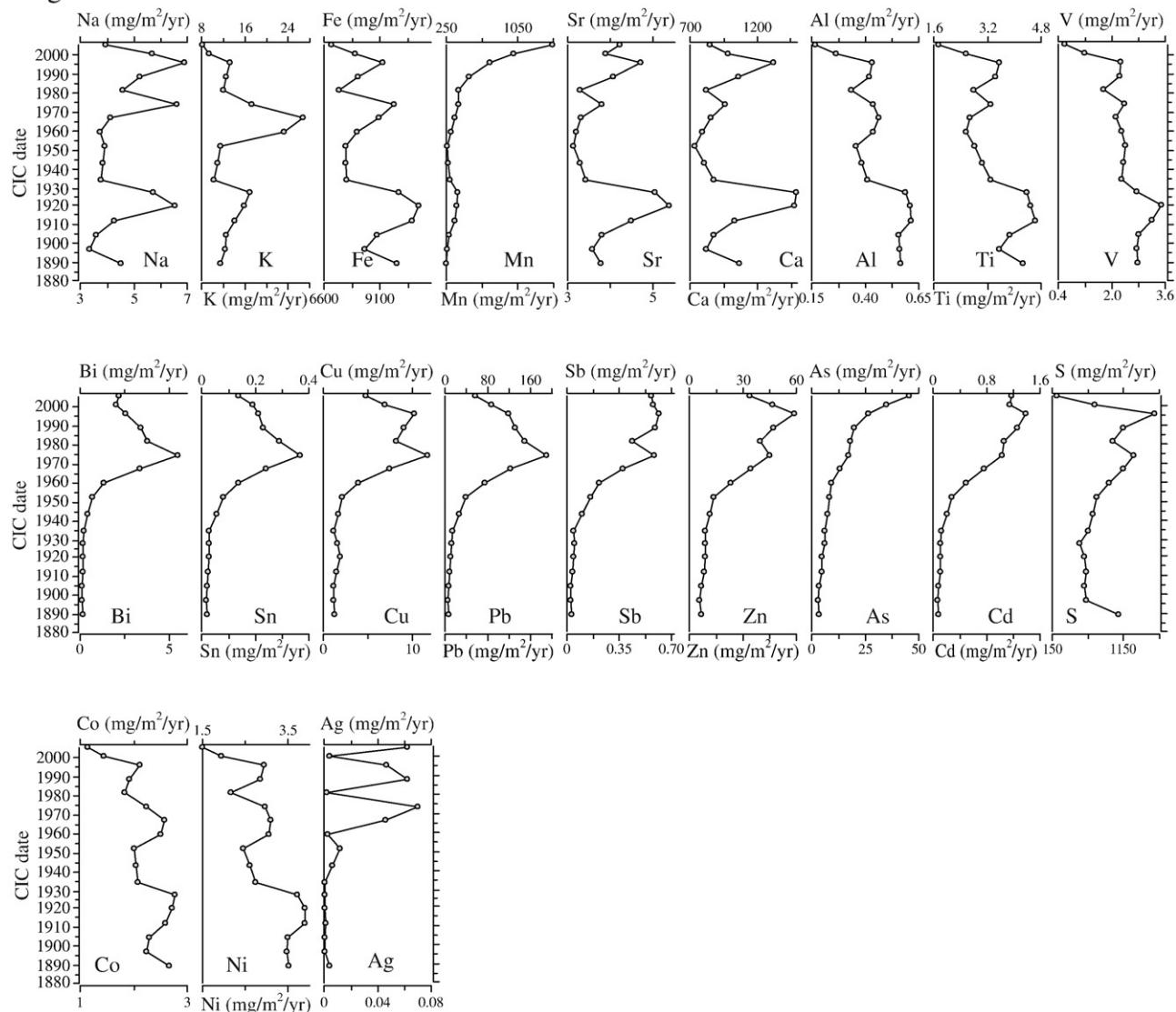
**Fig. 5—Geochemical concentration stratigraphies and CIC dates for Laguna Pirhuacocha. All elemental concentrations are reported as  $\mu\text{g g}^{-1}$  dry sediment mass except for Ca and Al which are in  $\text{mg g}^{-1}$ . Analytical error bars are smaller than the data points shown.**

exception of Co and Ni, the deposition of all trace metals increased dramatically after ~1950 AD. Subsurface peaks (~1975 AD) in both concentration and flux characterize Bi, Sn, Cu, and Pb. The increase in trace metal deposition is unrelated to organic sequestration, as organic content remains stable (~30%) for the length of the record (Fig. 5). Furthermore, Pb has been shown to be immobile in lake sediments (e.g. Gallon et al., 2004), and the close correlation

between Bi, Sn, and Cu with Pb would suggest that they too reflect depositional histories. Pb deposition has declined approximately 65% ( $170\text{--}50 \text{ mg m}^{-2} \text{ yr}^{-1}$ ) since the mid-1970s, with lower decreases recorded for Bi, Sn, and Cu (Fig. 6). Nonetheless, modern rates of Bi, Sn, Cu, and Pb deposition remain well above background values.

In contrast, Sb and Zn peak in concentrations (Fig. 5) in the uppermost surface sediment, and decline slightly in flux (Fig. 6)

## Laguna Pirhuacocha



**Fig. 6—Reconstructions of atmospheric deposition from Laguna Pirhuacocha plotted against CIC dates. Accumulation rates for Na, K, Fe, Mn, Sr, Ca, Al, Cu, Pb, Zn, As, S, and Ni are in  $\text{mg m}^{-2} \text{ yr}^{-1}$ , while the remainder are in  $\mu\text{g m}^{-2} \text{ yr}^{-1}$ .**

over the last decade, while the profiles of As, Cd, and Ag are characterized by a surface maxima in both concentration and, in the case of As, flux as well. The different profiles observed between metals likely reflect different depositional histories, but may also be due to a second-order diagenetic overprinting of the trace metal profiles. The geochemistry of Sb, Zn, Cd, and Ag in lake sediments is complex (Alfaro-De la Torre and Tessier, 2002; Chen et al., 2003; Gélinas et al., 2000; Gobeil, 1999). If post-depositional alteration of the Sb, Zn, Cd, or Ag sediment record is occurring, it appears to be minimal as compared to the otherwise large anthropogenic increases which begin after ~1950 and are roughly coeval with increases in Bi, Sn, Cu, and Pb.

Amongst the metal profiles, the As profile appears to be unique in that it is highly correlated with Mn ( $r^2=0.88$ ;  $n=26$ ;  $p < 0.01$ ). While the overall increase in As concentrations (~50–1100  $\mu\text{g g}^{-1}$ ) can only be explained by anthropogenic enrichment of the sediment, the high correlation between As and Mn suggests some amount of post-depositional alteration of the

historical record. Diagenetic mobilization of As within contaminated lake sediment is widely recognized (Aggett and O'Brien, 1985; Senn et al., 2007; Spliethoff et al., 1995). Mobilization of As primarily occurs via the reductive dissolution of Fe, Mn, and S host phases (Keimowitz et al., 2005; Martin and Pedersen, 2002), followed by upward migration along with reduced species of Fe and Mn. The result is that anthropogenic As is continuously mobilized towards the sediment–water interface. During mobilization some of this As are available for export to the water column, and the export of As to overlying lake-water has been documented during both anoxic and oxic epilimnia (Senn et al., 2007). The observed combination of high surface sediment As concentrations and the mobile nature of As within Laguna Pirhuacocha sediment may therefore pose a threat to future lake health. This is especially true if redox conditions within Laguna Pirhuacocha sediment favor enhanced As release in the future.

Laguna Pirhuacocha is located 11 km up-valley from the Morococha mining center and ~25 km down valley from the La

Oroya smelting complex (Fig. 1D). Mining at Morococha is primarily focused on silver extraction, while La Oroya, which was built in 1922 AD, is the largest and oldest industrial-scale smelting and refining center in Peru. Production processes at La Oroya are focused on lead, copper, and zinc but also exist for bismuth, silver, gold, selenium, tellurium, cadmium, antimony, and indium (Purser, 1971). Strong increases in Bi, Cu, Pb, Sb, Zn, Cd, and Ag are all noted at Laguna Pirhuacocha beginning during the mid-20th century. The geochemical history recorded at Laguna Pirhuacocha likely reflects both the evolution of mining activity at Morococha, and the smelting of ores at nearby La Oroya. Unfortunately, there is no historical data regarding the extent and timing of mining at Morococha. As shown previously (Cooke et al., 2007) significant metal pollution from mining activity at Morococha significantly predates the industrial era. Therefore, the industrial portion of the record likely records a mixture of metal pollution from both Morococha and La Oroya. The most significant increase in trace metals occurs ~1925 AD, which coincides with the construction of the La Oroya smelting complex. Therefore, it seems entirely likely that La Oroya rapidly accelerated local metal emissions, and has contributed to the Laguna Pirhuacocha sediment record since ~1925 AD. In this light, it appears that emissions of Bi, Sn, and Pb peaked during the early 1970s, while Cu and Sb exhibit a later increase from 1980 to 1990 AD (Fig. 6). As discussed previously, the secular increase in As observed at Laguna Pirhuacocha likely results from some diagenetic overprinting of the sedimentary As record. The cycling of S in lake sediments is complicated, but broadly reflects geographical gradients in anthropogenic S deposition (Bindler et al., 2008). In contrast to the aforementioned trace metals, the Co and Ni profiles suggest little anthropogenic disturbance to the natural geochemical cycling of these elements.

Unfortunately, emission trends for La Oroya to which our sediment record can be compared are only available for Cd, Pb, and As, and only span the last decade (1996–2005 AD) (Cederstav and Barandiarán, 2002; Kcomt, 2007). During this period, atmospheric Cd concentrations at every station increased with maximum annual concentrations (ranging from 0.025 to  $0.35 \mu\text{g m}^{-3}$ ) occurring in 2005. These atmospheric concentrations are 5x-higher than the World Health Organization (WHO) guidelines of  $0.005 \mu\text{g m}^{-3}$ . Emissions of Pb and As during the same period have also increased and both exceed their respective WHO limits of  $0.5 \mu\text{g m}^{-3}$  and  $0.25 \mu\text{g m}^{-3}$ . In addition, 99% of children (6 months–10 years of age) living in and around La Oroya have blood lead levels in excess of  $10 \text{ g/dl}$  (avg= $33.6 \text{ g/dl}$ ; n=346), the WHO/Centers for Disease Control blood level of concern (Centers for Disease Control, 2005). While these emission and population data are limited in both time and space, they highlight the need for continued monitoring in this highly developed region. The Laguna Pirhuacocha sediment record suggests that these recent increases in trace metal emissions represent a small fraction of the cumulative industrial emissions that have occurred over the past century.

## 5. Conclusion

The central Andes of Peru are an area of rapid industrial development. The findings presented here highlight a pressing need for future research in the magnitude of atmospheric

metal pollution in the region. They also highlight the regional nature of metal pollution in the Andes, as both archives record unique histories of metal deposition, despite being only ~100 km apart. Previous research in the Andes has also underscored the local to regional nature of metal pollution in the Andes. For example, Chirinos et al. (2006) found local-scale evidence atmospheric deposition of spheroidal carbonaceous particles (SCPs), but no evidence for long-distance transport of SCPs to remote lake systems. Furthermore, Biester et al. (2002) found no evidence for anthropogenic Pb enrichment to Chilean bog sediments. While comparable research is still lacking for the Peruvian Andes, the suggestion is that long-distance atmospheric transport of trace metals is negligible. This is in contrast to remote Northern Hemisphere lakes to which local trajectories of metal pollution are superimposed over hemispheric signals. The implication is that Andean reconstructions of metal pollution have the ability to track unique, local trajectories of industrial development.

The rates of metal deposition to Lagunas Chipian and Pirhuacocha are comparable to some of the more polluted regions in Europe and North America. Encouragingly, at Laguna Chipian, the depositions of all trace metals investigated here have declined in recent decades and are roughly one-half to one-third peak levels attained during the 1950s. At Laguna Pirhuacocha, the depositional fluxes of some trace metals have declined since peaking during the 1970s (Bi, Sn, and Pb) while others have steadily increased (Sb, Zn, and Cd). The Peruvian Andes have a long history of pre-Colonial, Colonial, and industrial metallurgy, and the cumulative effects of these activities on the environment are only just beginning to be documented.

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