# $^{210}$Pb chronology and trace metal geochemistry at Los Tuxtlas, Mexico, as evidenced by a sedimentary record from the Lago Verde crater lake

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## Abstract

Lago Verde is a fresh-water maar found on the lower slopes of San Martin volcano, at the Sierra de Los Tuxtlas, Mexico, currently the northernmost remnant of the tropical rain forest in America. $^{210}$Pb and $^{137}$Cs analyzed in a sediment core were used to reconstruct the historical fluxes of Ag, Cd, Cu, Pb, Hg and Zn to the site during the last ~150 yr. The $^{210}$Pb$_{xs}$-derived sediment accumulation rates, the magnetic susceptibility, C/N ratios and $\delta^{13}$C data evidenced background conditions at the lake until 1960s, when enhanced erosion related to the clearing of large forested areas at Los Tuxtlas promoted higher accumulation rates of a heavier and more magnetic sedimentary material. Recent sediments from Lago Verde were found enriched by Pb (26-fold natural concentration level [NCLs]) and moderately enriched by Cd>Cu>Zn and Hg (6-, 5-, 4- and 4-fold corresponding NCLs, respectively). The fluxes of Cu, Hg, Pb and Zn have significantly increased since 1940s, with peak ratios of total modern to pre-industrial fluxes of 11, 11, 19 and 49, respectively. The lake occupies a relatively pristine, non-industrialized basin, and therefore the increased metal fluxes might be related to long-distance aeolian transport of trace metals.
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## Introduction

The reconstruction of environment and climate changes over the past few centuries is essential to understanding the impact of natural processes and human activities on the ecosystems and to forecast their future evolution. Among components of global change, land-use conversion has the greatest impact on terrestrial ecosystems, profoundly altering land cover, biota and biogeochemical cycles (Walker and Steffen, 1999). High-resolution (decadal to annual) lake records are useful to assess natural environmental changes over long periods of time and their potential links with cultural development. However, quantitative reconstruction of either natural or anthropogenic events requires a precise chronology. The recent age–depth relationships in sediment cores are commonly calculated by $^{210}$Pb ($t_{1/2}$=22.26 yr), a natural radionuclide byproduct of $^{238}$U decay, which is supplied to lakes by atmospheric precipitation and has been shown to be an ideal tracer for dating lake sediments deposited during the last 100–150 yr (Krishnaswami and Lal, 1978), a period of time during which appreciable environmental changes occurred due to industrialization.

$^{137}$Cs ($t_{1/2}$=30.14 yr) is commonly used to corroborate $^{210}$Pb dating, since these radiotracers provide two independent measurements of the same burial processes occurring within a given sediment core. The artificial radionuclide $^{137}$Cs is present in the environment mainly due to fallout from the atmospheric testing of thermonuclear weapons. Significant fallout on a global scale began shortly after the initial test in the early AD

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1950s, peaked in AD 1963 and then rapidly declined following implementation of the international treaty banning such tests (Delaune et al., 1978). The history of this fallout is frequently preserved in lakes and reservoir sediment records, and where this is the case the peak value in the $^{137}$Cs activity versus depth profile may be used to identify the 1963 depth.

This paper presents an assessment of the modern sediment accumulation patterns in Lago Verde and evaluates how human activities have contributed to remobilize the trace metals burden in the area. The $^{210}$Pb-derived geochronology allowed us to date the upper 34 cm of the sediment core, representing the last ~150 yr; sediment accumulation rates at the lake have significantly increased during the last 40 yr, as a result of the deforestation and consequent erosion at the Sierra de Los Tuxtlas. Trace metal fluxes significantly increased from the 1940s, likely due to atmospheric fallout.

## Methods

### Study site

The Sierra de Los Tuxtlas is located in the state of Veracruz at the coastal plain of the Gulf of Mexico. This upland region is the result of Miocene, Pleistocene and Holocene volcanism (Santley et al., 2000) with lavas consisting of basanites and alkali basalts (Nelson and González-Caver, 1992). The soil type is andosoles derived from recent volcanic ash (Vázquez et al., 2004). This area is covered by dense tropical vegetation that constitutes the northernmost remnant of lowland tropical rainforest in America (Dirzo et al., 1997). The climate at the Sierra de Los Tuxtlas is hot and subhumid on the coastal plains, and temperate and humid in the highlands (García, 1981). The temperature in the area ranges between 32°C (May–June) and 18°C (December–January) and has a summer to early-autumn rainy season with annual precipitation of 2500 mm (Coates-Estrada and Estrada, 1986). The prevailing winds in the Sierra are the northeastern trade winds; however, strong cold winds from the north (nortes), peaking at over 100 km h$^{-1}$, strike the region from September through March; and hot–dry air masses (suradas) sweep in from the south toward the coast, during the dry season, from March through May (Buckles and Erenstein, 1996).

San Martín is the highest mountain at Los Tuxtlas (1,680 m a.s.l.) and is a broad alkaline shield volcano with more than 250 pyroclastic cones and maars on its lower slopes, some of which contain a lake, including Lago Verde (GVP, 2004). Lago Verde (Fig. 1) has a shallow water table and is about 400 m diameter and 4 m maximum depth. The water column has a reduced transparency (0.3–0.5 m depth) due to high content of suspended matter, influenced by eutrophic conditions and runoff during rainfalls. As a closed volcanic lake, groundwater and rainfalls are the most significant water inputs, and water is lost only through evaporation.

### Sampling

Two parallel sediment cores (VRUI and VRUII, 5-cm diameter, 6-m long) were collected in February 2001 at the center of Lago Verde (18°36.72′N, 95°20.87′W, 149 m a.s.l.) under 4 m of water using a piston corer. The cores showed undisturbed mud–water interfaces, and no evidence of bioturbation was observed along the sequences. This paper presents the findings from only the top 50 cm of VRUI sequence, where
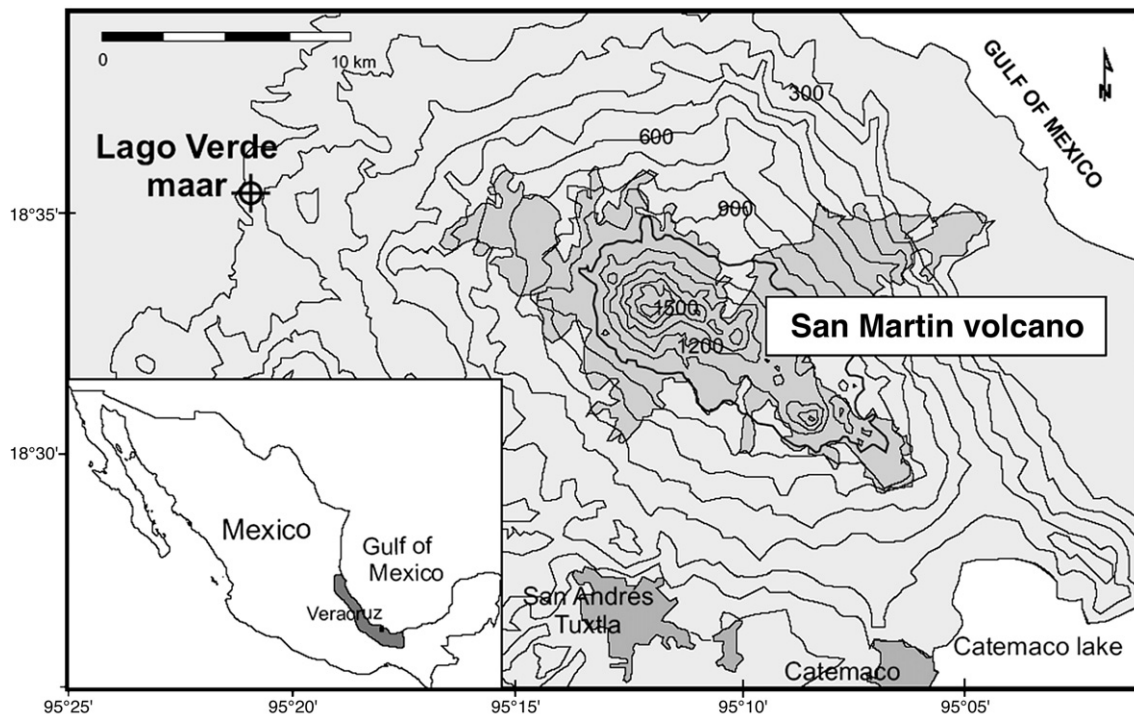


Figure 1. Location of Lago Verde crater lake in San Martin Volcano, Los Tuxtlas, Mexico.

[210]Pb-derived dates were expected to be reliable. The core was sectioned into 1-cm intervals and the samples were freeze-dried to constant weight, ground to a powder with an agate mortar and pestle, and stored in polyethylene bags.

### Laboratory analysis

Organic carbon (OC) and total N ($N_{tot}$) content were measured with a Carlo-Erba™ elemental analyzer, and uncertainties were determined from replicate measurements of standard materials, averaging ±5%. Inorganic carbon (expressed as $CaCO_3$) was determined from coulometric measurements. C/N ratios represent OC to $N_{tot}$ atomic ratios. [13]C content was measured on acidified aliquots loaded on the carousel of a Carlo-Erba™ elemental analyzer on-line with a Micromass IsoPrime™ instrument; overall analytical uncertainty, also determined from replicate measurements of standards, was ±0.15‰.

Magnetic susceptibility measurements were made with a Bartington Core logging sensor, with values being expressed in SI dimensionless volume units.

Sediments for metals and ^{210}Pb analysis were digested in a mixture of 5:4:1 $HNO_3 + HCl + HF$ (Loring and Rantala, 1992) using a microwave system (CEM MDS 2000).

Metals were analyzed by Atomic Absorption Spectrometry (Al, Cu, Fe, Mn and Zn by flame and Cd, Li and Pb by graphite furnace). Hg was analyzed after reduction with $SnCl_2$ in a Cold Vapor Mercury Analyzer (Buck Scientific™). Analytical checks were made on reference material IAEA-SL-1 and MESS-2. Recovery (in %) varied according to the metal, as follows: 89–101 for Al, 81–104 for Fe, 89–93 for Mn, 96–116 for Cd, 90–93 for Cu, 102 for Hg, 105–109 for Pb, 95–97 for Zn; variation coefficients estimated were less than 8%; and detection limits ($\mu g\ g^{-1}$) were found to be 0.01 for Ag and Cd; 0.02 for Hg, 0.05 for Cu, Li, Mn, Pb and Zn; and 0.1 for Al and Fe.

Total [210]Pb ($^{210}Pb_{tot}$) was determined by alpha spectrometry through its granddaughter [210]Po, assuming secular equilibrium. [210]Po and [209]Po (yield tracer) were spontaneously deposited onto a silver disc (Flynn, 1968) which was counted on a standard silicon surface barrier detector. [137]Cs (663 keV) and [226]Ra were measured by gamma-ray spectrometry; pre-weighed sediment samples were sealed glass vials for at least 21 days before being counted until obtaining an uncertainty <10%. [226]Ra was measured indirectly through [214]Pb (241.9,

295.2 and 351.9 keV) and [214]Bi (609.3 keV), assuming secular equilibrium. Replicate analyses ($n = 12$) of the certified reference material IAEA-300 confirmed good agreement of activities determined for [137]Cs. For [210]Po analytical method, accuracy and precision were estimated to be 99% and 4.6% respectively.

## Results and discussion

### Sediment properties

Sediment analyzed consisted of brown organic-rich silts. The dry bulk density profile (Fig. 2a) showed two types of sediment, one lighter from 8–50 cm depth ($0.17 \pm 0.02$ g cm$^{-3}$) and a heavier one from 8-cm depth to surface ($0.42 \pm 0.04$ g cm$^{-3}$).

The magnetic susceptibility (Fig. 2b) exhibited background values between 12 and 50 cm depth ($\sim 10 \times 10^{-5}$ SI; Ortega et al., in press) indicating a steady composition of the sediment until the late 1940s, when susceptibility values drastically increased and peaked at 5-cm depth. Above this level, the values gradually decreased toward the surface until reaching values as low as the background. The trend and levels found at Lago Verde are comparable to those previously reported for recent lacustrine sediments in the basin of Mexico (values in $10^{-5}$ SI): Chalco Lake, 0.2–30.0 (Lozano-García and Ortega-Guerrero, 1994) and Espejo de los Lirios Lake, 0.9–5.8 (Ruiz-Fernández et al., 2005) for which, in both cases, increasing susceptibility values were attributed to erosion at the surroundings resulting from land-use changes.

Aluminum and Li profiles (Figs. 3a and b) showed moderate variations with depth (1.4–6.9% and 2.3–6.5 $\mu g\ g^{-1}$, respectively) although an increasing trend towards the surface was observed at the uppermost 10 cm of the core. Fe content ranged from 2.6% to 6.3% and Mn concentrations from 254 to 945 $\mu g\ g^{-1}$, with the maximum values found at about 16-cm depth. From above this depth to the surface, however, the Fe and Mn profiles (Figs. 3c and d) showed the typical profile of an oxic sedimentary environment, with the highest concentrations at the sediment–water interface. Both metals are diagenetically mobile in aquatic systems, depending on redox conditions; reduced metal species, dissolved in the pore water, can migrate to the sediment surface where they will be reoxidized and precipitated as oxyhydroxides, yielding higher concentrations (Cochran et al., 1998).
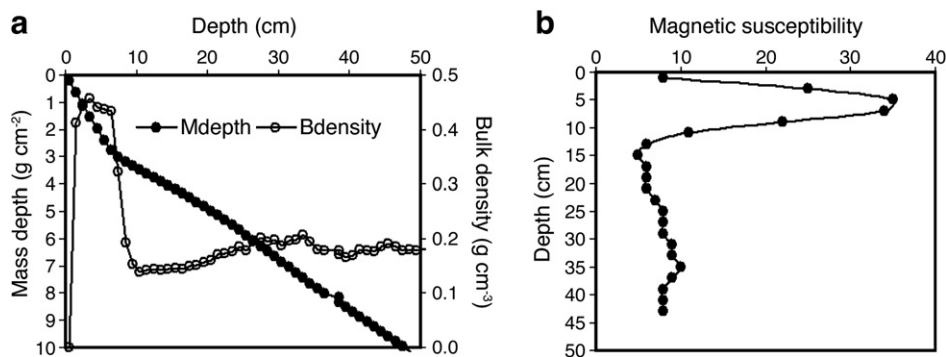


Figure 2. (a) Mass depth and bulk density and (b) magnetic susceptibility in sediment core VRUI from Lago Verde crater lake.
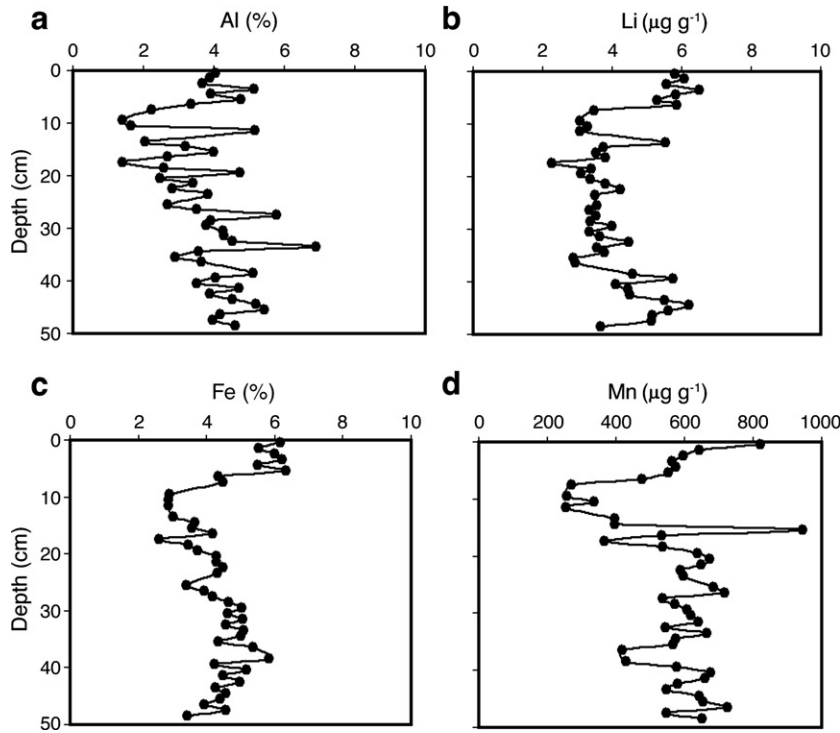
Figure 3. Al, Li, Fe and Mn profiles from sediment core VRUI.

*Radioisotope dating*

[137]Cs peak activity (Fig. 4a), which is assumed to correspond to sediments deposited in the years 1962–1964, was located at 7.5-cm depth (107 Bq kg^{−1}). It was higher than those previously found in other Mexican lakes such as Chapala Lake in Jalisco State (30–50 Bq kg^{−1}; Fernex et al., 2001), Zirahuén in Michoacán State (∼18 Bq kg^{−1}; Davies et al., 2004) and Espejo de los Lirios lake in Mexico State (13.5 Bq kg^{−1}; Ruiz-Fernández et al., 2004).

Total [210]Pb ([210]Pb$_{tot}$) activities ranged from 35 to 506 Bq kg^{−1}. The supported ^{210}Pb activity ([210]Pb$_{sup}$) was derived from the almost constant value found between 45 and 50 cm depth (38.1±1.9 Bq kg^{−1}) and it was used to calculate the excess ^{210}Pb activities ([210]Pb$_{xs}$=[210]Pb$_{tot}$−[210]Pb$_{sup}$). The [210]Pb$_{xs}$ inventory in the core was estimated to be 1343±15 Bq m[−2] (Table 1), which would require to be supported by a mean [210]Pb$_{xs}$ supply rate of about 42±0.5 Bq m[−2] yr^{−1}, which is comparable to the lowest [210]Pb$_{xs}$ depositional fluxes found in two other studies developed in Mexican lakes: 45 Bq m[−2] yr^{−1} in Chapala lake (20°15′N, 103°09′W, 1,500 m a.s.l.; Fernex et al., 2001); and 48 Bq m[−2] yr^{−1} in Zirahuén lake (19°26′N, 101°44′W, 2075 m a.s.l.; Davies et al., 2004), confirming that atmospheric origin is the main source of ^{210}Pb supply.

The logarithmic [210]Pb$_{xs}$ profile versus the cumulative dry mass of the sediments (g cm^{−2}) presented two major discontinuities at 7.5- and 19.5-cm depth (Fig. 4b). In order to verify that such anomalies were not promoted by changes in sediment composition (mineral type, grain size distribution, OC or CaCO$_3$ content), the [210]Pb$_{xs}$ profile was normalized by OC, CaCO$_3$, Al and Li concentrations; however, the effect was to

increase [210]Pb$_{xs}$ activities without removing the features. The non-monotonic features in the [210]Pb$_{xs}$ profile suggested that sediment accumulation have varied during the period recorded in the core and, therefore, the ^{210}Pb chronology was first calculated using the "Constant Rate of [210]Pb Supply" (CRS) dating model that allows to estimate changes in sedimentation rates through time, providing that the atmospheric flux is the dominant factor controlling the ^{210}Pb supply (Appleby and Oldfield, 1992). However, a discrepancy of ∼8 yr observed between the CRS and the ^{137}Cs-derived dates for the 7.5-cm depth layer (1963) signaled a significant change in the initial ^{210}Pb concentration in sediments accumulating ∼40 yr ago.

The mean ^{210}Pb flux (P) registered at the uppermost 8 cm of the sedimentary core was calculated using the following equation (Appleby, 2001):

$$P = \frac{\lambda \Delta A}{e^{-\lambda t_1} - e^{-\lambda t_2}}$$

where $\Delta A$ is the ^{210}Pb inventory between $x_1$ and $x_2$, i. e. the surface and 7.5-cm depth. The measured value (40 Bq m[−2] yr^{−1}) indicated a slight dilution of the atmospheric ^{210}Pb flux to the site, which could have various causes such as flood events, sediment slumps or major land-use changes.

Corrected ^{210}Pb dates and sedimentation rates for the intermediate depths were calculated assuming that P was uniform within the section and the age (t) of the sediment layer at depth x, intermediate to $x_1$ and $x_2$, was determined as (Appleby, 2001):

$$t = \frac{\text{Ln}\left(e^{-\lambda t_1} + \frac{\lambda}{P}\Delta A_{(x_1,x)}\right)}{-\lambda}$$
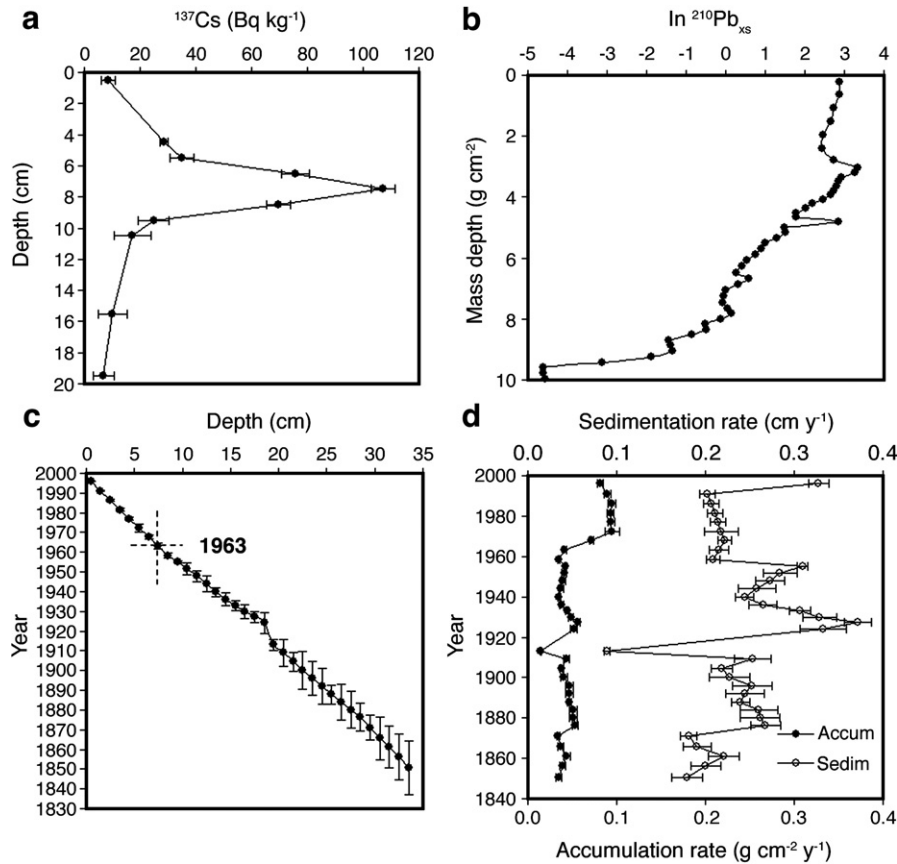
Figure 4. (a) $^{137}$Cs, (b) ln $^{210}$Pb$_{xs}$ versus mass depth, (c) $^{210}$Pb-derived choronology and (d) sedimentation and accumulation rates depth profiles from sediment core VRUI.

where $\Delta A_{(x_1,x)}$ is the $^{210}$Pb inventory between $x_1$ and $x$. The dates below 8-cm depth were corrected adding the $\sim 8$-yr difference previously found between CRS and $^{137}$Cs dates. Thus, the composite $^{137}$Cs–CRS dating model allowed to date the sediment core up to 34-cm depth, corresponding to a time span of $\sim 150$ yr (Table 1, Fig. 4c). The accumulation rates (0.003–0.095 g cm$^{-2}$ yr$^{-1}$) were quite steady until the late 1960s, when values almost doubled; but the sedimentation rates (0.02–0.37 cm yr$^{-1}$) have shown a higher variability throughout the period studied (Fig. 4d).

Further confirmation for $^{210}$Pb and $^{137}$Cs geochronologies was obtained upon the presence of charcoal particles ($>100$ mm) that were found at the topmost 30 cm of the parallel core VRUII (which correlated with the topmost 10 cm of VRUI core; Caballero et al., 2006). Charcoal fragments are the result of vegetation burning either for agricultural purposes or from sugar

cane industry (burning the sugar-cane trash during harvesting or crushing). Sugar cane is not cultivated within Lago Verde basin, but particles could have been transported by the winds from the surroundings. Sugar-cane cropping area nearly doubled between 1960 and 1970, reaching a historical maximum in the late 1960s (Azucar S.A. de C.V., 1983). However, large forested areas of Los Tuxtlas were subjected to slash-and-burn clearing of land for agriculture and development during the 1960s in the framework of government-subsidized programs.

### Carbon, nitrogen, C/N ratios and $\delta^{13}C$

Sediment samples from the top 50 cm of the VRUI core had practically no carbonate ($<0.1\%$) and the OC content ranged from 7% to 20% (Fig. 5a). The surficial layers of the core (up to 10-cm depth) showed a significant inverse linear correlation between the OC content and depth ($P<0.05$, $r=0.87$); however, it also presented two sections (from 10–32 and from 35–49 cm depth) in which OC content declined exponentially downcore (5b). The OC decomposition rates for these sections were evaluated by using the first-order G model (Zimmerman and Canuel, 2000) and the results (Fig. 5b and Table 2) indicated that both sections had an almost steady degradation, with comparable OC decay rates and high OC metabolization fractions at the sediment–water interface. However, OC half-life for the layers below 35-cm depth (older than 150 yr) is much higher than those

Table 1
$^{210}$Pb-derived accumulation and sedimentation rates in Lago Verde crater lake

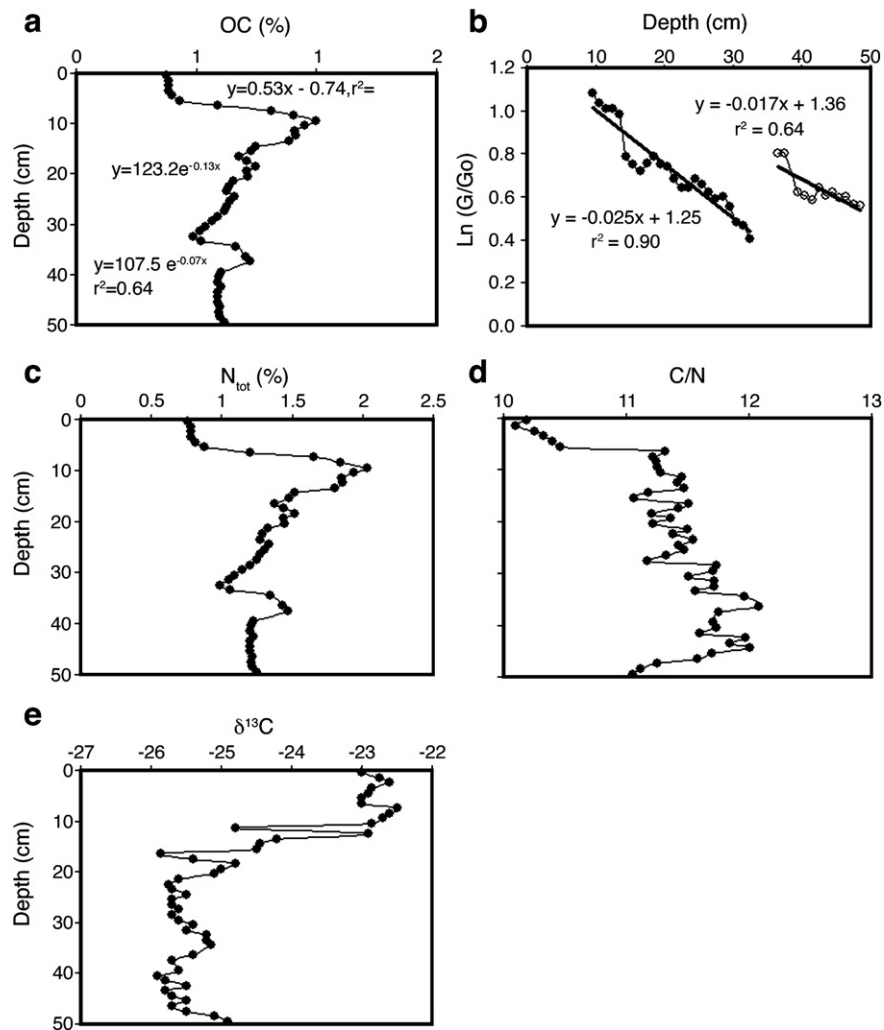| Depth interval (cm) | Mean CRS rates | |
|---|---|---|
| | Accumulation (g cm$^{-2}$ yr$^{-1}$) | Sedimentation (cm yr$^{-1}$) |
| 0–8 | 0.09±0.01 | 0.23±0.04 |
| 8–34 | 0.04±0.01 | 0.25±0.06 |
| 34–50 | 0.01±0.01 | 0.09±0.05 |

Figure 5. (a) Organic carbon, (b) first-order G-model for organic decay, (c) Total nitrogen, (d) C/N ratios and (e) $\delta^{13}C$ profiles in sediment core VRUI.

accumulated between 10 and 32 cm depth (AD 1860–1955), indicating that the younger layers contains more labile OC than the refractory OC preserved in the oldest ones.

$N_{tot}$ concentrations at Lago Verde varied from 0.8% to 2.0%, showing a depth profile very similar to that of OC (Fig. 5c) with a very significant correlation ($P<0.05$, $r=0.99$) between both constituents. The C/N ratios profile (Fig. 5d) showed an increasing trend with depth and could be divided into three sections according to their mean values, which were slightly but significantly different from each other (ANOVA, $P<0.05$): $11.67\pm0.27$ (28−50 cm), $11.33\pm0.13$ (6−28 cm) and $10.29\pm0.13$ (surface to 6 cm). The C/N ratios are typical of surface

Table 2
First-order G model for OC concentrations at core VRUI, Lago Verde crater lake

| Depth interval (cm) | 10–32 | 35–49 |
|---|---|---|
| G model equation | $y=-0.025x+1.25$ | $y=-0.017x+1.36$ |
| Determination coefficient ($r^2$) | 0.90 | 0.64 |
| Sedimentation rate (cm yr$^{-1}$) | 0.25 | 0.09 |
| OC decay rate ($k$, yr$^{-1}$) | $6.3\times10^{-3}$ | $1.5\times10^{-3}$ |
| OC half-life ($t_{1/2}$, yr) | ~160 | ~654 |
| OC metabolized fraction (%) | 71 | 74 |

sediments from mesotrophic–eutrophic lakes (Punning and Tõugu, 2000), suggesting a mixture of algal and higher-plant sources (C/N > 10–12; Tyson, 1995) with a predominant autochthonous contribution. Based on the simple equation for the mixing of two components and considering a C/N ratio of 6 for planktonic matter (Ho and Meyers, 1994) and 30 for vascular plants that might have been transported into the lake from the catchment, the phytoplanktonic contribution was estimated as a minimum of 76% to 82% for C/N of 11.67 and 10.29, respectively.

Two factors might be contributing to the diminution in C/N values: (a) an increasing contribution of OC-impoverished soils to the lake and (b) the enhancement in the primary productivity and the eutrophication of the lake associated with human impact. The traditional agriculture system at Los Tuxtlas region included frequent burning to clear the field for planting, to control weeds and plagues, and to reduce vegetation and crop residues. Burning leaves the soil almost bare, which in turn increases the risk of soil erosion and will cause exposure and remobilization of deeper OC-impoverished soil (Buckles and Erenstein, 1996). On the other hand, according to findings in the second sediment core collected in Lago Verde (core VRUII,

Ag (µg g⁻¹)

Cd (µg g⁻¹)
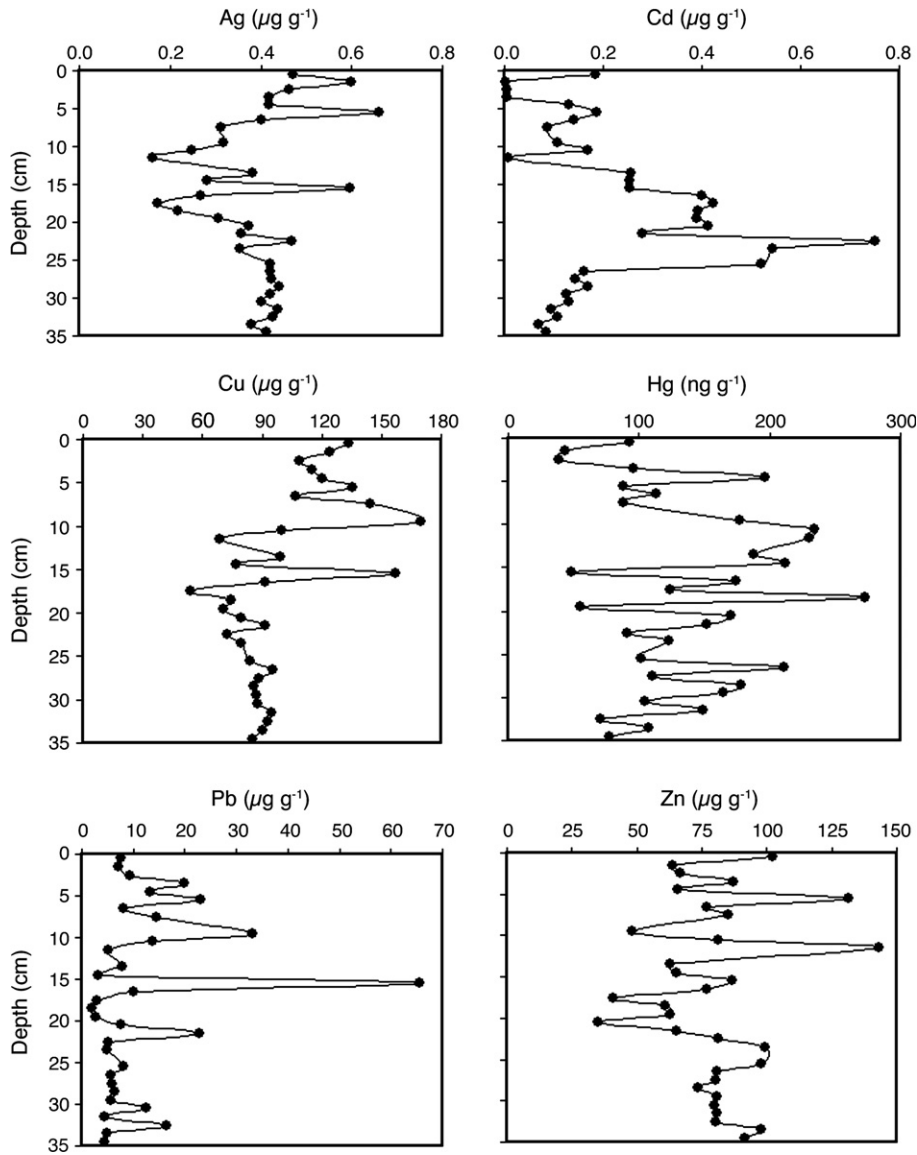
Cu (µg g⁻¹)

Hg (ng g⁻¹)

Pb (µg g⁻¹)

Zn (µg g⁻¹)

Figure 6. Trace metal profiles from sediment core VRUI.

Caballero et al., 2006), high erosion rates taking place since ca. 1963 in the surroundings of Lago Verde have led to a more turbid, and productive, eutrophic lake.

$\delta^{13}C$ values ranged from $-25‰$ to $-26‰$ from the bottom of the sediment core up to 16-cm depth; afterwards, $\delta^{13}C$ values tended to increase and showed the most enriched at the

Table 3
Natural concentration levels in Lago Verde crater lake

| Metal [a] | Lago Verde | Earth Crust [b] |
|---|---|---|
| Ag | 0.6±0.1 | 0.1 |
| Al | 4.0±0.3 | 8.8 |
| Cd | 0.2±0.1 | 0.2 |
| Cu | 95.0±9.0 | 100 |
| Fe | 4.0±0.6 | 8.6 |
| Hg | 0.2±0.1 | 0.08 |
| Li | 5.0±1.0 | 10 |
| Mn | 642±89 | 1500 |
| Pb | 4.0±2.0 | 5 |
| Zn | 57.0±5.0 | 100 |

[a] Metal concentrations are in $\mu g\ g^{-1}$, except Al and Fe (%).
[b] Taylor (1964).

Table 4
Enrichment factor (EF) for metals analyzed in sediments from Lago Verde

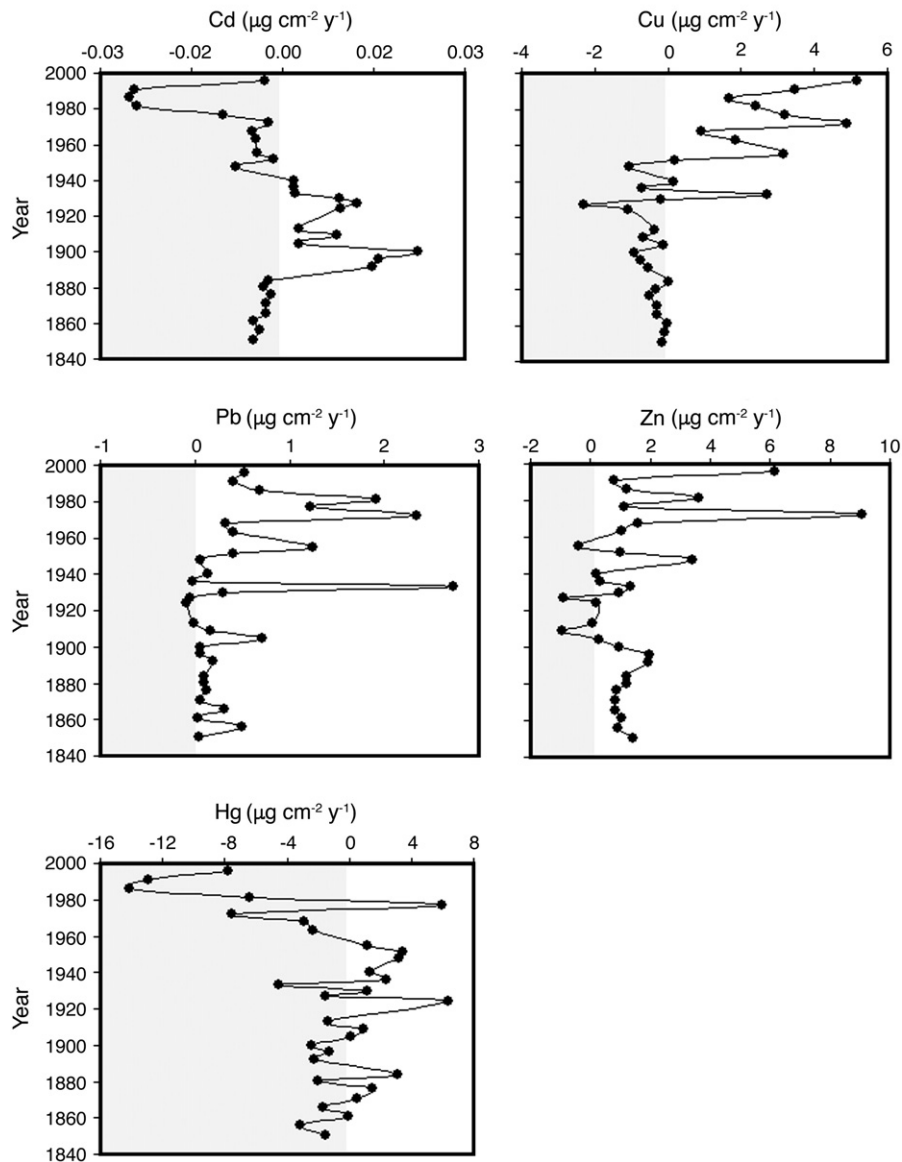| Metal | Normalizing element | |
|---|---|---|
| | Al | Li |
| Ag | 0.2–1.7 | 0.4–1.5 |
| Al | – | 0.4–2.1 |
| Cd | 0.1–6.2 | 0.1–4.3 |
| Cu | 0.6–5.3 | 0.7–2.7 |
| Fe | 0.6–2.2 | 0.6–2.1 |
| Hg | 0.1–4.0 | 0.1–2.5 |
| Li | 0.5–2.5 | – |
| Mn | 0.3–1.8 | 0.5–1.9 |
| Pb | 0.4–26 | 0.4–22.3 |
| Zn | 0.8–3.8 | 0.7–3.7 |

Figure 7. Excess metal fluxes profiles from sediment core VRUI. Shaded areas show negative excess fluxes produced by strata with metal concentrations lower than natural concentration levels (NCLs).

top sediment layers of the core with values ranging around a mean of $-22.8\pm0.2‰$ (Fig. 5e). The increment in $\delta^{13}C$ by approximately 3.4‰, observed in the most surficial sediments of the core, may be explained from greater rates of algal productivity in the lake waters; however, changes in vegetation type in the surroundings, such as the introduction of C4 plants (such as corn or sugar cane) into a typical C3 woody plants forest, should also be considered (C4 plants show a $\delta^{13}C$ range of $-8$ to $-14$; Bender et al., 1981).

The profiles of bulk density, magnetic susceptibility, $^{210}Pb_{xs}$-derived sediment accumulation rates, OC, C/N ratios and $\delta^{13}C$ have shown the steady conditions prevailing on the lake at the beginning of the 20th century, when autochthonous material dominated the sedimentation of the lake; however, from late 1960s, the steady OC decay process was replaced by a dilution mechanism with a heavier and more magnetic sedimentary

material (as indicated by the bulk density and magnetic susceptibility profiles) which accumulated at accelerating accumulation rates, as shown by the $^{210}Pb_{xs}$ geochronology.

Between AD 1960 and 1970, several countries in Latin America undertook actions for massive conversion of tropical landscapes from old-growth forests to agriculture and ranching areas (Reyes Hernández et al., 2006). In Mexico, large forested areas were also cleared to create croplands and to serve as induced or cultivated pasture for extensive cattle production. Forest clearance at Los Tuxtlas peaked between the 1960s and 1980s, by which time 84% of the original forest area had been lost (Dirzo and García, 1992). Thus, the changes recorded at the most surficial layers of the core indicated the accelerated accretion of sediments enriched by volcanic material supplied by runoff, resulting from the enhanced rate of erosion within and around the watershed, most likely promoted by changes in land
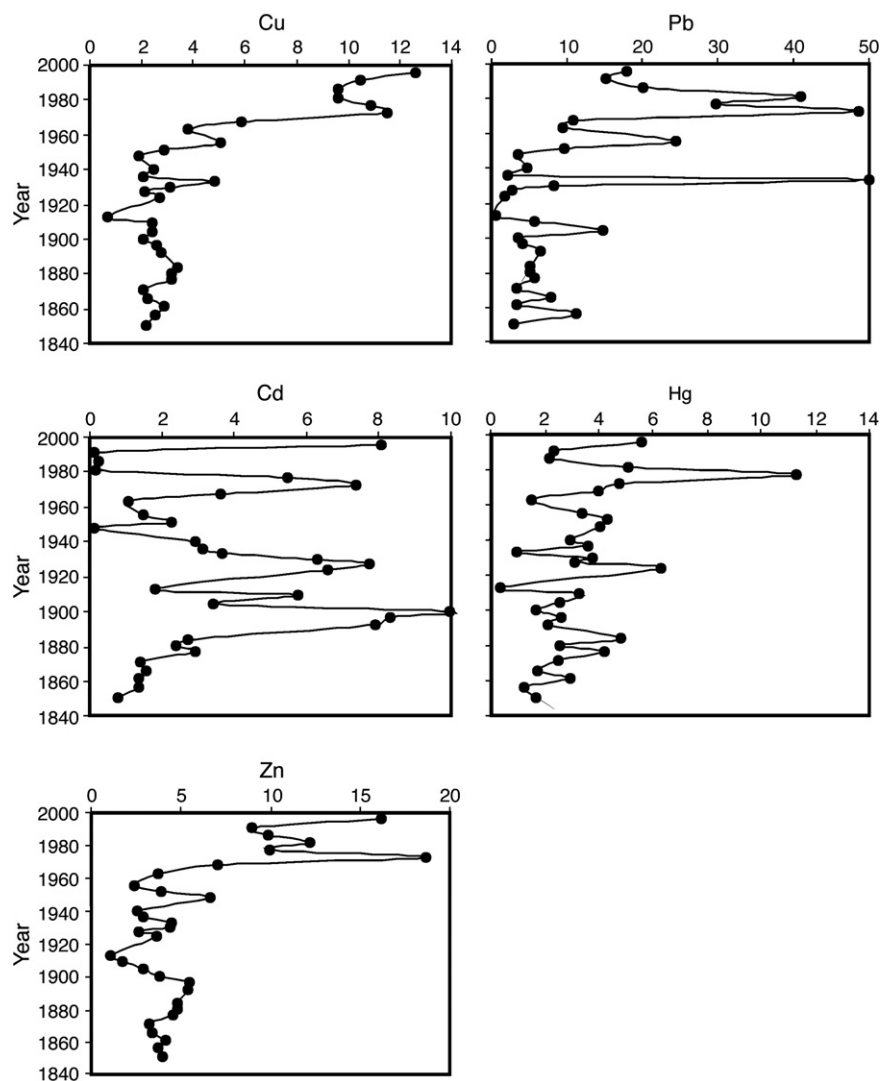
Figure 8. Metal flux ratios profiles from sediment core VRUI.

use (as suggested by C/N ratios and $\delta^{13}$C) and the heavy deforestation that have occurred at the tropical rain forest of Los Tuxtlas in the past 40 yr.

*Trace metals concentrations, enrichment and fluxes*

Trace metal profiles in core VRUI are shown in Figure 6. All the profiles showed considerable variability and subsurficial maxima. Ag, Al and Li profiles showed a slight decreasing trend from the deepest layers of the core up to 18-cm depth and then an increasing trend to the surface; Cu, Pb and Zn showed moderate variability between 50- and 20-cm depth, and then a higher variability with the highest values toward the surface. Cd profile showed the highest concentrations between 11- and 27-cm depth and a second maxima at 45-cm depth. Hg profile was completely erratic.

Trace metal enrichment in surface sediments can be attributed to anthropogenic mobilization, but it can also be the result of diagenesis. Trace metals tend to complex with OM as well as to adsorb onto particulate Fe and Mn oxyhydroxides in surface

sediments; upon OM decay and/or reductive dissolution of Fe and Mn oxyhydroxides, reduced metal species can be captured by authigenic sulfides or, due to sedimentation compaction, can migrate to the oxic sediment surface where trace metals can be readsorbed by the Fe and Mn oxyhidroxides or by OM (Tessier et al., 1985). In order to evaluate if trace metal distribution observed in VRUI sediments was shaped by diagenesis, a correlation analysis was performed. No evidence was found that Cd, Cu, Hg Pb or Zn profile distributions were influenced by redox diagenesis; Mn and Fe concentrations presented significant positive correlations ($P<0.05$) only between them and with Al and Ag (which was attributed to a common detrital origin); and OC significantly correlated with Hg only if using the data from surface to 20-cm depth (explaining the 40% of Hg variability).

The natural metal concentration levels (NCL) in Lago Verde were calculated as the average value of the three deepest layers of the core (where excess $^{210}$Pb was no longer present) to guarantee that levels found were due to pre-industrial contribution (Table 3). The NCLs found for Cd, Cu and Pb were

consistent with the natural abundance of metals in the basaltic component of the continental crust (Taylor, 1964). The NCLs for Cu and Zn also fell within the concentration ranges found at San Martin volcano young lavas (32–84 and 50–87 $\mu g\ g^{-1}$, respectively; Nelson and González-Caver, 1992).

Metal enrichment over NCLs was evaluated by the enrichment factor (EF) proposed by Glasby and Szefer (1998):

$$EF = [X/Al,\ Li]_{sample}/[X/Al,\ Li]_{NCL}$$

where $[X/Al,\ Li]_{sample}$ is the ratio of concentration of any metal to concentration of Al or Li in the sample at a given depth and $[X/Al,\ Li]_{NCL}$ is the ratio of NCL of any metal to Al or Li.

EFs values obtained for all the metals analyzed were close to one for most of the metals below 26-cm depth of the core (Table 4), indicating that natural concentrations prevailed up to the beginning of the 20th century except for Pb, which appeared to be moderately enriched (EF 3–4) before this threshold. After this period, EFs values allowed us to differentiate two metal groups: (a) detritic metals, such as Ag, Fe and Mn, which appeared slightly enriched (maximum 2-fold increase with respect to the corresponding NCLs); and (b) anthropogenic metals, which presented higher enrichments with maximum increases in NCLs of 4- (Zn, Hg), 5- (Cu), 6- (Cd) and 26-fold (Pb). Most increases occurred between 1960 and 1970 with exception of Cd, which showed peak EF values between 1890 and 1950. After the 1970s, the EFs of almost all metals returned to ∼1, indicating a return to natural conditions, except for Pb, which showed a moderate enrichment after this date (EF 2–8).

Excess metal fluxes ($MF_{xs}$) were calculated as follows (Cochran et al., 1998):

$$MF_{xs(i)} = W_i[M^+]_{xs(i)}$$

where $MF_{xs(i)}$=metal flux for the $i$th depth interval ($\mu g\ cm^{-2}\ yr^{-1}$), $W_i = ^{210}Pb$-derived accumulation rate for the $i$th interval ($\mu g\ cm^{-2}\ yr^{-1}$) and $[M^+]_{xs(i)}$=excess metal concentration for the $i$th interval ($\mu g\ g^{-1}$).

$MF_{xs}$ profiles obtained for all the metals studied exhibited a high variability (Fig. 7). Ag, Al and Mn showed no excess fluxes during most of the period studied (negative $MF_{xs}$) while positive $MF_{xs}$ were found for Cd (0.002 to 0.022) between 1890 and 1950; for Hg (0.07–6.35) between 1880 and 1985; for Li and Cu (0.03–0.22 and 0.15–5.2, respectively) from the 1940s to present; and for Fe, Pb and Zn (0.01–0.30, 0.03–2.70, 0.08–9.05, respectively) all along the 150 yr examined.

The metal fluxes changes over time were evaluated by the flux ratio (FR) proposed by Heyvaert et al. (2000) that, unlike the EFs, has the advantage of its independence from historical variation in the mass sedimentation rate, and providing a unitless measure for the comparison of changes in metal deposition between sites and geographic regions. It is calculated dividing the modern metal fluxes (using the total uncorrected metal concentrations) by the pre-anthropogenic flux estimated from the product of the NCL of each metal and the mean accumulation rate of the oldest section of the core obtained from the $^{210}Pb$-

derived chronology. The FR profiles exhibited a high variability (Fig. 8) but all of them demonstrated that fluxes have notably increased from the very beginning of the 20th century. The peak FR for Cd (10) was found in AD 1910, whereas maximum FR values for Cu (11) was found in late 1990s. Maximum values for Hg (11), Zn (19) and Pb (49) were observed during the early 1980s (although during 1942, Pb presented a comparable peak FR value). Maximum FRs for Hg, Zn and Pb at Lago Verde appeared to be higher than those found at Espejo de los Lirios lake, in the Metropolitan Zone of Mexico City (Ruiz-Fernández et al., 2004) between 1970 and 1990 (2, 12 and 13, respectively), while maximum FRs for Cd and Cu were equivalent (11).

The metal concentration profiles, the Al-normalized EFs, the $MF_{xs}$ and the FRs obtained from the sediment core VRI showed that natural levels of most metals prevailed up to the beginning of AD 1900. Even when the highest EFs for Cu, Hg, Pb and Zn were found during the 1960s, the flux ratios (FRs) have signaled that there was an important increment for all metal fluxes that started around the 1940s and peaked during middle 1980s.

*Metal provenance*

Principal component analysis (PCA) was used to identify associations among 14 geochemical variables at the sediment core VRUI, and to corroborate the metal provenance. Two principal components were found (eigenvalues>2; Table 5) to explain the 53% of the total variance (33% and 20% for factors 1 and 2, respectively). The PC1 (lithogenic fraction) had positive loadings for Ag, Al, Fe, Li and Mn, the assemblage of metals that characterize the detritic mineral matrix; and negative loadings for OC and $N_{tot}$ that represents the allochtonous production at the lake and a diluting factor for the terrigenous input. The PC2 (atmospheric input) included positive loadings for Cu, Pb and $^{210}Pb$ representing the wind-blown material. The atmospheric input of Pb and Cu as signaled by the PC2 could be related to gasoline combustion, since leaded gasoline con-

Table 5
PCA for geochemical data from sediment core VRUI, Lago Verde, Mexico

| Variable | Factor loadings (Varimax normalized) | |
|---|---|---|
| | Factor 1 Lithogenic input | Factor 2 Atmospheric input |
| Ag | **0.72** | 0.05 |
| Al | **0.68** | −0.10 |
| Cd | −0.14 | −0.50 |
| Cu | 0.07 | **0.87** |
| Fe | **0.79** | 0.23 |
| Hg | −0.40 | −0.40 |
| Li | **0.64** | 0.30 |
| Mn | **0.68** | −0.14 |
| Pb | −0.13 | **0.65** |
| $^{210}Pb$ | −0.39 | **0.78** |
| Zn | 0.12 | 0.20 |
| $N_{tot}$ | **−0.94** | −0.09 |
| OC | **−0.91** | −0.17 |
| Susceptibility | 0.16 | 0.53 |
| Expl.Var | 0.33 | 0.2 |

Significant loadings (>0.6) are in bold.

sumption used to be the most significant source of Pb to the environment. The use of fossil hydrocarbons as fuels also provides an opportunity for metal emissions to the atmospheric environment, including Hg, Cd, Cu and Zn. According to Stigter et al. (2000), these metals are present in crude oils in low concentrations, but all the metals eventually make their way into refined petroleum products and are released to the environment upon combustion. Soto-Jiménez et al. (2006) have used $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios to determine that the contaminant Pb found in VRUI sediments is mostly derived from Mexican lead ores that were used in the production of tetraethyl lead (TEL) additives for Mexican gasoline from the 1930s to the 1990s.

Considering that Lago Verde is located in a rather isolated, relatively pristine, non-industrialized basin, surrounded mostly by pasture lands and secondary vegetation, the increased metal fluxes are most likely the result of atmospheric fallout. One of the most important oil processing zones of Mexico is located about 50 km southeast from Lago Verde, including the oil refinery of Minatitlán and the petrochemical complexes Morelos, Pajaritos and Cangrejera. Considering that the Minatitlán oil-refinery started operations from early 1900s, it could be possible that some of the exhausts released from these processing plants were enriched by trace metals, transported through the atmosphere and incorporated in the sedimentary record of Lago Verde. Further research would be necessary to verify this hypothesis.

## Conclusions

A $^{210}Pb$ chronology of trace metals enrichment was studied in a single sediment core collected at Lago Verde crater lake (Los Tuxtlas, Mexico). The sedimentary record studied have shown increasing sediment accumulation rates that peaked between AD 1960 and 1980 related to the intense deforestation of the tropical rain forest of Los Tuxtlas as a consequence of agriculture and ranching projects. Trace metals enrichment factors and excess metal ratios indicated trace metals remobilization since the beginning of 1900s that peaked during 1940s and 1980s. PCA has demonstrated an important lithogenic contribution of trace metal, as well as an aeolian supply of Cu and Pb probably originating from the oil industry located in the region. Conclusions derived from this study are limited by the representativeness of a single core to reconstruct the geochemical history in the region; therefore, further research is recommended to quantify the atmospheric contribution to the enrichment of trace metals.

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