Historical reconstruction of small-scale gold mining impact in tropical wetland sediments Bajo Cauca-Antioquia, Colombia.

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Abstract

Global mining investment in Latin America has increased exponentially over the last decade, resulting in the release of vast amounts of toxic metals into the environment. Here, historical trends of trace metals (i.e., Hg, Cr, Cu, Ni and Pb) of small-scale Gold Mining (ASGM) were reconstructed using a dated (^{210}Pb and ^{137}Cs) sediment core collected from a tropical wetland located in Antioquia (Colombia), a region characterized by increased mining development over the past century. Results showed that metal concentrations at the beginning of the 20th century were similar to background values, indicating that there is no impact of any previous anthropogenic activities. The significant increase in both sediment accumulation rates and total organic carbon (TOC) that occurred in the 1940s

reflects the deforestation of the area due to the diversification of the economy (e.g. coffee cultivation, mining or animal husbandry). Both concentrations and accumulation rates of metals increased exponentially after the 1980s due to the reactivation of alluvial gold exploitation, reaching concentrations that exceeded up to 2-5 times the background values.

Keywords: *gold Mining, heavy metals, contamination, ^{210}Pb dating, tropical wetland*

1. Introduction

Artisanal and Small-scale Gold Mining (ASGM) is one of the main activities that introduces vast amount of heavy metals (e.g. Ag, Cr, Cu, Hg, Ni, Pb, Zn) into the environment (Adriano, 2001; Lar et al., 2015; Camizuli et a. 2018; Aliyu et al., 2018). Although mining activities provide large economic benefits for companies and governments, high amounts of metals introduced into the biosphere may have adverse effects on human and environmental health (Singh and Kalamdhad, 2011; Niane et al., 2014; Hilson, 2016; Gerson et al., 2018). According to the United Nations Environment Programme - UNEP (2018), the ASGM sector contributes for approximately 15% of total global Hg emissions and accounts for up to 80% of the metal emissions from South America and Sub-Saharan Africa. Surprisingly, activities such as ASGM are still not regulated in more than 70 countries (WHO, 2013).

Although mercury (Hg) is often the focus of studies investigating ASGM (Silva-Filho et al., 2006; Grimaldi et al., 2008; Balzino et al., 2015; Diringer et al., 2015; Mora et. al., 2018), there are other heavy metals released during these activities such as silver (Ag), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). The combination of their toxicity and the resulting loss of biodiversity has led to dramatic consequences for human population, such as migration due to the destruction of subsistence resources as well as the development of endemic diseases (Palacios-Torres et. al., 2018, Betancur-Corredor et. al., 2018). This increases the conflict between economically profitable ventures and natural ecosystems (Kahhat et al., 2019). An example of this conflict is Colombia, where ASGM constitutes about 2% of Gross Domestic Product GDP (Güiza and Aristizabal, 2013) and plays an important role in the national economy. In 2010, the ASGM sector in Colombia had 200000 miners officially producing 30 t of gold per year. In the administrative department of Antioquia, there were 17 mining towns (including Nechí municipality) and about 15% artisanal gold miners all over the country. This intensive mining activity positioned the Department of Antioquia as the world's largest mercury polluter per capita from ASGM (Cordy et al., 2011). By the 2013, after a substantial effort of the government, annual mercury releases into the environment were reduced by 63%, resulting in 46 to 70 tons (García et al., 2015). The amount of metals released and their impacts were greatest for nearby aquatic systems (lakes, streams or rivers) and wetlands due to the need for access to water (Ho et al., 2010; Rungwa et al., 2013, Manoj et. al., 2018). Other activities, such as intensive livestock farming and agriculture, also contribute to the increase in metal concentrations in aquatic systems in the region (Marrugo-Negrete et al., 2017).

During ASGM activities rocks and ore are first crushed into small pieces by hand that is then added with water into motorized mills. Because water is used, ASGM facilities are often built near waterways such as rivers, which can later be subject to severe metal pollution. The impact of ASGM in the environment can be monitored checking the quality of suspended particles in rivers and streams (Ji et al. 2016; Lartiges et al. 2001). However, to integrate changes in the quality of the particles over long time periods river sediments as environmental archive is often more useful. However, the temporal metal trends in fluvial sediments are frequently punctuated by higher-order fluctuations related to geomorphologic control of fluvial sedimentation, grain size, hydrological factors and short-term redistribution events such as floods (Herr and Gray, 1996; Nguyen et al., 2009; Bábek et al., 2011). Therefore, the historical reconstruction of metal fluctuations make the interpretation of past contamination flowing through river a difficult task.

Wetlands are considered as sinks for a wide range of chemical compounds, because of the presence of fine grain sediments and high organic matter content that increases the influence on the cation exchange capacity and therefore, the retention of those contaminants (Devesa-Rey et al., 2011; Gu et al., 2015; Kang et al., 2017). Sediment records collected in wetlands are commonly used to study the quality of these ecosystems (Gan et al., 2013; Chen et al., 2016; Zhu et al., 2019), as they allow to quantify the degree of pollution or contamination of the system. Pollution occurs when there is damage to organisms and the ecosystem. Contamination is defined as the presence of a chemical above natural concentrations in the area; however, this concentration does not cause damage (Chapman, 2007). Moreover, the use of dated sediment records is a common way of providing important information on past environmental changes in aquatic ecosystems, especially in situations where there is lack of past data (Puig and

Palanques, 1998; Garcia-Orellana et al., 2011). To this purpose, the natural radionuclide ^{210}Pb ($T_{1/2}$ = 22.3 years) is often used to establish the chronology of recent sedimentary records accumulated over the past 100-150 years (Appleby and Oldfield, 1992), period when the most dramatic changes due to anthropogenic activities have occurred in the environment. Because anthropogenic, physical or biological processes could alter the ^{210}Pb record, the ^{210}Pb-derived chronology should be verified with other dating tracers such as artificial radionuclides (^{90}Sr, ^{137}Cs, $^{239,240}Pu$ and ^{241}Am) (Smith, 2001; Sang-Han et al., 2005) that were introduced in the environment during the nuclear weapons testing in the 50-60s and later, and mainly in Europe, during the 80s due to the Chernobyl accident.

Several studies carried out in lakes in Colombia provided accurate estimations of the impact of ASGM activities in South America (Telmer and Veiga, 2009; Adler et. al, 2013; Moreno-Brush et. al., 2016; Adler et. al, 2017; Marshall et. al., 2018). But some other sediment reservoirs in highly impacted areas such as wetlands, have not yet been widely studied over time, making it difficult to estimate the regional impact of mining activities in tropical zones. A study conducted by the United Nations Office on Drugs and Crime in 2018 determined that out of the 83,620 ha with gold mining operation identified in 2016 in Colombia, more than 30,900 ha were part of the territory of Antioquia (37% of the total Colombia territory). Thus, this area contributed to the 41% of the Colombia national gold production (UNODC, 2018). However, there are not studies that have determined accumulation of heavy metals in Antioquia to assess the current impact of ASGM. With this objective, we reconstructed recent (past 100-150 years) historical trends in both concentrations and accumulation rates of trace metals (Cr, Cu, Hg, Ni, Pb, and Zn) using a wetland sediment core. Thus, comparing metals concentrations, released by anthropogenic activities, with background values helped us to evaluate the historical impact of ASGM on nearby wetland ecosystems.

2. Materials and methods

2.1 Study area

Las Palmas wetland is located in the district of La Concha – Nechí (7°07'53.69'' - 8°01'45.87'' N and 74°54'46.20'' - 74°47'45.43'' W), region of Bajo Cauca, department of Antioquia (Colombia) (Figure 1). The region has a tropical climate, with annual temperatures and precipitation ranging between 28 and 30 °C and from 2000 to 4000 mm, respectively. The dry season is from January to March and from July to September, while the rainy season is from October to December and from April to June (Betancur et al., 2009, OECD, 2016).

Las Palmas wetland is located on the left margin of the Nechí River, which is the most important tributary of the Cauca River. The wetland is located within two geological formations: the alluvial deposits of the Nechí River and the Caucasia Formation, which is of a great economic importance for its gold reserves (Zapata et al., 2013). Geomorphological units in the wetlands include floodplains, flooded lowlands, and partially flooded high plains with a low undulating topography between 30 and 600 m above sea level. Lateral erosion by scouring affects the margin of the rivers in some stretches. The high biodiversity and natural resources (e.g. wood and minerals) of Las Palmas is currently threatened by anthropogenic activities such as mining and agriculture (Alcaldía Municipal de Nechí, 2000).

The most important gold deposits in Colombia are located in three regions. One of them is the drainage basin of the Cauca River that belongs to Las Palmas wetland

(Acemoglu et al., 2012). Las Palmas is one of the areas with the highest mining exploitation in the Bajo Cauca Antioqueño, and represents one of the main wetlands of the riverine complex. Moreover, the department of Antioquia has yielded the most significant gold outputs over the last 10 years, with around 40% of the total national production (Betancur-Corredor et al., 2018). Thus, studying this area is essential to understand the impacts that mining activity have and still cause to the wetland ecosystems.

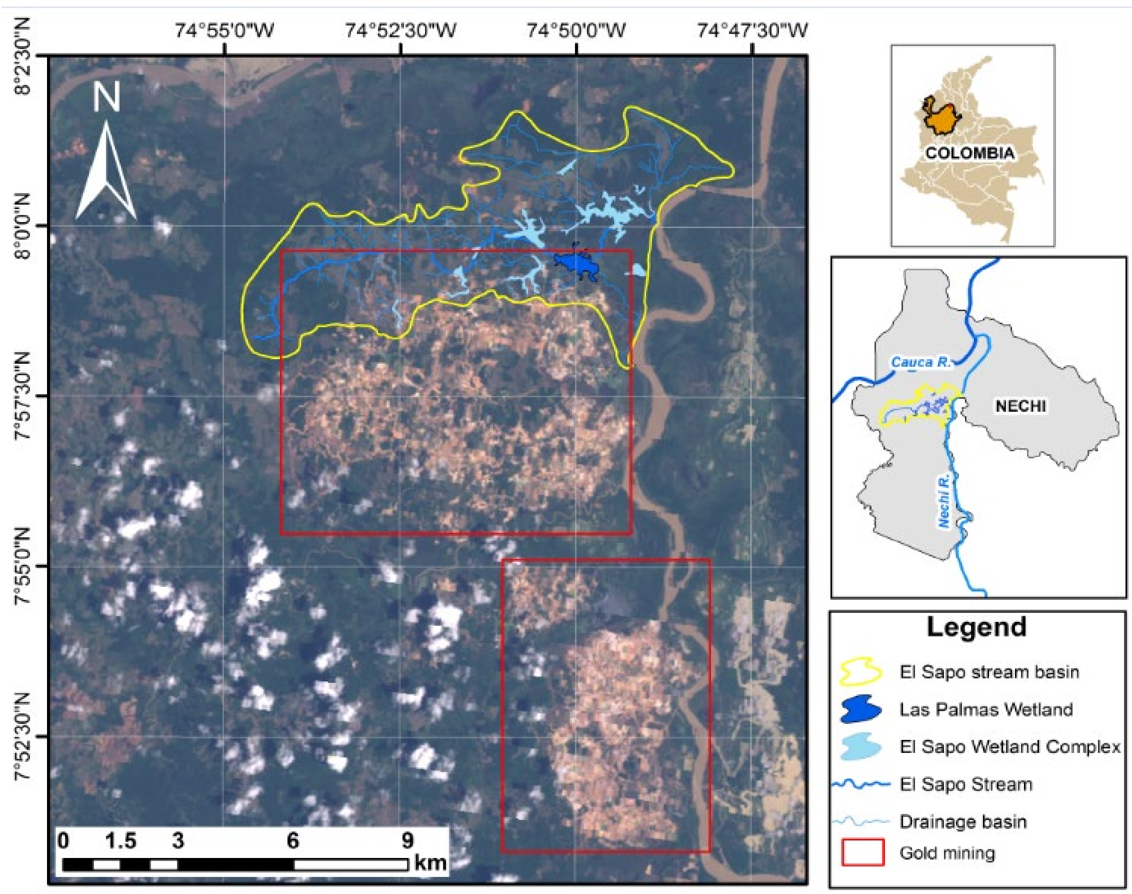

Figure 1. Location of Las Palmas wetland (Antioquia department, Colombia)

2.2 Sampling

Due to that the objective of a radiochronology is to describe the temporal evolution of the contamination recorded due to anthropogenic activities as accurately as possible, the information contained in one core is intrinsically valid, since it represents the evolution of this part of the ecosystem over time (Sanchez-Cabeza et al., 2012). Core sampling was based on the criteria established for the sampling of sediment cores provided in Sanchez-Cabeza et al. (2012), where the fundamental objective is to obtain an unaltered sediment record, avoiding the mixing of the strata, and thus guaranteeing the adequate resolution of environmental changes. The center of Las Palmas complied with the conditions defined above, since this was the area that had the least influence of the tributaries of the wetland (Río Nechí and Quebrada El Sapo) and the anthropogenic activities that take place in the wetland area of influence.

A sediment core (6.6 cm diameter, 371 cm length) was collected in 2014 from the center of Las Palmas wetland during the rainy season using a Livingstone/Bolivia corer following the procedure outlined by the Limnological Research Center (http://lrc.geo.umn.edu/laccore/assets/pdf/sops/livingstone-bolivia.pdf).

Sampling was carried out in the rainy season (November) due to difficult access to the area during the dry season, when channels of access to the wetland dry up and impedes access to the area. Once collected, the core was transported to the laboratory and stored at 4 ºC until further analysis. The core was sliced every 1 cm following the procedures established by Loring and Rantala (1992). Samples were weighed before and after freeze drying to determine water content and bulk density. Subsamples of each section were ground using an agate mortar and stored in polyethylene bags for further analysis.

2.3 Laboratory analysis

Intact samples were analyzed for grain size following a standard laser diffraction method (ISO, 2009) and using a particle size analyzer (Beckman Coulter LS 230) after an oxidative treatment with H_2O_2 (10%). For the analysis of total organic carbon (TOC), approximately 0.3 g ground sediment samples were oxidized with a mixture of $K_2Cr_2O_7$ and H_2SO_4 (2.5:3.75 mL, respectively) in a hot plate (120 ºC, 60 min). TOC content was determined using a spectrophotometer UV/VIS (Merck Pharo 300) (ISO, 1998). Precision was evaluated by measuring the values of relative standard deviation (RSD) of a set of data. The RSD values obtained for repeatability tests was 2.92% and recovery was evaluated through six replicates of the certified reference material NIST SRM-1944- New York/New Jersey Waterway Sediment and the resulting was 92.9%.

Metals analysis (Al, Cr, Cu, Ni, Pb and Zn) was carried out by atomic absorption spectrophotometry (Thermo Scientific AA iCE3300). Mercury (Hg) content was analyzed by cold vapor generation technique (Buck 410) after acid digestion (HNO_3 + HCl + HF, 5:4:1 mL) of dried sediment samples in closed Teflon PFA containers on a microwave oven (700 W, 70 s). The limit of quantitation (LoQ) values found were of 0.750 mg L^{-1}, 0.1 mg L^{-1}, 0.010 mg L^{-1}, 0.020 mg L^{-1}, 0.050 mg L^{-1}, 0.047 mg $L^{-1}$and 0.025 µg for Al, Cr, Cu, Ni, Pb, Zn and Hg respectively. Precision was evaluated by measuring the values of relative standard deviation (RSD) of a set of data. RSD values obtained for repeatability tests were 3.10% (Al), 6.22% (Cr), 8.21% (Cu), 13.76% (Ni), 13.55% (Pb), 12,39% (Zn) and 12.62% (Hg). The recovery study was carried out by spiking technique. Known concentration of standard solutions (Al, Cr,Cu, Ni, Pb, Zn and Hg) were added to certified reference material - IAEA SL-1 (Trace and Minor Elements in Lake Sediment), and the resulting spiked samples compared to the known value of standard solutions added. The average recovery values were 104 ± 3% (Al), 95 ± 7% (Cr), 102 ± 2% (Cu), 101 ± 2% (Ni), 100 ± 2% (Pb), 105 ± 2% (Zn) and 100 ± 5% (Hg). Total activities of ^{210}Pb were estimated by alpha spectrometry through its daughter product ^{210}Po, assumed in secular equilibrium with ^{210}Pb (Flynn, 1968; Hamilton and Smith, 1986, Sanchez-Cabeza et al. 1998). Briefly, sediment samples were acid digested with HF and HNO_3 (3:9 mL) after spiking with a known amount of ^{209}Po yield tracer. After this, Po isotopes were plated onto silver disks immersed into a solution of HCl (1M) for 6 hours. To ensure the analytical quality of the process and to assess the reproducibility of the results, a replicate was prepared for each group of samples. Recovery of the method was evaluated by measuring a certified sediment reference material IAEA-315 (103 ± 4 %). Discs were measured using Passive Implanted Planar Silicon (PIPS) (CANBERRA, model PD-450.18 A.M.) and silicon surface barrier (EG&G Ortec Mod. SSB 450R) alpha spectrometers. Discs were measured until achieving less than 5% of uncertainty in the ^{210}Po counting rate or a maximum counting time of 400,000 s. In order to constrain the age model and to determine the supported ^{210}Pb from ^{226}Ra, some samples were analyzed by gamma spectrometry. Thus, activities of ^{137}Cs and ^{226}Ra were measured by using a calibrated geometry high-resolution, high-purity germanium (HPGe) detector (Canberra) for 2 - 3 days. Dried and grained samples were sealed and stored for three weeks before counting to ensure secular equilibrium between ^{226}Ra daughters. ^{137}Cs was quantified via its γ-emission at 662 keV (MDA= 3 - 8 Bq kg^{-1}) and ^{226}Ra via the γ-emission at 351 keV (MDA= 6 - 12 Bq kg^{-1}) of its daughter nuclide ^{214}Pb.

2.4 Sediment chronology

Sediment core chronology was determined by applying the Constant Rate of Supply (CRS) model (Appleby and Oldfield, 2001). This model assumes a constant flux of ^{210}Pb (excess ^{210}Pb – $^{210}Pb_{xs,}$ derived from subtracting the supported ^{210}Pb from the total ^{210}Pb) to the sediment and allows the rate of sedimentation to vary over time. The CRS model also provides estimation of both mass accumulation rates (MAR, g m^{-2} y^{-1}) and sediment accumulation rates (SAR, cm y^{-1}).

2.5 Statistical analysis

A correlation analysis was applied on the entire data set (grain size, TOC, mass accumulation rates and metal concentrations) using raw or normalized metal concentrations according to the degree of correlation with Al content. In order to understand the processes that control metal distribution in the wetland, the distribution of the selected elements was studied using a principal component analysis (PCA) Logarithmic transformation and data standardization were carried out to carry (Reimann et. al., 2002; Rencher, 2002). Here, the Spearman correlation matrix to compensate the differences in the scale of the values between variables was analyzed. The analysis was carried out using R-version 3.5.3: R (Core Team, 2018).

3. Results and discussion

3.1 Sediment chronology and sedimentation rates

^{210}Pb activities decreased exponentially with depth (Figure 2a). However, an almost constant ^{210}Pb activity (mean of 92 $\pm$ 3 Bq kg^{-1}) was observed between 0.9 and 2.8 g cm^{-2} (between 2 and 8 cm). Considering the assumptions stated by the

CRS model, this constant activity in ^{210}Pb is ascribed to an increase in mass accumulation rate. This increase in sediment accumulation rates is consistent with the metal concentration profiles that showed a similar pattern in the same sections (see section 4.2). This type of ^{210}Pb distribution can also be obtained by physical and biological mixing. However, the application of the CRS in these altered ^{210}Pb profiles would introduce a deviation from the real age up to only 4%, which is of the same order that the uncertainty associated to the age-depth model (Arias-Ortiz et al., 2018). Thus, the CRS model seems to be the most suitable model to derive consistent chronologies for our core. At the bottom of the profile, ^{210}Pb activities were almost constant and similar to the mean measured activity of ^{226}Ra (35 ± 4 Bq kg^{-1}). This constant value was taken as representative of the supported ^{210}Pb and subtracted from the total ^{210}Pb activities to obtain the excess ^{210}Pb fraction, used for dating. The CRS model was applied to the unsupported ^{210}Pb distribution, and an age of 159 ± 24 years was obtained for the upper 4.5 g cm^{-2} (15 cm) of accumulation.

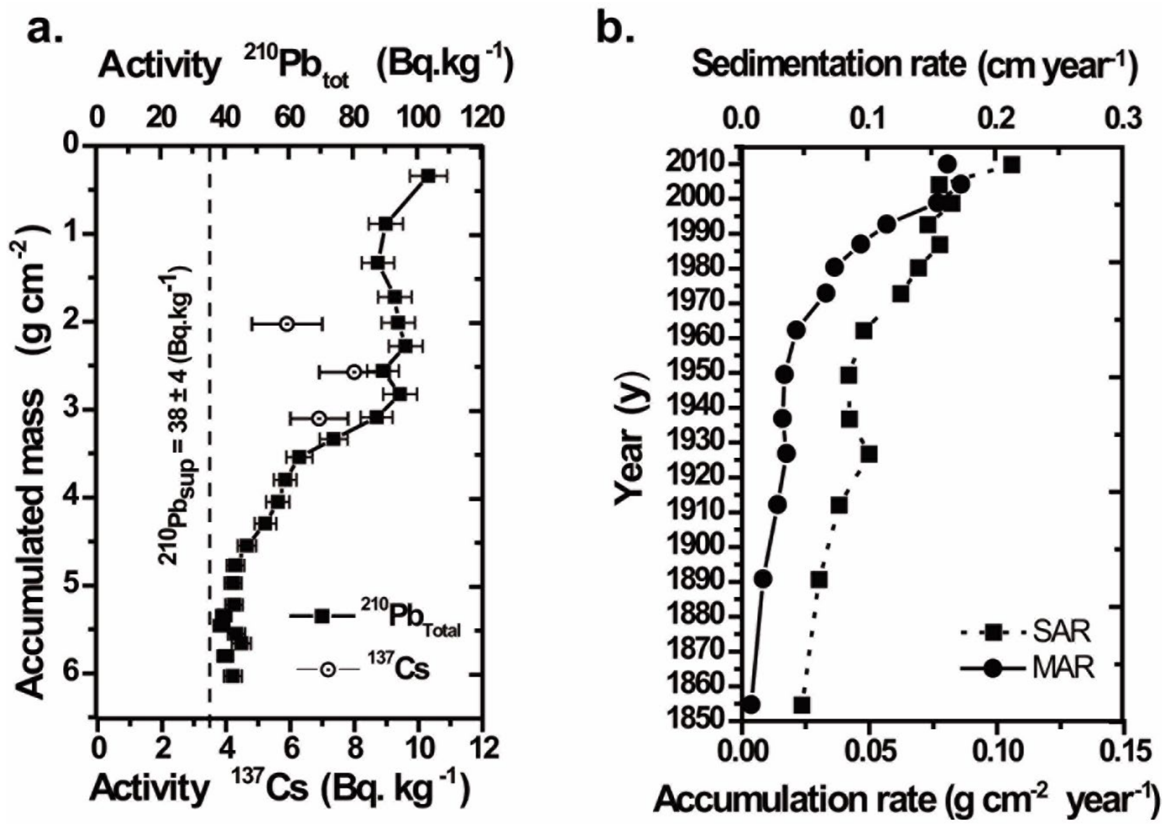

Figure 2. a) Total ^{210}Pb and ^{137}Cs concentration profile and b) Mass Accumulation Rates (MAR) and Sedimentation Rates (SR) in Las Palmas wetland sediment core.

Activities of ^{137}Cs were detected between 2.0 and 3.1 g cm^{-2}, with concentrations ranging from 5.9 and 8.0 Bq kg^{-1} (Figure 2a). A peak of ^{137}Cs, corresponding to the year 1973 ± 2, can be inferred, which is in good agreement with the historical deposition of ^{137}Cs in the south hemisphere (Pennington et al., 1973). The deepest layer with detectable ^{137}Cs activity was located in 1950 ± 4, also consistent with the beginning of the global fallout period (1954). The consistency of the temporal changes of ^{137}Cs activities with the historical deposition of ^{137}Cs confirms the validity of the ^{210}Pb-derived ages.

Estimated sediment accumulation rate (SAR) increased one order of magnitude since the beginning of the 19th century, from 0.02 ± 0.01 cm y^{-1} (MAR of 0.004 ±

0.003 g cm^{-2} y^{-1}) in the oldest layers to 0.12 ± 0.02 cm y^{-1} (MAR of 0.033 ± 0.005 g cm^{-2} y^{-1}) in 1970s. After this, the increase in sediment accumulation rates is more pronounced, reaching 0.23 ± 0.02 cm y^{-1} (MAR of 0.081 ± 0.009 g cm^{-2}·y^{-1}) at the surface, which exceeds the background values in a factor of 12.

3.2 Temporal changes in sediment composition

Las Palmas wetland sediment core was composed mainly (> 96%) of silt and clay sized material (Figure 3). On average, bulk sediments contained 2.5 ± 2.4 % of sand (>63 μm), 75 ± 4 % of silt (2 - 63 μm) and 22 ± 5 % of clay (<2 μm). The sediment profile showed a clear decreasing trend of sand content from the bottom to the surface, with a clear peak in 1910. An opposite trend was observed for the clay fraction, with an increase from 20-25% in 1900 to 40% at the beginning of the 21th century. TOC content showed values between 2 and 8% (Figure 3b), with a clear peak in ~1940 and decreasing values towards recent times. The range of TOC content in the wetland was similar to those observed in lacustrine sediments from South America (Bertrand et al., 2009; Irurzun et al., 2014), although higher values (between 10 - 40%) have been found in the Quistococha Lake in Peru (Aniceto et al., 2014).

Aluminum content ranged from 11% to 16%, increasing from 1930 until a subsurface peak in 1960s (Figure 4). After a short decline, Al content increased again up to maximum values of 16% in recent times. Metal concentrations (Ni, Pb, Cr, Cu and Hg) increased from the basal core sections to the surface (Figure 4).

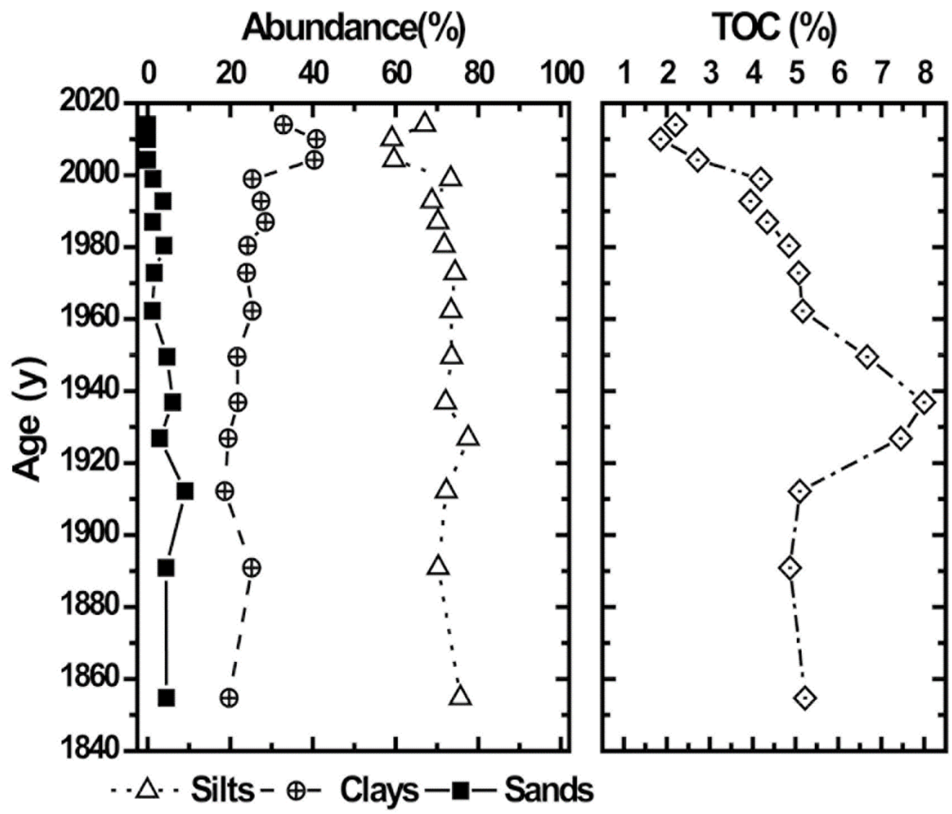

Figure 3. Vertical profile of grain size ((a) Sands, (b) Silts, (c) Clays) and (d) TOC.

Surface metal concentrations were higher than background values by a factor of 1.4, 1.7, 1.3, 1.7 for Ni, Pb, Cu, Cr, respectively. Maximum values of Cu (55 mg·kg^{-1}) and Pb (37 mg·kg^{-1}) were found in sites with low contamination levels (Feria et al., 2010). Unlike these metals, Zn concentrations were almost constant (around 160 mg·kg^{-1}) between 1855 and 1970s. After this, Zn concentrations decreased to values of 93 mg kg^{-1} at the surface. Trends in Hg concentrations differed from the rest of metals, with two peaks of maxima concentrations in 1960 and 1980. Maximum Hg concentrations of 406 µg kg^{-1} at recent times exceeded two times the values observed at the beginning of the 19th century. Maximum Hg concentrations were higher than those reported in sediments of Bajo Cauca - Antioquia 240 µg·kg^{-1} (UPME and Universidad de Córdoba, 2015) and sediments of Lake Pillo (20 μg·kg^{-1} to 180 μg·kg^{-1}) in Chile (Alvarez et al., 2017). However measured concentrations were lower than those obtained in sediments of Lake La Señoraza - Chile (734 μg·kg^{-1}), where Hg concentrations are associated with the opening of a chlor-alkali plant of a cellulose industry in the early 1960s (Alvarez et al., 2017).

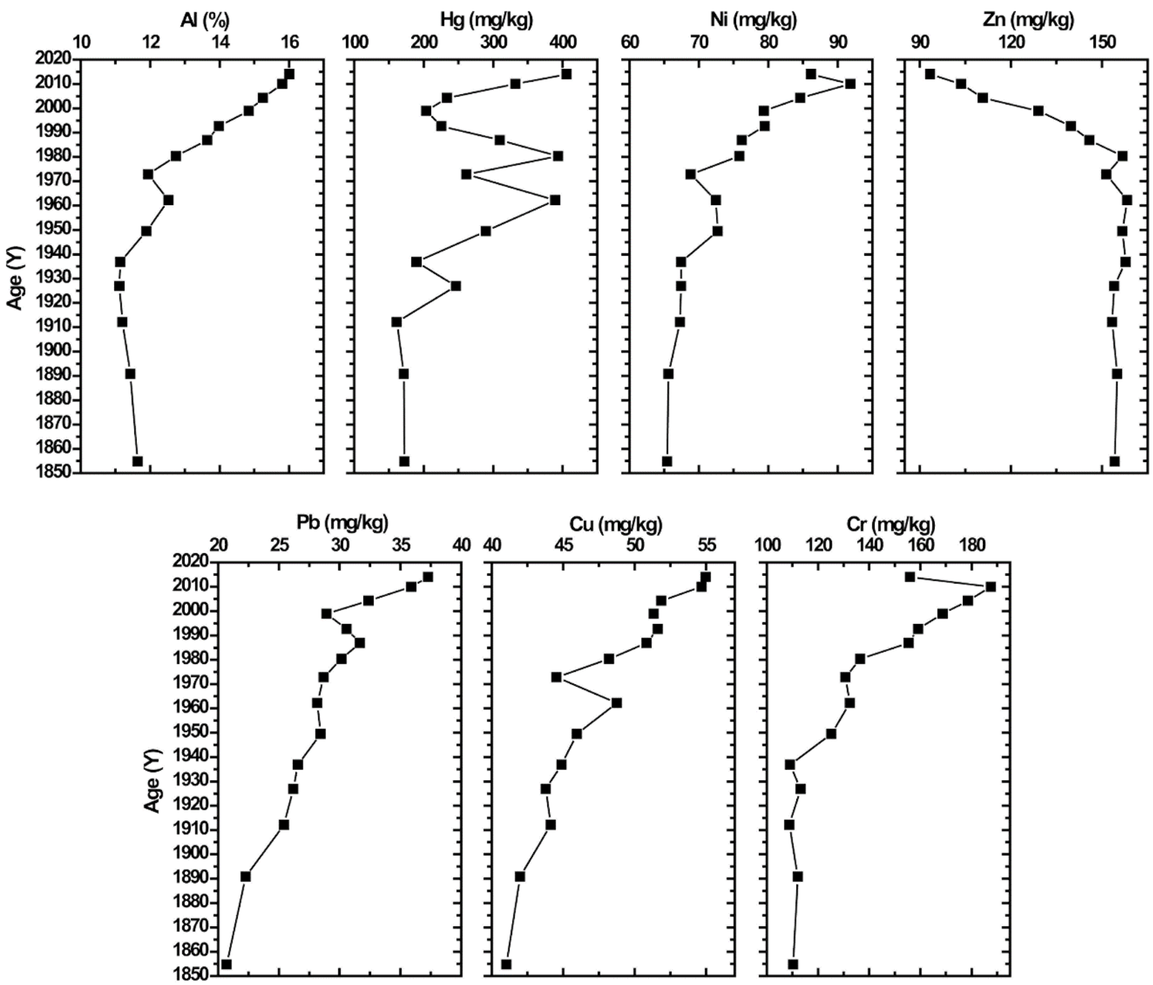

Figure 4. Concentrations profiles of trace metals (Al, Hg, Ni, Zn, Pb, Cu and Cr).

Trace metal concentrations in sections older than 1850 are usually taken as pre-anthropogenic values and considered background or natural levels (Matschullat et al., 2000; Wei and Wen, 2012). In Las Palmas record, metal concentrations at these deep layers were within the range of reported background concentrations for other lakes from South America (Urrutia et al., 2002; Marrugo, 2007; UPME, 2014).

However, they were considerably higher than other values observed in other wetland ecosystems in Colombia, for example, Hg background level in Las Palmas was higher than those values reported by Marrugo et al. (2007) in Mojana, likely due to lithological differences between systems. Regarding Hg, concentrations were similar to those determined for Lake La Señoraza (Chile), but considerably higher than in other studies (Urrutia et al., 2002; Feria et al., 2010; Rua et al., 2014; Alvarez et al., 2017). High and variable concentrations during pre-industrial times have been previously observed in other studies that demonstrate that natural concentrations of metals on a scale of thousands of years can be highly changing. This fact may cause a great variability in the metals concentrations in sediments and make difficult to establishing basal values. Background values observed in our core are shown in Table 1, where other background values for other sites of the world are also referenced.

331

3.3 Sediment chemistry: responses to natural and human induced changes

In order to understand and delimit the historical evolution of metals concentrations in Las Palmas wetland, a sedimentation temporal framework should be defined considering the ^{210}Pb-derived age model. We used a Principal Component Analysis (PCA) to visualize the temporal variation of the different variables measured in Las Palmas wetland. The result of the PCA applied to metal concentration, granulometry, SAR and TOC distribution together with the age of each sediment section is shown in Figure 4. The PCA showed that Al, Cr, Cu, Ni and Pb were inversely related to TOC, silt and sand content. The analysis also showed that the most important associations occurred between Hg and clay content, and Hg and TOC ($r = 0.39$, $p < 0.05$ and $r = 0.44$, $p < 0.05$, respectively). Unlike the rest of metals, Zn showed a positive relationship with TOC ($r = 0.83$, $p = 0.0001$) that indicates the enrichment or deficit of Zn in the presence of organic matter. This is in agreement with previous studies that showed that metals such as Cd and Zn can be absorbed by living plants in areas of high biological activity (Livett et al., 1979; Shotyk, 1996; Espi et al., 1997; Olid et al., 2010). Thus, the presence of macrophytes (*Ludwigia sedoides, Paspalum repens and Utricularia foliosa*) in the wetland might have played a fundamental role in the sequestation of Zn, as well as influence the regulation processes in these ecosystems (Van der Hammen et al., 2008 Kumar and Tripathi, 2008; Maine et al., 2009; Martelo and Lara-Borrero, 2012). The TOC concentration shows a considerable increase between 1910 and 1960, consistent with the exponential population growth, technological changes in the agricultural sector, rural–urban migration and recolonization of lowlands around Cauca river during that period. Total population grew from 6 million to 20 million, while urban population doubled from 30% to 60%. This rapid population growth let to land use changes and also accelerated deforestation processes. The estimated national rate of clearing was around 70000 ha per year, with 18000 ha per year corresponding to zones where coffee and other products continued to be grown. The clearing of lowland forests increased with large areas of subhumid and humid forests of the Caribbean, now being cleared at annual rates greater than 2 %. The impact of the cattle industry continued to increase. Of the 28 Mha of cleared land at the end of the period, it is estimated that grazing accounted for more than 80 % (Etter et al., 2008).

Finer suspended sediment particles (clays and silt) usually accumulate higher concentrations of heavy metals due to the high content of secondary minerals (Fe, Mn, Al oxides and hydroxides, and carbonates) and organic matter (Hardy and Cornu, 2006). Sand and silt fractions in sediments are largely composed of the primary mineral quartz (e.g., SiO_2), which is a very weak adsorbent for heavy metals. The statistical results of the PCA shows how clays are correlated with Al and heavy metals (Ni, Pb, Cu and Cr) and lesser to extend to Hg. These correlation between clays, Al and metals indicate that the increase of metals in the Las Palmas wetland is due to the presence of higher content of clays (aluminosilicates). Although the correlation of the increase of Al and heavy metals with the increase of the sedimentation rates in the Las Palmas sediment record could be associated with natural processes such as climatic change, the fact that the highest concentrations of Al and metals have been recorded since the 1980s would indicate that such accumulation of metals is due to an increase in anthropogenic activities. In fact, the highest concentrations of metals were recorded since the 1980s.

According to the PCA, sediment could be divided into four groups of sediment sections that correspond to different temporal framework (Figure 5). The four group of samples (Group 4) is formed by sections located along the positive axis of the first component and accumulated between 1885 and 1937, characterized by the highest concentrations of sands, silts, TOC and Zn. Sections accumulated between 1950 and 1980 are mainly correlated with mercury (Hg) (Group 3), containing the highest Hg concentration. Younger sections of this group 3 accumulated between 1950 and 1973, however, are also associated with high concentrations of Zn, TOC and silts. Sections accumulation between 1987 and 1999 showed the strongest correlation between SAR, Clays, Cr, Cu, Ni and Pb (Group 2). Finally, the most recent sections accumulated between 2004 and 2014 (Group 1) are located along the negative axis of the first component, being characterized by the highest values of SAR, Clay, Cr, Cu, Ni and Pb. Both groups (1 and 2) show lower Zn and TOC concentrations with increasing sedimentation rate and clays content.

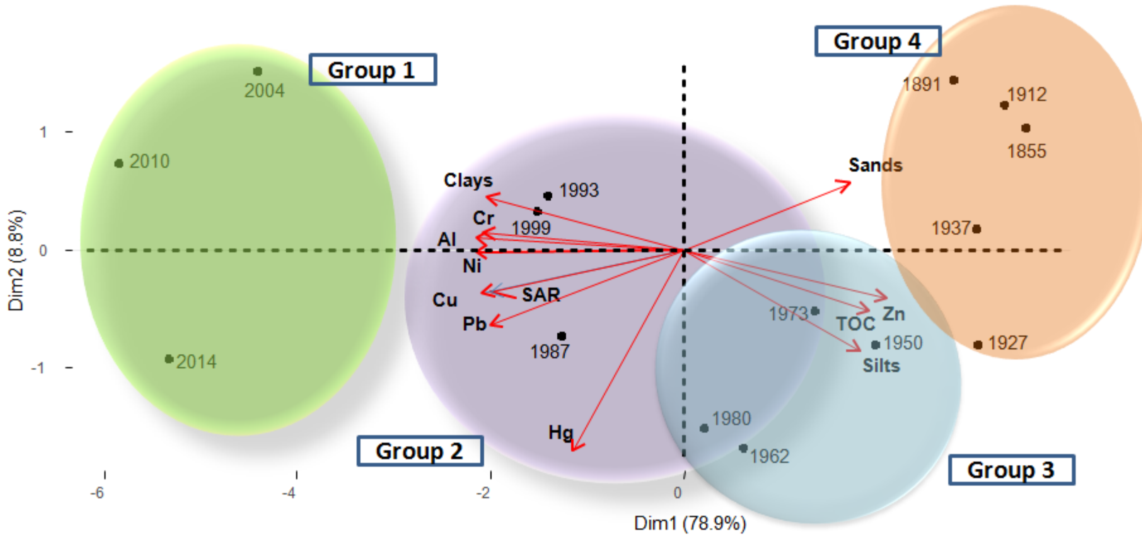

Figure 5. PCA applied to a set of sedimentary characteristics.

3.4 . Historical evolution of metal fluxes

Background metal fluxes showed values of 6.3 µg·m^{-2}·y^{-1} for Hg and 4.1, 1.5, 2.4 and 0.8 mg·m^{-2}·y^{-1} for Cr, Cu, Ni and Pb, respectively (Figure 6). All metals had similar trends, with a steady increase since the early 20th century. We observed a first slight increase in metal fluxes from 1910 - 1920 to 1930 - 1940 and a second significant increase from 1970 - 1980 to 2010. For Hg, fluxes increased from 13 µg ·m^{-2}·y^{-1} in 1910 to 327 µg g·m^{-2}·y^{-1} in 2014, equivalent to a 24-fold increase. Cr, Cu, Ni and Pb showed similar fluxes trends, with an increase from 1910 to maximum values in 2010 and a subsequent decrease thereafter. In this period of time, fluxes increased from 9.0, 3.7, 5.6, and 2.1 mg·m^{-2}·y^{-1} to 161, 47, 79, and 31 mg·m^{-2}·y^{-1} for Cr, Cu, Ni, and Pb, respectively, that represent enrichments up to factor of 13 - 18.

Maximum estimated fluxes of Cr, Cu, Ni and Pb are greater than those reported in other studies performed in other South American lakes. For example, Cooke et al.

(2009) reported metals fluxes of 170 - 50 $mg \cdot m^{-2} \cdot y^{-1}$ for Pb, 3.9 $mg \cdot m^{-2} \cdot y^{-1}$ for Hg, 2-10 $mg \cdot m^{-2}\ y^{-1}$ for Cu and 1.5 - 3.5 $mg \cdot m^{-2} \cdot y^{-1}$ for Ni, and 5 - 60 $mg \cdot m^{-2} \cdot y^{-1}$ for Zn in Cerro de Pasco (Peruvian Andes). Cooke and Abbott (2008) reported maximum metal fluxes of 30 $mg \cdot m^{-2} \cdot y^{-1}$ for Pb, 10 $mg \cdot m^{-2} \cdot y^{-1}$ for Zn, 4 $mg \cdot m^{-2} \cdot y^{-1}$ for Cu and 1.5 $mg \cdot m^{-2} \cdot y^{-1}$ for Ni, for Chipian lake (Peru) and 200 $mg \cdot m^{-2} \cdot y^{-1}$ for Pb, 60 $mg \cdot m^{-2} \cdot y^{-1}$ for Zn, 10 $mg \cdot m^{-2} \cdot y^{-1}$ for Cu and 3.5 $mg \cdot m^{-2} \cdot y^{-1}$ for Ni for Pirhuacocha lake (Peru). Therefore, although the Pb fluxes reported in this study are similar to those presented in other studies, the rest of the metal fluxes are considerably larger.

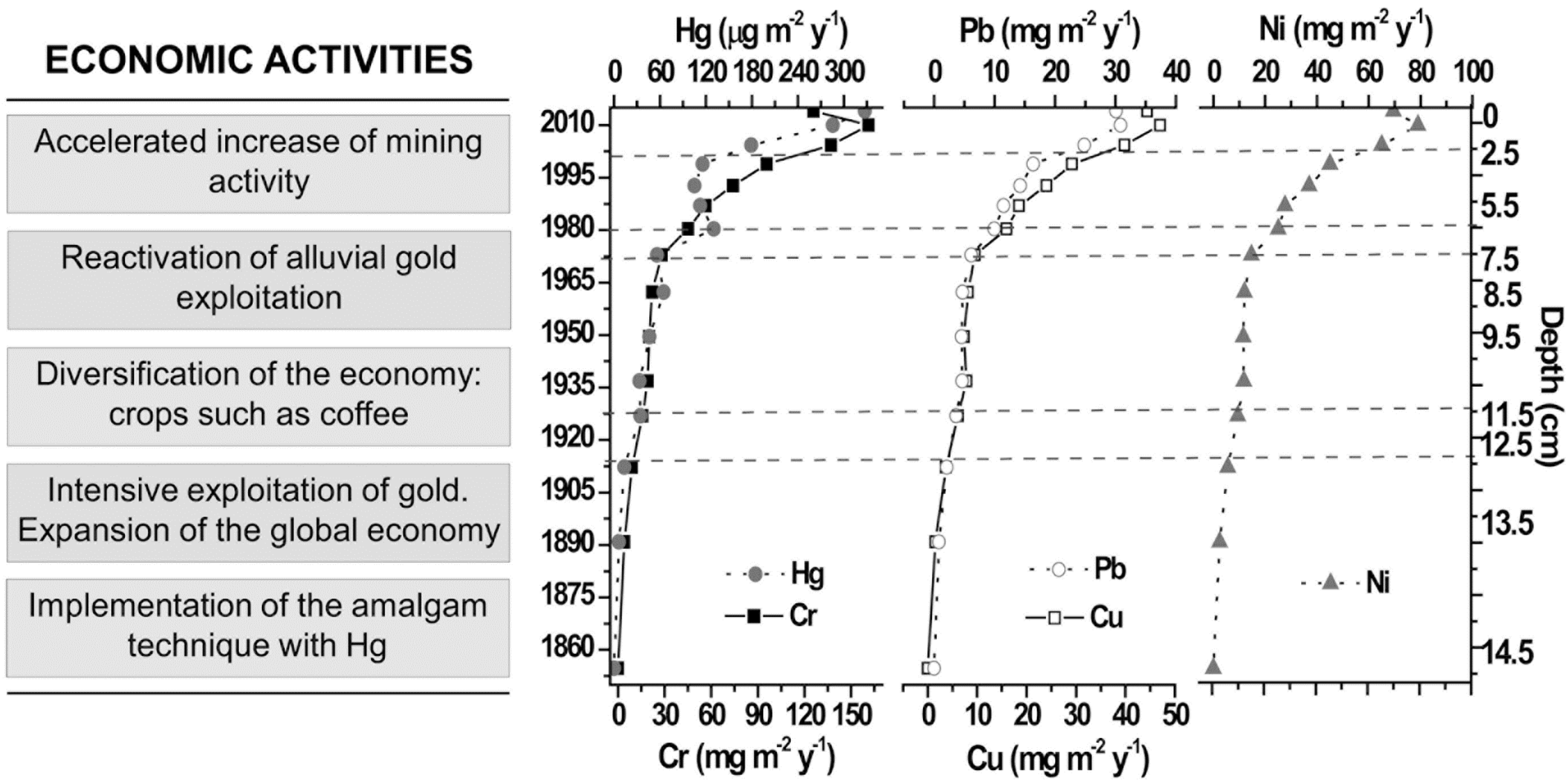

Figure 6. Historical metal fluxes calculated for the Las Palmas wetland according to the economic activities.

The historical reconstruction of the metal fluxes in Las Palmas wetland reflects the economical evolution of the regional economy mainly related to the agricultural and mining activities (Figure 7). The slight increase in metal fluxes observed from 1910 - 1920 to 1930 - 1940 is likely related to the expansion of the world economy during the 1920s and after the First World War, with the consequent demand of gold. During the beginning of the past century, the international prices of gold increased due to of the Great Depression, going from US $ 18.50 ozt in 1934 to US $ 35 in 1970. In the late 1930s and early 1940s, there was a wave of colonization in the Bajo Cauca guided by the expectation of a better life based on the gold mining (OECD, 2016). This new settlement process led to changes in vegetation cover as a consequence of changes in land use (e.g. mining, agriculture and wood industry) that probably, increased dramatically the organic matter content in the wetland over several years (Figure 4). However, deforestation and the opening of new ASGM activities increased erosion rates and piles of ground rocks (commonly known as "jales mineros"), which, due to runoff and dust dispersion, reduced TOC content and increased the amount of fine particles entering into Las Palmas wetland. After this period, with the advent of the Second World War, world economies began to recover and world gold exports declined, justifying the almost constant metal fluxes during the 1940 - 1980 period. During this period, the economy of the area diversified based not only on mining, but also on agriculture (e.g. coffee crops, cassava), which used fertilizers such as superphosphate and other phosphates with high concentrations of Cr, Cu, Ni, Pb and Zn (Feria et al., 2010), which probably helped to increase the metal fluxes to the wetland. These deforestation processes established changes in vegetation cover in the wetland area, pasture mosaics (18.4%), mining extraction areas (18.1%) and shrublands (11.4%) (Corantioquia, 2015). However, during this mid-20th century period no significant changes in metals are observed.

Between 1970 and 1980, a clear increase in both sedimentation rates and metal fluxes is observed (Figure 6). This is consistent with the reactivation of the mining activities in Colombia and, specifically, with the reactivation of alluvial gold exploitation (AGE) in Antioquia (Betancur-Corredor et al., 2018). This is also in agreement with the fact that at this time, a channel was opened through the wetland to facilitate the access to the area to market the harvested products. The new channel was much shorter, wider and straighter than the natural fluvial connections, which were progressively closed naturally (Corantioquia, 2015). That probably led to the retention of TOC and sands transported to the wetland from the natural connection and reduced the inputs of these materials to Las Palmas, as observed in Figure 4. These changes in the natural dynamics between the river and the wetland reduced significantly the accumulation of silts and increased the accumulation of clays, Al and heavy metals.

Finally, the accumulation of heavy metals in recent wetland sediments observed in the late 20th century, is also due to the physical and chemical erosion of the mining waste. These wastes are constituted by crushed polymetallic material cotaining high specific surface area and high levels of heavy metals such as Pb, Zn, Mn, Cu, Cd, etc., which can be released and subsequently deposited in the bed sediments of the wetland. These changes allowed for foreign investment and exploitation in the area (Duarte, 2012), which considerably intensified mining activities in the Las Palmas wetland. Thus, in recent years, foreign direct investment in mining has almost tripled. This increase in investment implied that Colombia was the largest importer of mercury in Latin America and the Caribbean, with about 130 tons of mercury imported in 2011, 75% of which was used in ASGM activities. That represented the release of between 50 and 100 tons of Hg into the environment (Güiza and Aristizabal, 2013).

Mining is not the only activity that causes impacts on wetland ecosystem services. These impacts are more related to the increase of TOC rather than significant increase in metal fluxes as it is observed with mining activities after the 1980s. Changes in land use as crops (coffee, sugar cane, oil palm, coca, and rubber) and cattle ranching also represent a source of metals into the environment. It has been estimated that these activities are responsible for the transformation of 45% of the natural land cover (Etter et al., 2006; Ricaurte et al., 2017) and have led to violent clashes over land ownership and social marginalization, leading to the degradation of large wetland extensions and therefore the increase of metal fluxes. Impacts due to land use change include deforestation due to destruction and loss of vegetation, soil contamination, landscape changes, and soil loss due to disposition of tailings in the vicinity of mining sites and gutters. (Gómez-Rodríguez et al., 2017).

This study carried out in Colombia represents a clear example of how the historical evolution of metal fluxes and concentrations recorded in a sediment record reflects the evolution of the regional economy related mainly to agricultural and mining activities. This link is clearly evident between the close relationship between the evolution of the mining economy (% GNP) in Colombia and the flux of Hg recorded in the Las Palmas wetland area (Figure 7). Although there is a clear increase in the Hg flux since 1970, the income that contributes to the gross domestic product due to mining activity has decreased since 2005 due to intermittences in the international price of gold (Güiza and Aristizabal, 2013; Betancur-Corredor et.al., 2018) and not only related to the ASGM activities in Antioquia. Therefore, historical trends in metal concentration in sediments from Las Palmas wetland reflect the degree of socio-economic development in the basin and can be used as a good proxy for evaluating anthropogenic impacts in the area.

Conclusions

This study represents a clear example of how the historical reconstruction of metal fluxes using sediment cores in an impacted wetland reflects the economical evolution of the regional economy mainly related to the agricultural and mining activities in Antioquia (Colombia). Metal fluxes in the wetland evolved according to main three periods of time (Figure 6): from 1910 to 1930; from 1930 to 1970 and from 1970 to 2014. These periods coincide with the economical evolution of Antioquia and worldwide mining activities. Changes in national policies with respect to mining activities implied an increase in the exploitation of natural resources and, consequently, an increase of the release of metals into the environment. However, in order to study the real impact of mining, a more extensive study should be performed around where ASGM activities are carried out.

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