Variations of Pb in a mine-impacted tropical river, Taxco, Mexico: Use of geochemical, isotopic and statistical tools

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ABSTRACT

The potential environmental threat from Pb in Mexican rivers impacted by historic mining activities was studied using geochemical, isotopic and statistical methods. Lead geochemical fractionation and factor analysis of fractionated and total Pb indicate that anthropogenic sources have contributed significantly to Pb concentrations, while natural sources have contributed only small amounts. The analyses also indicate that two main processes are controlling the total Pb variation throughout the year in both rivers: erosion with discharge processes, and proportional dilution related to differences in grain-size distribution processes. Bio-available Pb in riverbed sediments was greater than 50% in 80% of the sampling stations indicating a high potential environmental risk, according to the risk assessment criteria (RAC). Nevertheless, based on the environmental chemistry of Pb and on multivariate statistical analysis, these criteria did not apply in this particular case. Significant differences ($p < 0.05$) in total Pb concentrations (from 50 to 5820 mg kg^{-1}) and in the geochemical fractionation were observed as a function of seasonality and location along the river flow path. In the Cacalotenango and Taxco rivers, the highest concentrations of total Pb were found at stations close to tailings during the rainy and post-rainy seasons. The geochemistry of Pb was mainly controlled, during the dry and post-rainy seasons by the organic matter and carbonate content, and in the rainy season by hydrological conditions (e.g., the increase in river flux), hydrological basin erosion, and the suspended solids concentration. Isotopic analyses of the $^{210}Pb/^{214}Pb$ ratio showed three processes in the Cacalotenango and Taxco rivers. First, the accumulation of atmospheric excess ^{210}Pb, favoured during calmer hydrodynamic conditions in the river basin commonly during dry periods, is recorded by a $^{210}Pb/^{214}Pb$ ratio of >1. In the case of the Cacalotenango river, ^{210}Pb did show preferential accumulation in sediments. Second, a $^{210}Pb/^{214}Pb$ ratio of <1 in some samples might be indicating (a) the presence of eroded material from weathered tailings with similar ^{210}Pb depletion (probably by secular disequilibrium caused by weathering or mining processes, which was observed in both rivers), or (b) preferential transport of Pb and sediments during high energy events (e.g., flow increase, as is the case of Taxco river). Third, no significant changes in the $^{210}Pb/^{214}Pb$ ratio might be reflecting a situation where mining material is not entering the system, or where hydrodynamic changes throughout the year of equal magnitude allow the system to reach a new equilibrium for the $^{210}Pb/^{214}Pb$ ratio. Finally, based on these results it is recommended that inhabitants of the studied area avoid using water from the Cacalotenango river in the rainy and post-rainy seasons, and to take precautions for its use in the dry season, such as allowing suspended material to settle before use, and that they should avoid use of Taxco river water at all times.

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1. Introduction

Spatial and temporal variations of potentially harmful metal concentrations in riverbed sediments are the result of a combination of chemical, biological and physical processes (Griethuysen et al., 2005; Nguyen et al., 2005; Okonkwo and Mothiba, 2005; Armienta et al., 2003). These sediments act as a record of anthropogenic disturbance to the environment, such as pollution by potentially harmful metals. Identification of source, measurement of total concentrations and determination of chemical forms are essential to asses the environmental risks associated with pollutant metals in aquatic systems (Lu et al., 2005; Talavera-Mendoza et al., 2005; Dias and Edwards, 2003; Dótor, 2002; Salomons, 1995).

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However, recent studies of metal concentrations in tropical river sediments have only reported total concentrations of metals and physicochemical parameters (Griethuysen et al., 2005; Nguyen et al., 2005; Okonkwo and Mothiba, 2005; Armienta et al., 2003). Because these studies did not evaluate geochemical fractionation, the possible chemical forms of these metals and their potentially dangerous environmental impact were not fully explored.

For example, Singh et al. (2005) used Tessier's analytical sequential extraction technique (Tessier et al., 1979) to demonstrate a medium environmental threat according to RAC (risk assessment criteria) from sediments in an Indian river (Jain, 2004). However, these results were not confirmed by multivariate analysis of the relationships among metals and physicochemical parameters, and therefore, the geochemical behavior of the metals was not fully assessed. Furthermore, studies of tropical river systems based on a single hydrological season can mask the impact of seasonal hydrological changes and associated concentration peaks that may result from leaching of river basins.

In Mexico, large quantities of waste are derived from mining and abandoned mines. According to Armienta et al. (2003), this waste constitutes a potential environmental risk. Solid waste produced from mineral processing results in fine-grained waste termed tailings, which are confined to tailings impounds. The stability of these impounds is limited; and their structural and geochemical equilibriums are constantly modified by hydrological changes (Sangupta, 1993; Ritcey, 1989). Tailings are routinely affected and transformed by processes such as erosion, wash out and runoff, which result in the release and further dispersion of their constituent solids and liquids.

Once the metals contained in the solid or liquid waste enter river sediments, their mobilization is controlled by a number of factors such as pH, Eh, cation exchange capacity, organic matter content, carbonate content and even the abundance of microbial populations (Balistrieri and Murria, 1993; McEldowney et al., 1993; Sangupta, 1993; Gerringa, 1990; Ritcey, 1989; Förstner, 1980). The bioavailability, pollution potential and, therefore, the probable environmental impact of metals are mainly controlled by their chemical form (Wolterbeek and Verburg, 2001; Salomons, 1993; Tessier et al., 1979).

Mining has been the main economic activity in Taxco de Alarcón (located 250 km south of México City), for five centuries. Ore extraction and processing have produced wastes posing an environmental threat to the area. Currently, Pb, Zn and Ag ores are extracted by selective flotation. Previous studies in this area have only focused on the total concentrations of metals. Castro (2002) reported an average concentration in sediments of the area of 430 ± 270 mg kg^{-1} of Pb, and a background value in soils of the area of 100 mg kg^{-1}. For the El Fraile tailings, Romero (2004) reported Pb concentrations of 3340 to 7760 mg kg^{-1}.

The vertical and lateral distribution of sediments that may indicate erosion and depositional processes (and hence of metal dispersion and accumulation) can be determined by means of their ^{210}Pb activity (Appleby and Oldfield, 1978). This is because ^{210}Pb (half-life 22.26 a) has a strong affinity for soil and sediment particles, resulting in rapid adsorption at the soil surface (Walling et al., 2003; Turnewitsch et al., 2004). Lead-210 is a naturally occurring radionuclide belonging to the ^{238}U decay series, produced from the decay of gaseous ^{222}Rn (half-life 3.82 days), the daughter of ^{226}Ra (half-life 1.622 ka) (Smith and Hamilton, 1992; Walling et al., 2003). Upward diffusion of naturally occurring ^{222}Rn to the atmosphere results in the subsequent fallout of ^{210}Pb onto surface soils and sediments. This fallout ^{210}Pb which is not in equilibrium with ^{226}Ra is known as excess or unsupported ^{210}Pb, and has an average world deposition flux of 118 Bq m^{-2} a^{-1} (Walling et al., 2003). The method estimates the residual radioactivity arising from unsupported ^{210}Pb present in the sediments. Supported

^{210}Pb is determined by establishing the ^{226}Ra content of the sample and assuming a secular equilibrium. Unsupported ^{210}Pb at specific depths in the sediments is then estimated by subtraction of this concentration (supported ^{210}Pb) from total ^{210}Pb (Smith and Hamilton, 1992; Appleby and Oldfield, 1978).

The aim of this study was to evaluate the mobility and the potential environmental threat of Pb from mining waste in bed sediments of the Cacalotenango river and compare them with a section of the Taxco river. Temporal and spatial variation of total Pb and fractionation were used to calculate the amount of bio-available Pb. RAC were used as a reference for its potential threat. Analytical results (geochemical fractionation and physicochemical parameters) and statistical methods were used to determine the geochemical behavior and the actual threat of Pb in the area. Isotopic analyses of ^{210}Pb and ^{214}Pb (a proxy for ^{226}Ra), were used to corroborate the results of sediment Pb accumulation and/or export processes.

2. Study area

The study area is located in the Mexican Federal State of Guerrero. It is located between 18°30′–18°33′ N and 99°36′–99°40′ W (Fig. 1). It lies 10 km SW of Taxco de Alarcón, a city of ∼100,000 inhabitants (INEGI, 2002). The area is a hydrological basin which
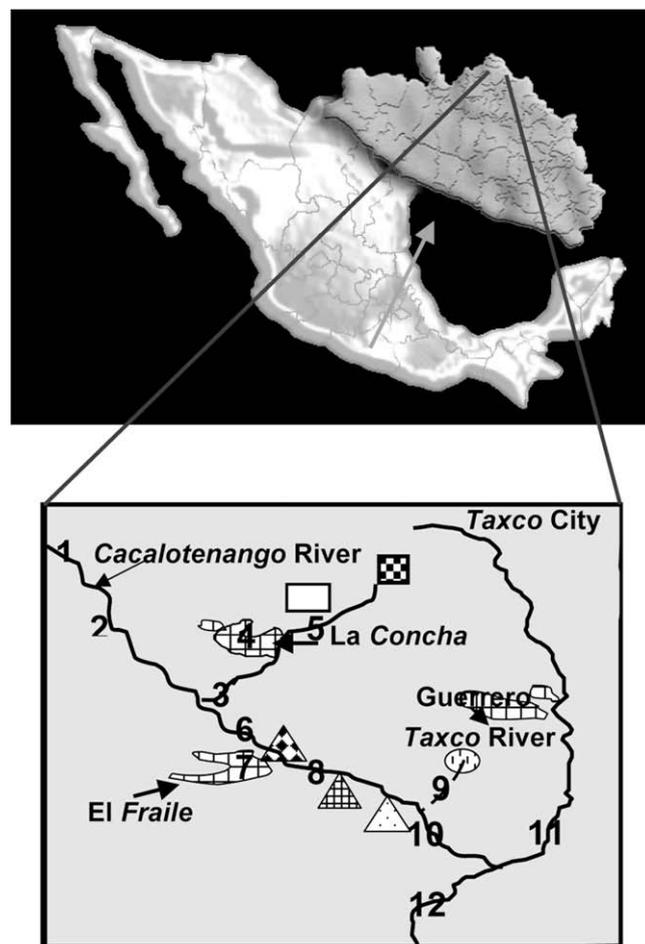

Fig. 1. Study area showing the location of the sediment sampling sites (1, 2, 3, 5, 6, 8, 9, 10, 11 and 12), tailings samples – stations 4, 7 and Guerrero, and main relevant features for this study: ☐ Rockwaste Dump, ▲ Town El Fraile, ▲ Town Santa Rosa, △ Town Dolores, ⊞ Tailings, ⬭ Jesus Mine, ▩ Carbonated rocks and ▬ Rivers.

forms a branch of the greater Rio Balsas-Mezcala basin and has two main rivers: Cacalotenango (RCA) with a total length of 11.5 km (INEGI, 2005), and Taxco (RTX) with a total length of 29.3 km (INEGI, 2005). The Cacalotenango river drains into the Taxco river; and the Taxco river continues until it joins the Cocula River, and discharges into the Infiernillo reservoir.

The Cacalotenango river receives mine waste from La Concha tailings, which are located at an active mine near La Concha stream (total length 3 km, INEGI, 2005), and from El Fraile tailings. Untreated urban wastewater, from approximately 5000 inhabitants in the towns of Dolores, Santa Rosa, El Fraile and Cacalotenango, pours directly into the river. The Taxco river receives mine waste from several tailings piles along its flow. For example, Armienta et al. (2003) report over 20 M tons of tailings in the area surrounding the city of Taxco. In addition, the Taxco river also receives untreated urban wastewater discharged from the city itself (approximately 50,000 m^3 d^{-1}).

The climate in the area is humid and warm with mean temperatures higher than 17.5 °C (SNM, 2005). The area experiences three main hydrological seasons, a dry season from December to the end of May (average monthly precipitation 7.7 mm), a rainy season from June to September (average precipitation 609.7 mm), and a post-rainy season from October to December (average precipitation 67.6 mm) (SNM, 2005; CONAGUA, 2001).

3. Materials and methods

3.1. Selection of sampling sites, sediment and water collection

Water and river sediment samples were collected at: stations 1, 2, 6, 8 and 10 located along the Cacalotenango river (RCA); stations 3 and 5 located along La Concha Stream (RLC); station 9 near a closed mine; and stations 11 and 12 located along the Taxco river (RTX). Stations 4 and 7 represent the two principal tailings dumps in the area, La Concha tailings (RLC4) and El Fraile Tailings (RCA7). In addition, three samples were taken from the Guerrero tailings (GRO1, GRO2 and GRO3), located along the upper Taxco river, for comparative isotopic analysis. All the stations are shown in Fig. 1.

Stations RCA1, RCA2 and RLC5 were selected to represent non-polluted sites, since they are located far enough away (approximately 2 km) and too high (approximately 100 m above the sources of contamination) to be influenced by transport from the tailings or mines. Stations RLC3, RLC4, RCA6, RCA7, RCA8, RCA9, RCA10, RTX11, GRO1, GRO2 and GRO3 were selected to represent the polluted sites related to each of the mines and tailings mentioned above. Distances between stations were variable and depended on the locations of pollution points. Station RTX12, located downstream, was selected to show the amount of Pb discharged into the rest of the hydrological basin.

All samples (water and sediments) were collected during the dry, rainy and post-rainy seasons of a single year using the methods of Rubio and Ure (1993) and Loring and Rantala (1992). Sediment and tailings samples were collected and placed in plastic bags. Water samples were placed in polyethylene bottles. Finally, all samples were packed in ice for transportation to the laboratory.

Samples from the tailings were used as reference values for the concentrations of Pb in mining waste and the isotopic signature from the study area. Approximate river flow was measured at the river stations where and when water samples were collected (RCA1, RCA2, RLC3, RLC5, RCA6, RCA8, RCA10, RTX11 and RTX12) based on the method of Ficklin and Mosier (2002) assuming a flat river bottom. The abundance of fine mud (particle size <62.5 μm, reported as % clay + silt) was measured with a Horiba LA910 laser/tungsten particle size analyzer.

3.2. Geochemical and isotopic analyses

Bulk Pb analyses were performed on air-dried samples sieved with a #10 nylon sieve (Rubio and Ure, 1993), with 76–99% of the sediment particles being <2 mm. The extraction of total Pb was performed using the Loring and Rantala (1992) technique. Quality control was assured by using reference sediment NIST-SRM 8704. A relative standard deviation below 10% and a mean recovery of 95% were obtained. Lithium was determined by means of atomic absorption spectrometry (AAS). Space–time variations in Li concentrations, which show the natural behavior of metals, were used to normalize the Pb concentrations. By performing a covariance analysis of Li and Pb concentrations, as proposed by Loring and Rantala (1992), Li becomes a natural-conditions tracer that allows detection of anomalous data such as a Pb input from an anthropogenic source.

The technique developed by Tessier et al. (1979), was used to determine Pb fractionation of sediments (for FX2, FX3 and FX4). The reactants proposed by Kersten and Förstner (1986) were used to extract FX1, whereas the Loring and Rantala (1992) method was used for the FX5 fraction. The sum of all fractions was compared with total Pb concentrations in order to obtain the percentage recovery. Relative difference between total Pb concentration and the sum of all fractions was below 10%.

The activity of ^{210}Pb and ^{214}Pb was measured with a Canberra hyperpure Ge gamma detector, using their energies of 7.5×10^{-15} J (46.6 keV) and 5.6×10^{-14} J (351.9 keV), respectively. Energy and efficiency calibrations were done using Isotope Products Laboratories standard sources of ^{210}Pb and ^{226}Ra, along with in-house built geometries and densities similar to those of the sediment samples. Homogenized sediment was kept in gas-tight jars and allowed to equilibrate for ^{222}Rn for 30 days. Counting took place for a maximum 72 h or until <5% error was achieved. Marine sediment reference material NIST-SRM 4357 was used for quality assurance, with results better than ±15% of those reported for this ocean sediment. Results are reported in Bq kg^{-1} dry weight.

Organic matter (OM) and carbonate (CO$_3$) concentrations were measured according to Loring and Rantala (1992). Suspended solids (SS) were measured following the technique used by APHA (1995).

3.3. Potential bio-available Pb

Using the results from the geochemical distribution, the method proposed by Kwon and Lee (2001) was used to determine the potential bio-available Pb. The bio-available fraction is defined as the sum of FX1 (labile fraction), FX2 (bound to carbonate fraction), and FX3 (bound to Fe and Mn oxy-hydroxides fraction). The unavailable Pb concentration is defined as the sum of the remaining fractions, FX4 (bound to organic matter or sulfides) and FX5 (lithogenic or residual fraction). The bio-available Pb percentages obtained were assessed against the RAC Code (Jain, 2004).
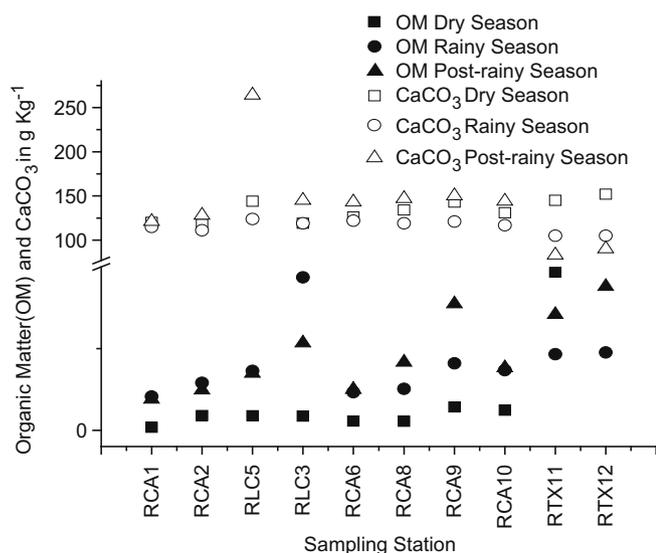
4. Results and discussion

4.1. Time–space variation of chemical and hydrological parameters

Flow variations between the hydrological seasons are shown in Table 1. Significant differences (ANOVA $p < 0.05$) were found between the Cacalotenango and Taxco rivers, and between the dry, rainy and post-rainy seasons.

Time–space variations of organic matter (OM) and carbonate (CO$_3$) contents are shown in Fig. 2. The significant differences found between sampling stations and hydrological seasons are the result of local conditions at stations RLC3, RTX11 and RTX12.

Table 1
Mean[b] flow and velocity seasonal variations in Taxco (RTX), La Concha (RLC) and Cacalotenango (RCA) rivers.

River	Season	Depth (m)	Width (m)	Velocity[a] (m s^{-1})	Flow[a] (m^3 s^{-1})
La Concha	Dry	0.5	2.5	0.1	0.2
Cacalotenango		1.0	7.0	0.2	1.4
Taxco		1.5	11.0	0.1	2.6
La Concha	Rainy	1.3	4.0	0.4	2.7
Cacalotenango		1.5	8.0	0.5	6.0
Taxco		3.5	13.0	0.8	36.4
La Concha	Post-rainy	1.0	2.5	0.3	0.5
Cacalotenango		1.2	7.5	5.3	3.0
Taxco		2.9	11	0.5	16.0

[a] Velocity and flow were calculated by Ficklin and Mosier's (2002) method.
[b] Mean velocity and flow were calculated using the obtained data for each sampling station at each river.

Fig. 2. Time–space variations of organic matter and percentage of carbonates.

Table 2
Abundance of mud in sediments collected from the riverbed at Taxco (RTX), La Concha (RLC) and Cacalotenango (RCA) rivers.

Sample	Season	% <63 μm
RTX11	Post-rainy	40
RTX11	Dry	50
RTX12	Post-rainy	58
RTX12	Dry	83
RCA2	Post-rainy	44
RCA2	Dry	69
RCA8	Post-rainy	63
RCA8	Dry	65
RLC3	Post-rainy	56
RLC3	Dry	69

4.2. Total Pb

Temporal and spatial variations of Pb concentrations for each sampling station are shown in Fig. 3. Significant differences (ANOVA $p > 0.5$) between the sample sites result from the presence of tailings and rock waste dumps. There are no recognizable sources of metal pollution in stations (RCA1, RCA2 and RLC5). According to RAIS (2000), Pb contents in these sites are about the expected concentration for a mine site (150 mg kg^{-1}) and might result from natural sources, such as the erosion and alteration of metal-rich rocks (Salomons, 1995).

At other sites, Pb concentrations are up to four times higher than in the non-polluted stations. The highest concentrations were

The peak of OM observed in the rainy season (47 g kg^{-1}) at station RLC3, was produced by wastewater released from the local school, located just a few meters away from La Concha tailings. OM concentrations in the dry, rainy and post-rainy season samples at stations RTX11 (48 g kg^{-1}) and RTX12 (57 g kg^{-1}) may result from the accumulation of organic matter along with fine sediments. The similarity of OM contents at stations RTX11 and RTX12 during the dry and post-rainy seasons (35 g kg^{-1} and 44 g kg^{-1}, respectively) may be explained by the settling of fine-grained organic covered particles during reduced river flow.

There were no significant differences in the concentration of carbonates between the sampling sites, except for station RLC5, which showed high concentrations in the post-rainy season. This pattern is probably due to carbonate-rich bedrock located near this station (Fig. 2). Erosion and wash-off from this outcrop may release carbonates into the river. A slight decrease was observed during the rainy and post-rainy seasons at stations RTX11 and RTX12. This indicates the transport of carbonates adsorbed to fine material downstream due to flow increase in the Taxco river. Further evidence of this process is provided by the high abundance of mud during the dry season (83%) compared to the post-rainy season (58%) in sample RTX12 and to a lesser extent in sample RTX11 (40% and 50% during the post-rainy and dry seasons, respectively; Table 2). As expected, fine-grained sediments are more abundant during the dry season at the studied sites, reflecting a decrease in hydrodynamic energy (Table 1).

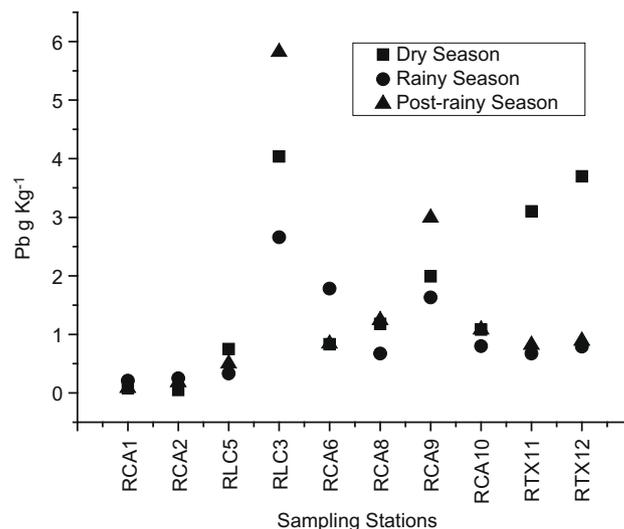Fig. 3. Time–space variations of Pb in river bed sediments.

found at station RLC3 (5820 mg kg^{-1}), located downstream from La Concha tailings, during the post-rainy season, and at Taxco river stations RTX11 (3110 mg kg^{-1}) and RTX12 (3720 mg kg^{-1}) during the dry season.

Significant differences (ANOVA $p > 0.5$) between the three hydrological seasons for the polluted stations (RLC3, RCA6, RCA8, RCA9, RCA10, RTX11 and RTX12) were also observed. These differences could be explained by seasonal changes (Griethuysen et al., 2005), since the tailings suffer from the "wash-off-effect" during the rainy season, allowing metals to be transported with run off to the river. The strongest evidence of this process is the accumulation of Pb at station RLC3 during the post-rainy season. Lead adsorbed to fine-grained organic or inorganic material may be deposited as a result of a decrease in flow rate. This phenomenon is known as discharge with erosion (Bradley, 1984; Bradley and Cox, 1986a,b). A proportional dilution related to differences in grain-size distribution (Salomons, 1995) was observed at stations RTX11 and RTX12 (Table 2). Space–time variations of total Pb (Fig. 3) corroborates the first phenomenon, while the suspended solids variations (Fig. 4) confirm the second one.

Suspended solids contents in the three hydrological seasons at Cacalotenango river stations 1 through 10 were not significantly different (ANOVA $p > 0.5$). However, Taxco river stations RTX11 and RTX12 showed a significant increase in the concentration of suspended solids in the rainy and post-rainy seasons, but not in the dry season. This increment in the transported material concentration may be explained by the increase in the Taxco river flow from approximately 2.6 m^3 s^{-1} in the dry season to 36.4 m^3 s^{-1} in the rainy season. This flow increase enhances the resuspension and transport of fine material.

4.3. Pb fractionation

To determine the bioavailability, potential pollution and probable environmental implications of Pb present in river sediments, a geochemical fractionation analysis was performed for the dry (Fig. 5a), rainy (Fig. 5b) and post-rainy (Fig. 5c) seasons.

In the dry season (Fig. 5a), the lithogenic fraction (FX5) represents more than 50% of total Pb in non-polluted samples (RCA1, RCA2 and RLC5). This percentage indicates a natural origin for Pb at these sites (Salomons, 1995; Kwon and Lee, 2001; Jain, 2004). Moreover, significant variations between hydrological seasons for these samples were not observed, showing that Pb is almost immo-

bile with respect to the changing hydrological conditions at these sites. The majority of Pb occurs in fractions FX1, FX2 and FX3 at the polluted stations in the dry season. This distribution confirms that Pb is mainly introduced by anthropogenic activities (Salomons, 1995; Kwon and Lee, 2001; Jain, 2004). Geochemical fractionation in these polluted stations shows a significant change during the rainy season (Fig. 5b), since Pb in FX1 diminished proportionally at the expense of an increase in the remaining fractions. Metals in the FX1 fractions are weakly bound to sediments (Gibbs, 1977) resulting in desorption of labile Pb from sediments.

The percentage increment of the lithogenic Pb fraction in all samples during the rainy season shows that natural Pb is eroded from the hydrological basin. Geochemical ratio changes indicate that naturally bound Pb will show a different geochemical fractionation than that of Pb bound to sediments under anthropogenically altered conditions (Salomons, 1995; Kwon and Lee, 2001; Jain, 2004).

Stations RTX11 and RTX12 best show the importance of the erosion effect on the change in geochemical fractionation ratios and total Pb concentration. It also corroborates the proportional dilution related to differences in grain-size distribution phenomena previously mentioned.

During the post-rainy season (Fig. 5c), total Pb concentrations and geochemical fractionation ratios close to that measured during the dry season were observed at nearly all the stations. Concentrations greater than those measured in the dry season were observed at station RLC3 during the post-rainy season (Fig. 3). The erosion of the tailings and subsequent transport of this material to the RLC3 station, where the water flux diminishes and allows settlement of the fine particles, explains this. The observed increase in Pb during the post-rainy season at station RCA9 may have been produced by the erosion of solid and liquid wastes from the Jesus mine, located upstream.

During the post-rainy season at stations RTX11 and RTX12, Pb concentrations were below those of the dry season, indicating that the river flow did not reach dry season flow conditions. Ratios between the geochemical fractions for these stations on the Taxco river, show that the source of the sediments present in the river could be controlling, for the most part, the binding geochemistry of Pb (probably from the Guerrero tailings) in a more significant way than physicochemical changes in the river.

4.4. Bio-available Pb and multivariate statistical analyses

The percentage of bio-available Pb is defined by Kwon and Lee (2001) and Jain (2004) as the sum of Pb in the exchangeable fraction (FX1), the carbonate fractions (FX2) and the Fe–Mn oxides fraction (FX3) (see Fig. 6). Some of the values are slightly above 100%, which could be explained by the relative standard deviation ($\pm$10%) of the extraction technique. It is noteworthy that bio-available Pb is above 50% in 80% of all samples. This shows that Pb present in the bed sediments of the Cacalotenango and Taxco rivers represents a potential environmental threat during all three hydrological seasons. According to the RAC (bio-available metal concentration >50%) (Jain, 2004), the study area could be considered as very high risk in terms of Pb pollution.

The polluted samples showed the highest values of bio-available Pb during the dry season. Lead-polluted water would be expected for this season since solid Pb (expected to be weakly bound to sediment particles) may equilibrate with the aqueous phase increasing the amount of dissolved Pb. Nevertheless, according to Burgess (1978) and Claudio et al. (2003), Pb^{4+} is not found in solution, since Pb(IV) species are strong oxidants. Therefore, the greater percentage of Pb in natural environments is present as a Pb^{2+} species, but it will usually be found as hydroxy or polynuclear species adsorbed to particulate of suspended material and not as a
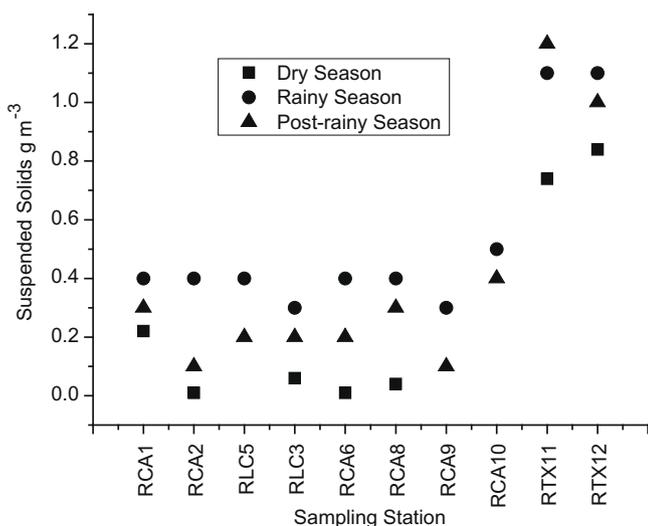

Fig. 4. Time–space variations of suspended solids along the Cacalotenango, La Concha and Taxco rivers.
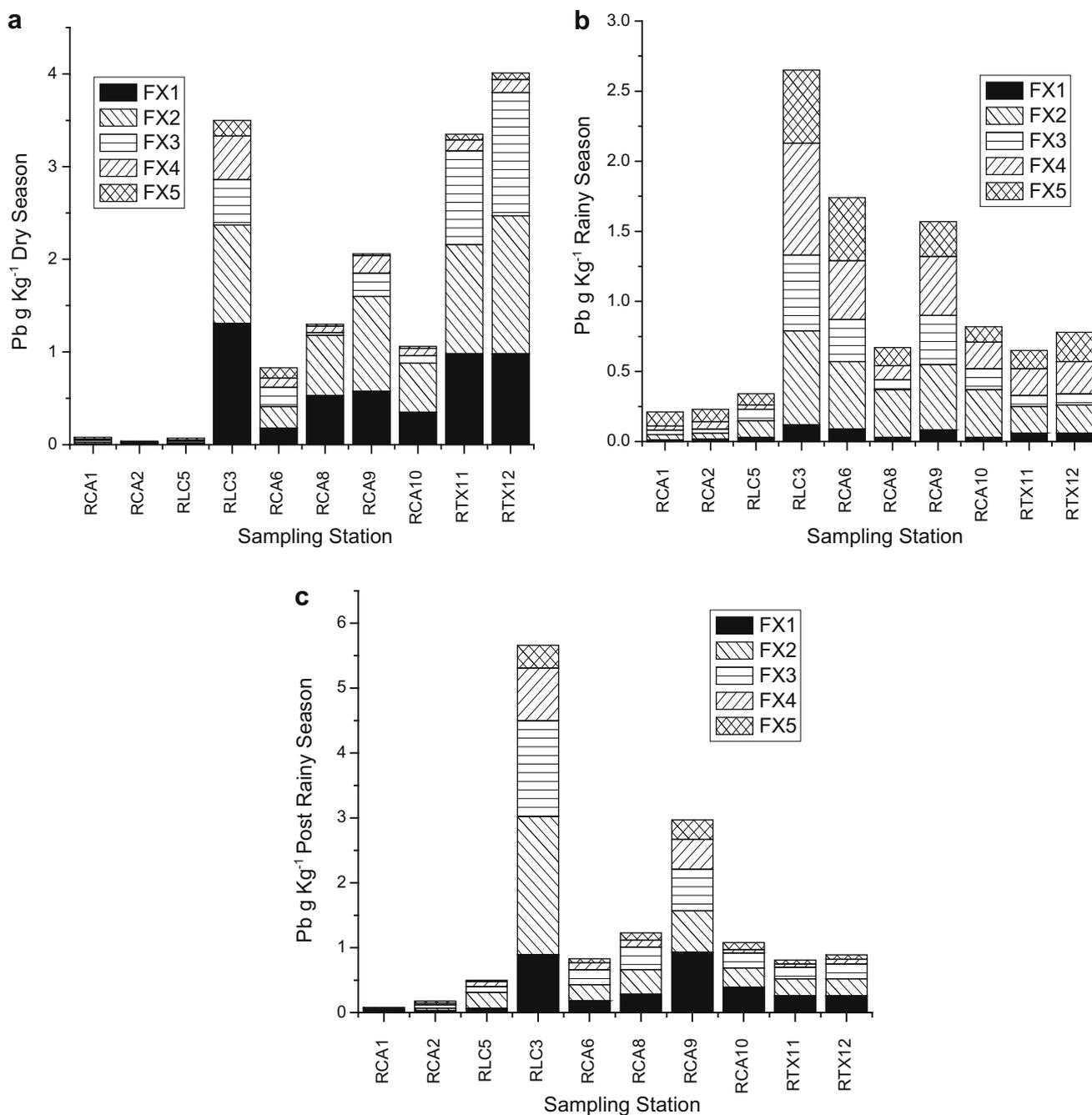
Fig. 5. Space variations of geochemical fractionated Pb in the (a) dry, (b) rainy and (c) post-rainy seasons. FX1 = exchangeable, FX2 = bound to carbonates, FX3 = bound to Fe and Mn oxides, FX4 = bound to organic matter and sulfides and FX5 = residual.

dissolved element in the water column. Consequently, although bio-available Pb in sediments is higher in the dry season, its release to the water column is not favoured by the chemical characteristics of Pb, and also because of the low flow conditions that allow settlement of fine particles, and a low concentration of suspended solids (Fig. 4). Lead concentration may not reach hazardous levels in Cacalotenango river water during the dry season, so the inhabitants of the area could extract water from the river, use a container to let particulate matter settle, and then carefully pour off the water so as not to resuspend the settled solids. The Taxco river stations showed a higher concentration of suspended solids (Fig. 4) than those of the Cacalotenango river, therefore Pb polluted water would be expected during the dry season. Nevertheless, this river water is not used by humans in the study area, since Taxco city

urban wastes are poured directly into it and it has a bad odour and an unattractive grey colour with a foam cover.

Bio-available Pb in sediments was lowest in the post-rainy season. Following the RAC, it suggests that this season is the best for the extraction and use of water (Liu et al., 2005). However, multivariate statistical analyses (Lucho-Constantino et al., 2005) indicated that this assumption might be wrong. In addition, factor and canonical analyses were applied to assess the processes governing the geochemistry of Pb and possible sources in the study area (Dias and Edwards, 2003).

Factor analyses results for the dry season (Table 3) show that 81% of the geochemical processes of Pb in sediments are explained by two varimax rotated factors. The first one includes total Pb, and Pb in labile geochemical fractions, OM, CO_3 and suspended solids
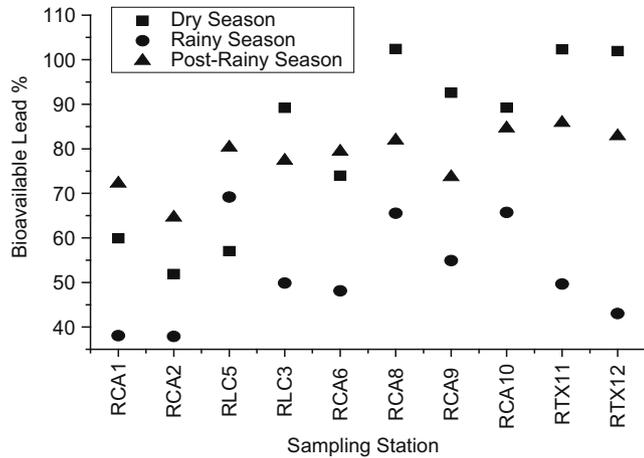
Fig. 6. Time–space variations of bio-available Pb in sediments of the Cacalotenango and Taxco rivers.

all show a significant (>0.7) and positive value. This factor indicates that nearly all the Pb present is anthropogenic (Garrett, 2000). The relationship of Pb with carbonates reflects its bioavailability and that it is bound or adsorbed to a significant extent to these minerals. Any change affecting carbonates would release Pb from the sediments (Arcega-Cabrera et al., 2005). The relationship of Pb with organic matter and suspended solids indicates that during the dry season, settling of fine-grained sediments (especially in the Taxco river where Pb increases concomitantly with% mud) could scavenge Pb from the water column into the river bottom (Gibbs, 1973; Bradley, 1984). Thus, sediments would show a relative Pb enrichment when compared with water during the dry season. However, in the Cacalotenango river and La Concha stream, the role fine-grained sediments may play as Pb scavengers is not evident.

The second factor, also varimax rotated, associated the FX4 and FX5 geochemical fractions with Li with a positive and significant (>0.7) value. It also showed that there is a natural source of Pb, probably from run off within the hydrological basin, that had a total Pb mean value of 120 mg kg^{-1}. The canonical analysis between these two factors gave a value of 0.998, indicating that the geochemistry of Pb in the dry season was mainly controlled by the chemical characteristics of the sediment and settling of suspended solids.

In the rainy season (Table 3), 82% of geochemical processes involved in Pb behavior in sediments were explained by two varimax rotated factors. The first one related Pb (total and all geochemical fractions) and carbonates with significant (>0.7) and positive val-

ues. It indicated that Pb in the sediments is being transported by the river. The inverse and significant (>0.7) relationship with suspended solids and the organic matter in the second factor suggested that the suspended solids were playing an important role in scavenging Pb from sediments to the water column (Gunn et al., 1991; Pestana et al., 1997; Tarras-Wahlberg et al., 2001), corroborating the co-transport hypothesis previously discussed. On the basis of this relationship, the use of river water should be avoided during the rainy season, since Pb concentration in the suspended solids of the water column may increase.

The presence of FX4 and FX5 in the first factor shows a lack of a relationship between these natural fractions and Li, that is the tracer of natural concentrations. It was an unexpected outcome but it might be due to the magnitude of concentration differences, since natural Pb (FX4 and FX5), entering the rivers through basin run off has a significantly smaller concentration compared to that from anthropogenic sources (FX1, FX2 and FX3). With this in mind, a factor analysis was performed using logarithmic data, and 85% of the geochemical behavior of Pb was explained by two varimax rotated factors. Magnitude differences were overcome and a significant positive relationship was found between FX4 and FX5 and Li. Also a negative and non-significant relationship between FX1, FX2 and FX3, and Li was shown (Table 4). This can be explained by natural Pb entering the river system with a different geochemical fractionation ratio than that of anthropogenic origin. This result corroborates the previous discussion on the geochemical fraction ratios changes (Section 4.3) and it is in accord with the expected results. The canonical value of 0.979 between the two factors shows that the river flow conditions and the source (natural or anthropogenic) of Pb, could be controlling the geochemistry of Pb during the rainy season.

Table 4
Factor analysis for the rainy season, performed in the data transformed to logarithmic values of total Pb, Pb in the different geochemical fractions, organic matter, carbonates, suspended solids and total Li. Significant value (>0.7).

Variable	Post-rainy season	
	Factor 1	Factor 2
Pb total	**0.87**	0.10
FX1	**0.95**	0.00
FX2	**0.83**	0.24
FX3	**0.89**	0.00
FX4	0.32	**0.70**
FX5	0.17	**0.73**
OM sediment	0.21	**−0.81**
CO$_3$ sediment	0.38	**0.74**
Suspended solids	−0.19	**−0.97**
Li total	0.54	**0.72**
% of total variance	0.62	0.23

Table 3
Factor analysis for the dry, rainy and post-rainy seasons variations of total Pb, Pb in the different geochemical fractions, organic matter, carbonates, suspended solids and total Li. Significant values (>0.7).

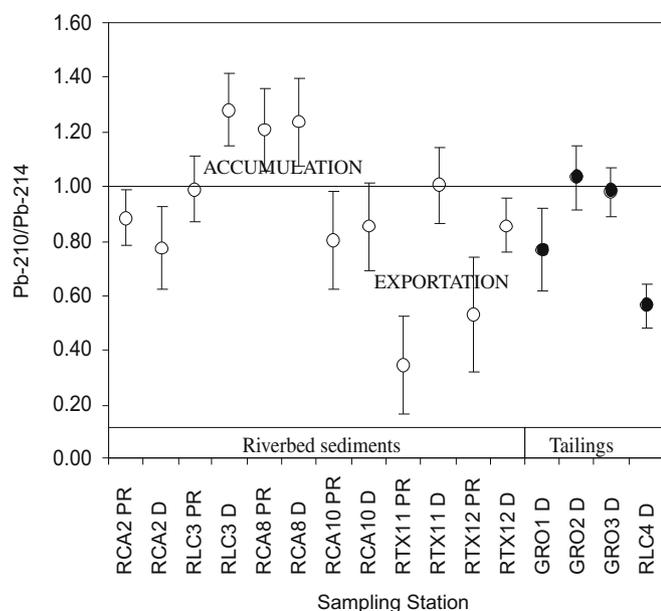| Variable	Dry season		Rainy season		Post-rainy season	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Pb total	**0.96**	0.25	**0.99**	0.01	**0.99**	0.10
FX1	**0.83**	0.47	**0.86**	0.08	**0.95**	0.00
FX2	**0.91**	−0.06	**0.98**	0.04	**0.83**	0.24
FX3	**0.95**	−0.06	**0.97**	0.09	**0.89**	0.00
FX4	0.21	**0.95**	**0.85**	−0.22	**0.92**	0.07
FX5	0.15	**0.86**	**0.84**	−0.11	**0.97**	0.03
OM sediment	**0.70**	−0.09	0.10	**−0.77**	0.21	**−0.71**
CO$_3$ sediment	**0.89**	0.24	**0.86**	0.43	0.38	**0.70**
Suspended solids	**0.80**	−0.44	−0.33	**−0.84**	−0.19	**−0.90**
Li total	−0.29	**0.70**	−0.05	**0.85**	0.54	0.15
% of total variance	0.54	0.27	0.59	0.23	0.57	0.19

Fig. 7. Isotopic ratios ^{210}Pb/^{214}Pb showing the zones of accumulation in the Cacalotenango river and exportation in the Taxco river. D = dry season, PR = Post-rainy season.

Seventy-six percent of the geochemical behavior of Pb is explained by two varimax rotated factors in the post-rainy station (Table 3). Factor one shows a positive and significant (>0.7) relationship of total Pb and all its geochemical fractions, indicating that the Pb present in the bed sediments mainly comes from erosion of tailings. This result is corroborated by the lack of significant association with Li, which, according to Loring and Rantala (1992), functions as a tracer of natural variations of metals and identifies anthropogenic inputs to a natural system. The presence of carbonates in the second factor, inversely and significantly (>0.7) related to organic matter, shows competition for Pb. While Pb bound to carbonates tends to settle, Pb bound to organic matter tends to stay in the water column (Gerringa, 1990; Axtmann and Luoma, 1991).

4.5. ^{210}Pb, ^{214}Pb and sedimentation processes

The results for the determinations of ^{210}Pb and ^{214}Pb by gamma counting are shown expressed as ^{210}Pb/^{214}Pb ratios in Fig. 7. Ratios >1 are interpreted as signalling an accumulation of excess (atmospheric) ^{210}Pb, and thus of sediment deposition. Ratios $\cong$1 indicate a secular equilibrium between these isotopes (and hence with ^{226}Ra) in river sediments, suggesting that no excess ^{210}Pb is accumulating or being transported. Ratios <1 suggest a disequilibrium which is responsible for depleting the lighter ^{210}Pb, suggesting sediment transportation. Overall, samples with low ^{210}Pb also have lower ^{214}Pb activities.

The seasonal variation in ^{210}Pb/^{214}Pb in the riverbed sediments probably results from seasonal changes in the rates of particle erosion, transport and deposition forced by the increase in river flow during the rainy season (Smith and Ellis, 1982; Roulet et al., 2000; Gacshin et al., 2005). In fluvial systems, slightly higher or lower ratios can result from changes in the temporal, spatial, textural and bio-geochemical patterns (El-Daoushy and García-Tenorio, 1998; Olley et al., 1996; Goodbread and Kuehl, 1998; Xiang et al., 2002). Thus, lower proportions of ^{210}Pb in post-rainy period samples might be reflecting (1) a contribution from tailings material (pollution), (2) the desorption and/or erosion of any previously deposited atmospheric ^{210}Pb (transport), or (3) a dominance of in situ ^{210}Pb and ^{214}Pb (as in situ decay products of ^{226}Ra) in the sediments (accumulation).

Except for RCA2, all the riverbed samples show a significant increase in ^{210}Pb/^{214}Pb during the dry season, signalling the accumulation of atmospheric ^{210}Pb during calmer hydrodynamic conditions, and the settling of finer-grained particles, as is also suggested by the higher abundance of mud during the dry periods (Table 2). One sample from the Cacalotenango river (RCA8) commonly has ^{210}Pb/^{214}Pb > 1, suggesting that sediment accumulation processes are dominant throughout the year at this site. This is also the case during the dry season for La Concha stream, where the site located near the school is evidently accumulating ^{210}Pb and Pb rich sediment; although, the abundance of mud increases only 13% from one season to another. Apparently deposition processes dominate the ^{210}Pb/^{214}Pb signal at these sites from the Cacalotenango river during the dry season. In the rainy season, all Cacalotenango river stations with the exception of RCA2 show an insignificant decrease in the ^{210}Pb/^{214}Pb ratio, this might be interpreted as evidence of limited transport of sediments or as low ^{210}Pb/^{214}Pb ratio sediments (0.56) entering to the river system, probably, from the La Concha tailings erosion.

In the Taxco river sampling stations, the change in the ^{210}Pb/^{214}Pb ratio is more significant than in the Cacalotenango river. A transport process or a low ^{210}Pb/^{214}Pb sediment entering process could also explain these results. When comparing the ratios in the two rivers, a preferential accumulation of sediment and Pb in the Cacalotenango river and a preferential export in the Taxco river during the post-rainy season is evident.

If the sum of errors of the counting method for each sediment sample (10–21%) is included, the RCA2 sample has ^{210}Pb/^{214}Pb ratios $\cong$ 1 in the dry and post-rainy seasons. It is probable that neither a significant transportation process nor an introduction of anthropologically altered material with low ^{210}Pb/^{214}Pb ratio is taking place at this site. Consequently, RCA2 is representative of a non-polluted site in the study area.

Samples RTX11 and RTX12 from the Taxco river show significant depletions of ^{210}Pb during the post-rainy season with a ^{210}Pb mean of 0.35 and a ^{214}Pb mean of 0.53. Depletions of ^{210}Pb are also seen in those tailings, which are known to be extensively weathered such as GRO1 (adjacent to the Taxco river). No depletions however are seen for the unweathered GRO2 and GRO3 tailings. Significant ^{210}Pb depletions, like those in samples RTX11 and RTX12 during post-rainy season, are indicative of processes that may have affected the secular equilibrium between ^{210}Pb and its parents. The two samples (the only ones available from the Taxco river), were selected for isotopic analyses because they were thought to contain material eroded from tailings, and thus could serve as tracers for tailings-pollutant transport. But the riverbed stations show a lower ^{210}Pb/^{214}Pb ratio than that of the GRO1 tailings, this was unexpected and can only be explained by the presence of material from other more weathered tailings entering the river system. It is likely that these and other unstudied weathered tailings are responsible for the low ^{210}Pb/^{214}Pb ratios in sediments in this region. Given 500 a of intensive mining in this region, there are probably numerous unstudied weathered tailings.

The low ^{210}Pb/^{214}Pb ratios in the Taxco river probably reflect the presence of eroded material from tailings along the course of the Taxco river (Armienta et al., 2004), which themselves have a secular ^{210}Pb/^{214}Pb disequilibrium, due to Pb ore extraction processes and/or extensive weathering of the tailings. The enhanced mobility of ^{210}Pb compared to ^{214}Pb in fluvial systems and weathered ores is a matter that needs to be assessed in more detail.

5. Conclusions

Space–time variations of total Pb in the Cacalotenango and Taxco rivers respond to both geochemical fractionation and the

hydrological conditions of the area. Two processes mainly drive total Pb variations due to hydrological conditions: (a) proportional dilution related to differences in grain-size distribution (Taxco river) and (b) discharge with erosion (Cacalotenango river). Among the measured physicochemical parameters, organic matter, carbonates and, in part, grain-size of sediments determine the space–time variations of total Pb and its fractionation during the three seasons. In the rainy and post-rainy seasons, these variations also depend on the behavior of suspended solids and on material entering from the erosion of the hydrological basin. The isotopic analyses indicate that preferential export of Pb occurs in the Taxco river, and preferential accumulation of Pb occurs in the Cacalotenango river. It is suggested that weathered tailings have distinctly low $^{210}Pb/^{214}Pb$, a feature that may aid when tracing tailings pollution at this and other sites. Also, statistical and isotopic analyses confirm that the main source of Pb in the area is anthropogenic, mainly derived from La Concha tailings for the Cacalotenango river, and from the Guerrero and other unstudied tailings for the Taxco river. Bio-available Pb is >50% in most of the samples in both rivers, implying a very high risk according to RAC. Nevertheless, when these results were analyzed using multivariate statistical analysis, and by taking into account the environmental chemistry of Pb, it was shown that RAC criteria did not apply for this study area. Based on the geochemical and statistical results, it would be advisable to avoid using the water of the Cacalotenango river during the rainy and post-rainy seasons, but it could be used during the dry season, with the precaution of letting the suspended particulate material settle before consumption. Water from the Taxco river should not be used during any of the three hydrological seasons since higher concentrations of suspended solids, which function as a co-transport vehicle for Pb, are found throughout the year.

Acknowledgements

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