Ecological Risk Assessment of Heavy Metals in Sediments from the Soubeira Reservoir, a Small-Scale Reservoir in North Central Burkina Faso, West Africa

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Abstract

Small-scale reservoirs play a central role in socio-economic development of Burkina Faso. In the absence of a best environmental management plan, these reservoirs can be potential factors of water pollution and ecological deterioration. In the present study, we investigated ecological status of sediments from the Soubeira reservoir, using concentrations of a series of heavy metals. Concentrations of the metals ranked as follows: Fe> Mn> Cr> Zn> Cu> Pb> As ~ Co> Hg ~Mo> Cd. Based on the correlation analysis, Fe, with weaker relationships with other metals, may be derived from the local ferruginous soil, whereas Cd, Cu and Cr could be mainly originated from anthropogenic sources and carried by clay minerals into the reservoir. In contrast, Hg and As abundance could be related to artisanal gold mining in the surrounding environment. Negative correlations between heavy metals (except As) with pH were consistent with desorption and mobility of the majority of heavy metals under low pH values. The significant negative correlations were also observed between CEC and As ($r = - 0.75$) and between clay and As ($r = -0.64$). This could be an indication of As mobility under the physico-chemical conditions of the reservoir. Both potential ecological risk and adverse effect indices suggested that the reservoir sediments were highly polluted. Five heavy metals (As, Cd, Cu, Cr and Hg) could cause adverse effect to biota, whilst only Hg and Cd appeared to show high and moderate potential ecological risk indices, respectively. The study demonstrated that the Soubeira reservoir requires a heavy metal pollution control program.

Keywords: small-scale reservoirs, sediment pollution, heavy metals, benthic organisms, physico-chemical parameters

1. Introduction

In Burkina Faso, the agricultural sector contributes about 40% to the Gross National Product and employs more than 80% of the workforce (INSD, 2011). In this semi-arid country, the rainfall regime is erratic and unevenly distributed with the northern region receiving less than 500 mm rainfall per year (Mahé and Paturel, 2009; Ibrahim et al., 2012). To meet the growing demands for freshwater, more than 1700 small- and medium-scale reservoirs were built across the country (Cecchi et al., 2009; Venot and Cecchi, 2011). Most of these reservoirs were constructed within the Nakambe River Basin (formerly White Volta) where population densities are high (~ 100 inhabitants /km²; INSD, 2000). These reservoirs have attracted many farmers and artisanal gold miners from distant villages, putting more pressure on water resources (Morin, 1990). Consequently, domestic wastewater, agricultural runoff and mining waste, rich in heavy metals (defined here as metallic and metalloid elements of density equal to or greater than 6 g/cm³), are discharged into the adjacent reservoirs.

Because of their persistence in the aquatic environment and their accumulation in biota, heavy metals may enter foodweb and pose serious threats to human health (Nüremberg, 1984; Cook et al., 1990; Deniseger et al., 1990; Förstner, 1990; Harte et al., 1991). Some heavy metals such as Zn, Co, Cu, Cr, Mo, Fe and Mn are involved in numerous biochemical processes in organisms, but can be toxic at high concentrations (Sandstead, 1995). In contrast, non-essential heavy metals (notably As, Pb, Cd and Hg) may cause acute or chronic toxicity even at low concentrations (Muñoz-Olivas and Cámara, 2001; Kabata-Pendias, 2011).

Once introduced into the aquatic environment, heavy metals are redistributed throughout the water column, adsorbed or accumulated in bottom sediments (Macklin *et al*., 2006; Martin, 2000; Nouri *et al*., 2008; Reza and Singh, 2010). Depending on the physico-chemical conditions such as mineralogical composition, pH, cation exchange capacity (CEC) and the presence or absence of inorganic and organic ligands, previously adsorbed heavy metals onto sediments can be released back into the underlying water, making sediments a secondary source of water pollution (Calmano *et al*., 1990). Due to fluctuations in discharge and short water residence time, monitoring of pollutants in the water column alone is not conclusive (Förstner and Wittman, 1983). Moreover, in streams and rivers, reduced water velocity in some reaches may result in sediment accumulation in localized areas, whereas, in lakes and reservoirs, sediments are more uniformly distributed (Yi *et al*., 2011; Rosen, 2015). Thus, the impact of anthropogenic pollution on atmosphere, hydrosphere, biosphere and pedosphere is well preserved in lacustrine and reservoir sediments compared to those of streams and rivers (Mackay, 2001; Choi and Wania, 2011).

Several studies have investigated biological pollution and its health impacts related to small-scale reservoirs in Burkina Faso (e.g., Poda, 1996; Poda and Traoré, 2000; Cecchi *et al*., 2004; Leboulanger *et al*., 2008), but heavy metal contamination of these reservoirs has been generally ignored. Given the paucity of published data on heavy metal contamination of small reservoirs in semi-arid climatic zones, the objectives of the present paper are (1) to evaluate concentration levels of 11 heavy metals (As, Cd, Co, Cr, Cu, Pb, Fe, Mn, Mo, Hg and Zn) in the Soubeira reservoir, (2) to identify the geogenic and anthropogenic sources of these metals in the reservoir, using correlation analysis and (3) to assess the degree of potential environmental risk and adverse biological effect of selected potentially harmful heavy metals (i.e., As, Cd, Cr, Cu, Hg, Pb and Zn), using potential ecological risk index (PERI) and adverse effect index (AEI). The findings of this study can be used to ascertain the suitability of a small-scale reservoir in semi-arid environmental settings for different water uses and to provide baseline data for an effective water quality monitoring program within a given watershed.

1.1 Site Description and Environmental Setting

The Soubeira reservoir is an earth-fill reservoir that was built in 1986 on the Nakambe River drainage basin in the north central Burkina Faso (Fig. 1). The reservoir is underlain by Birimian volcanic and volcano-sedimentary rocks (Hottin and Ouédraogo, 1972). With a storage capacity of 494000 m^3 and a height of 3.70 m, this small-scale reservoir is fed by numerous tributaries of the Nakambe River. The study area is situated in the Sudano-Sahelian climatic zone characterized by an extended dry season from November to May with an average annual rainfall of 751 mm (BUNASOL, 1990). The catchment of the Soubeira reservoir has an area of 110 km^2 and it is mainly occupied by farmlands and perennial grassland (Fontes and Guinko, 1995). The predominant soil types in the area are ferruginous tropical soils (Boulet, 1968).

The main activities in this rural area are agriculture, animal husbandry and artisanal gold mining. As a result, water of the Soubeira reservoir is used for livestock watering and irrigation of off-season vegetable and crop growing, domestic water supply, brick making and ore processing. Although the reservoirs may have potentiality to significantly improve livelihood of the local population (Savy *et al*., 2006; Cecchi, 2007), their multifunctional use will inevitably deteriorate surface water quality (Vincent, 1994; Ersado, 2005; Boelee *et al*., 2009).
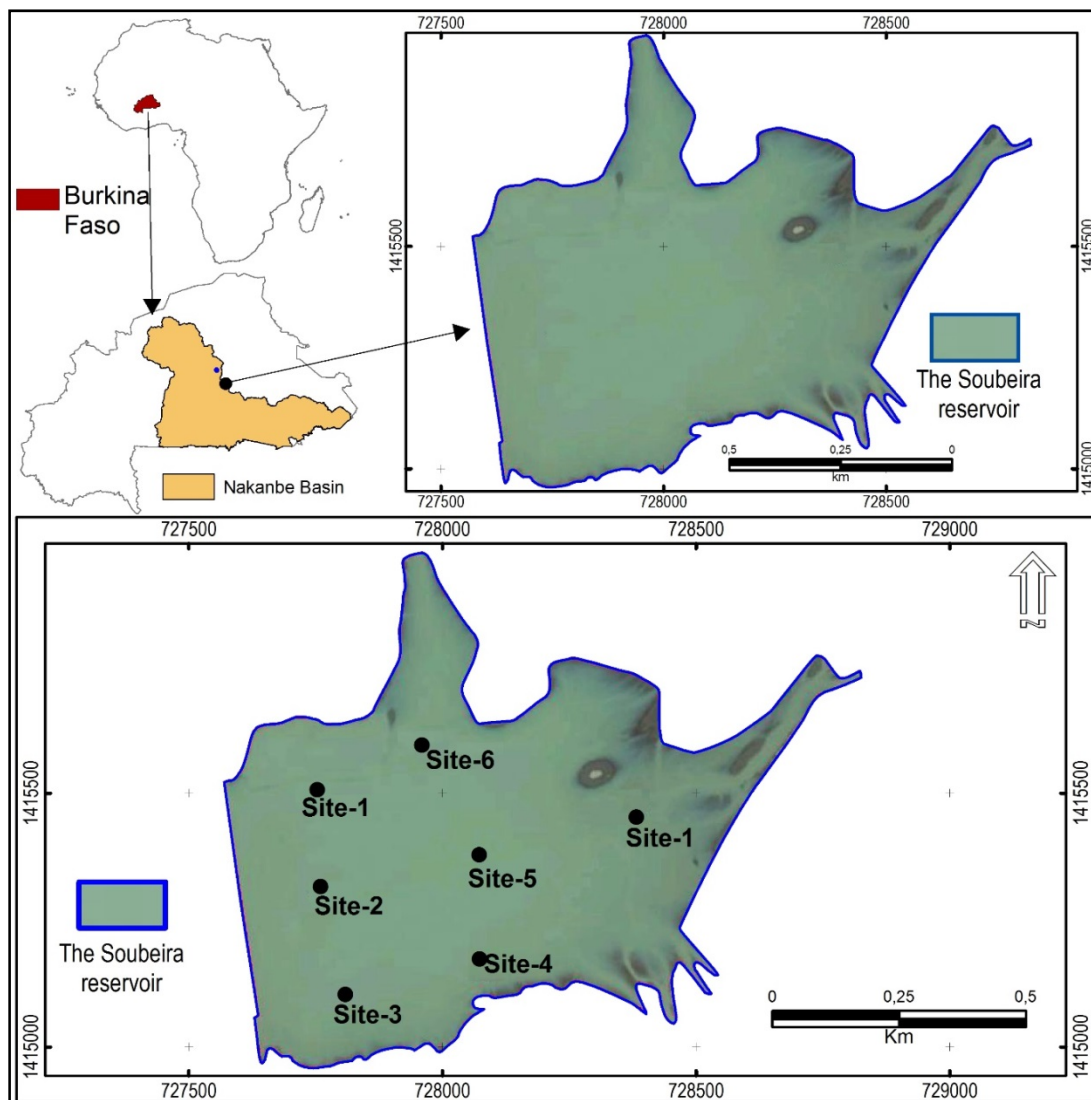
Figure 1. Map of Burkina Faso showing the Nakambe River Basin and the Soubeira reservoir with sampling sites

2. Materials and Methods

Core sediment samples were collected from seven sites within the reservoir using a hand-held stainless steel corer (Beecker 0.23. SA). Sites 7 and 6 are located in the reservoir intake and sites 1, 2 and 3 in the overflow discharge points, whereas sites 4 and 5 are located between inlet and discharge points (Fig. 1). The depth of sampled cores varied between 44 and 57 cm. All samples were sealed in clean polyethylene bags and stored in an ice box. Once in the laboratory, cores were carefully mixed to form composite samples. The samples were subsequently air-dried at room temperature and sieved to remove coarse debris. A subset of each sample was used to determine granulometric composition, using physical separation method (Rouiller et al., 1994). A second subset was finely powdered in an agate mortar for chemical analysis. The pH values of the samples were measured in 1: 2.5 mgL^{-1} sediment/water ratio, and total organic carbon contents (TOC) were quantified using the Walkey-Black wet digestion method (Nelson and Sommers, 1992). The Ag-Thiourea (AgTu) method was used to extract basic cations (Pleysier and Juo, 1980). Glycol-ethnol was used to remove soluble salts in 1 g air-dry (<2 mm) of each sediment sample. Subsequently, 50 mL of AgTu (0.01 M) solution was added to the soluble salt-free samples, shaken, centrifuged at15 rpm for 4 h and filtered through a 0.2 μm nylon membrane. Extractable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and exchangeable Ag^{+} concentrations of the filtrates were measured by Flame Atomic Absorption Spectrophotometer (Perkin Elmer AA100). The unbuffered CEC of the sediments was assumed to be the total reactive site concentrations of the solids.

Total heavy metal concentrations were measured in a mixture of HN_3, HCl and HF in the laboratories of the

"Bureau des Mines et de la Géologie du Burkina" (BUMIGEB). A subsample (~ 0.5 mg) of each sample was transferred into a Teflon container and 15 mL of ultrapure HNO_3, HCl and HF were added it. The mixture was digested in a microwave (CEM Mars5) for 60 min. The digested samples were diluted to 100 mL with double deionized water (Milli-Q water) and their heavy metal concentrations were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, Perkin Elan 9000). The Blanks and the Laterite Ore (GBM397-1) standard were digested and analyzed according to the same protocol as for sediment samples in order to evaluate the accuracy of the digestion method. The analytical results obtained for GBM397-1 differed by less than 15% from the certified values. The detection limits (LD) for Fe and Mn were 0.07 and 0.04 mg/kg, respectively. In contrast, LD was 0.01 mg/kg for As, Cd, Co, Cu, Hg and Zn and 0.001 mg/kg for Mo and Pb.

3. Results and Discussion

3.1 Sediment Characteristics

In aquatic environments, positively charged heavy metal ions tend to be associated with sediments through a set of geochemical processes such as adsorption onto aluminosilicate and oxyhydroxides minerals, co-precipitation with Fe and Mn-oxyhydroxides and complexation with organic and inorganic ligands (Bruder *et al*., 2002; Sutherland and Tack, 2002). Following changes in physico-chemical parameters (e.g., pH, organic matter and clay content), sediments may release the heavy metals into the water column. As a result, a heavy metal control and monitoring program of a surface water system should take into account distribution patterns of physico-chemical parameters in sediments.

In the present study, physico-chemical parameters such as pH, clay, TOC and CEC were uniformly and normally distributed in the Soubeira reservoir (CV < 50% and low skewsness values; Tables 1 – 2). Thus, the texture ranged from loam to clay, suggesting that the sediments are likely to have a great affinity for heavy metals (Zhang *et al*., 2014; Saeedi *et al*., 2013). However, the slightly acidic pH (5.4 – 6.0), except site 3 (pH = 8), indicates that the Soubeira sediments may have a low buffering capacity. Therefore, a small decrease in pH may lead to remobilization of previously sediment-adsorbed heavy metals into the adjacent water column, and thereby increasing the metal bioavailability and their ecological risk (Calmano, 1988; Calmano *et al*., 1993; Kelderman and Osman 2007).

Organic matter content constitutes and important property of sediments, as it controls heavy metal mobility within the aquatic system (Violante *et al*., 2010). Because of the semi-arid climatic conditions (low rainfall and high temperatures), which reduce the input of organic matter, TOC was generally low in the sediment samples, and it ranged from 0.3 to 1.3% with the maximum values measured in sediments from sites 4, 5 and 7 (Tables 1). The sites 1, 3 and 6, with the highest contents of sand also exhibited relatively low CEC and TOC contents. The overall low CEC (5.3– 13.2 cmol$_c$/kg) suggests that kaolinite, according to McBride (1994), could be the dominant clay type in the Soubeira sediments. With little or no permanent negative charges, heavy metal adsorption on kaolinite is pH-dependent (McBride, 1994). Hence, a small variation in pH will result in adsorption/desorption of heavy metals onto the Soubeira reservoir sediments. It can be reasonably concluded that pH is unlikely to play an important role in the heavy metal immobilization in the Soubeira sediments.

Table 1. Physico-chemical parameters and potentially toxic heavy metal concentrations in seven surface sediment samples collected in the Soubeira reservoir

Parameter	Unit	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6	Site-7
pH$_{H2O}$	-	6.0	5.5	8.8	5.4	5.5	5.8	5.4
TOC	%	0.5	0.8	0.3	1.3	1.1	0.5	1.1
CEC	cmol$_c$/kg	8.5	12.1	7.3	10.8	11.6	5.3	13.2
Clay	%	39.2	47.1	33.3	47.1	47.1	33.3	54.9
Silt	%	31.4	39.2	27.5	39.2	43.1	37.3	33.3
Sand	%	29.4	13.7	39.2	13.7	9.8	29.4	11.8
Texture[a]		ClLm	Cl	ClLm	Cl	Lm	ClLm	Cl
Fe	mg/kg	22195	21192	22138	21659	24089	14620	29024
As	mg/kg	12.4	10.1	11.0	11.3	16.6	10.9	12.1
Cd	mg/kg	0.9	0.9	1.0	0.9	1.0	1.1	0.9
Co	mg/kg	13.2	12.4	11.5	12.6	12.7	8.6	17.7
Cr	mg/kg	63.2	70.6	71.8	72.4	76.6	54.2	68.8
Cu	mg/kg	33.1	41.5	26.8	37.5	44.3	27.6	52.6
Hg	mg/kg	2.4	2.6	1.4	1.5	4.9	4.8	2.8
Mn	mg/kg	508.5	542.7	522.9	629.7	539.6	517.2	648.4
Mo	mg/kg	3.0	3.4	2.5	2.6	2.9	3.2	3.1
Pb	mg/kg	17.4	21.8	13.5	13.3	12.7	16.4	22.6
Zn	mg/kg	44.1	50.1	92.7	69.3	60.6	100.2	80.3

[a] ClLm: clay loam; Cl: Clay; Lm: loam

Table 2. Summary statistics of physico-chemical parameters and eleven potentially toxic heavy metals in sediment samples collected in the Soubeira reservoir

Parameter	Unit	N	Min.	Max.	Average	Median	SD[a]	CV (%)[b]	Skewness
pH$_{H2O}$		7	5.4	8.8	6.1	5.5	1.2	20.1	**2.7**
TOC	%	7	0.3	1.3	0.8	0.8	0.38	47.8	-0.1
CEC	cmol$_c$/kg	7	5.3	13.2	9.2	10.7	2.9	29.0	-1.0
Clay	%	7	33.3	54.9	43.1	47.1	8.09	18.7	-0.1
Silt	%	7	27.5	43.1	35.9	37.3	5.40	15.0	-0.3
Sand	%	7	9.8	39.2	21.0	13.7	11.47	54.6	0.7
Fe	mg/kg	7	14620	29024	22131	22138	4259	19.0	-0.3
As	mg/kg	7	10.1	17	12.1	11.3	2.15	17.9	1.9
Cd	mg/kg	7	0.9	1.0	0.9	0.9	0.07	7.4	1.2
Co	mg/kg	7	8.6	18	12.7	12.6	2.69	21.2	0.7
Cr	mg/kg	7	54.2	77.0	68.2	70.6	7.4	10.8	1.6
Cu	mg/kg	7	26.8	53.0	37.6	37.5	9.3	24.8	0.4
Hg	mg/kg	7	1.4	5.0	2.9	2.6	1.44	49.2	0.7
Mn	mg/kg	7	508	648	558	539	57	10.1	1.1
Mo	mg/kg	7	2.5	3.0	2.9	3.0	0.32	10.8	-0.4
Pb	mg/kg	7	12.7	23	16.8	16.4	4.05	24.1	0.6
Zn	mg/kg	7	44.1	100	71.1	69.3	21.13	29.7	0.1

[a] SD: standard deviation; [b] CV: coefficient of variance (CV = (SD/average)*100)

3.2 Spatial Distribution Patterns of Heavy Metals

The concentrations of heavy metals in the Soubeira reservoir decreased in the following sequence: Fe> Mn> Cr> Zn> Cu> Pb> As ~ Co > Hg ~ Mo> Cd. The relative high Fe concentrations observed in the present samples reflect the presence of ferruginous nodules in the sediments. Thus, the high concentrations of Mn and Fe could be due to erosion of the parent rock and its subsequent transport into the reservoir. With skewness values less than 2, all heavy metals were normally distributed. The total concentrations of the heavy metals in the sediment samples followed the order of site-7> site-5> site-3> site-1> site-2> site-1 > site-6 (Fig. 2). The average concentrations of As, Hg and Cr in the sediments exceeded the average world's soil concentrations (Kabata-Pendias, 2011).

Spatial distribution maps of heavy metals in the sediments were produced using PAST3 software (Hammer *et al.*, 2001). After normality test and semivariogram modeling, an ordinary kriging interpolation method was used to construct spatial distribution maps of individual heavy metals (Fig. 3). Patches of maximum concentrations of Co, Mn, Cu, Hg, Fe, Pb and Zn were found around the reservoir inlet (Sites 6 and 7). On the contrary, As spread from site 5 to sites 4 and 7, whereas Cd was concentrated around site 6. Because of their high affinity for fine-grained particles, the maximum concentrations of Cr and Pb were observed in sites (2, 5 and 3) with the highest clay contents. The spatial distribution of Mo showed a homogenous pattern across the reservoir with the highest concentrations around site 2.
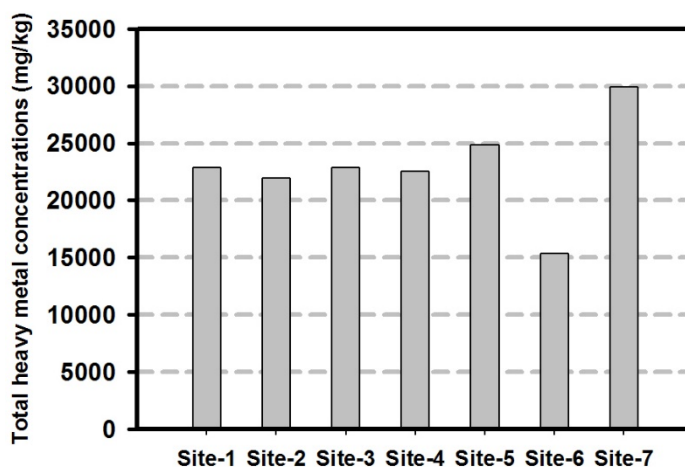

Figure 2. Total concentrations of 11 heavy metals (Fe, As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Pb and Zn) in the Soubeira reservoir sediments
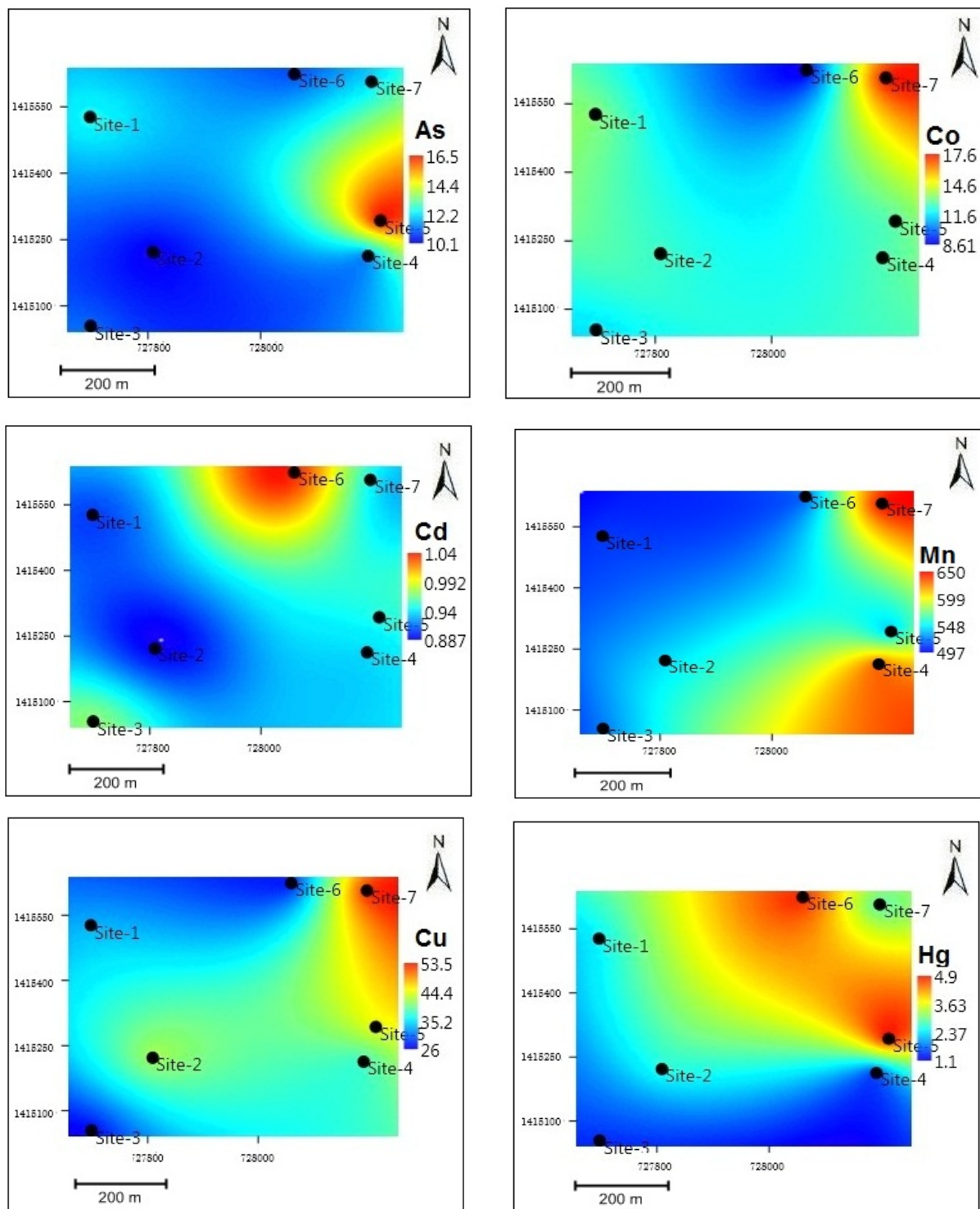
Figure 3. Spatial distribution patterns of As, Co, Cd, Mn, Cr, Cu, Hg, Pb, Mo and Zn in the sediment samples from the Soubeira reservoir
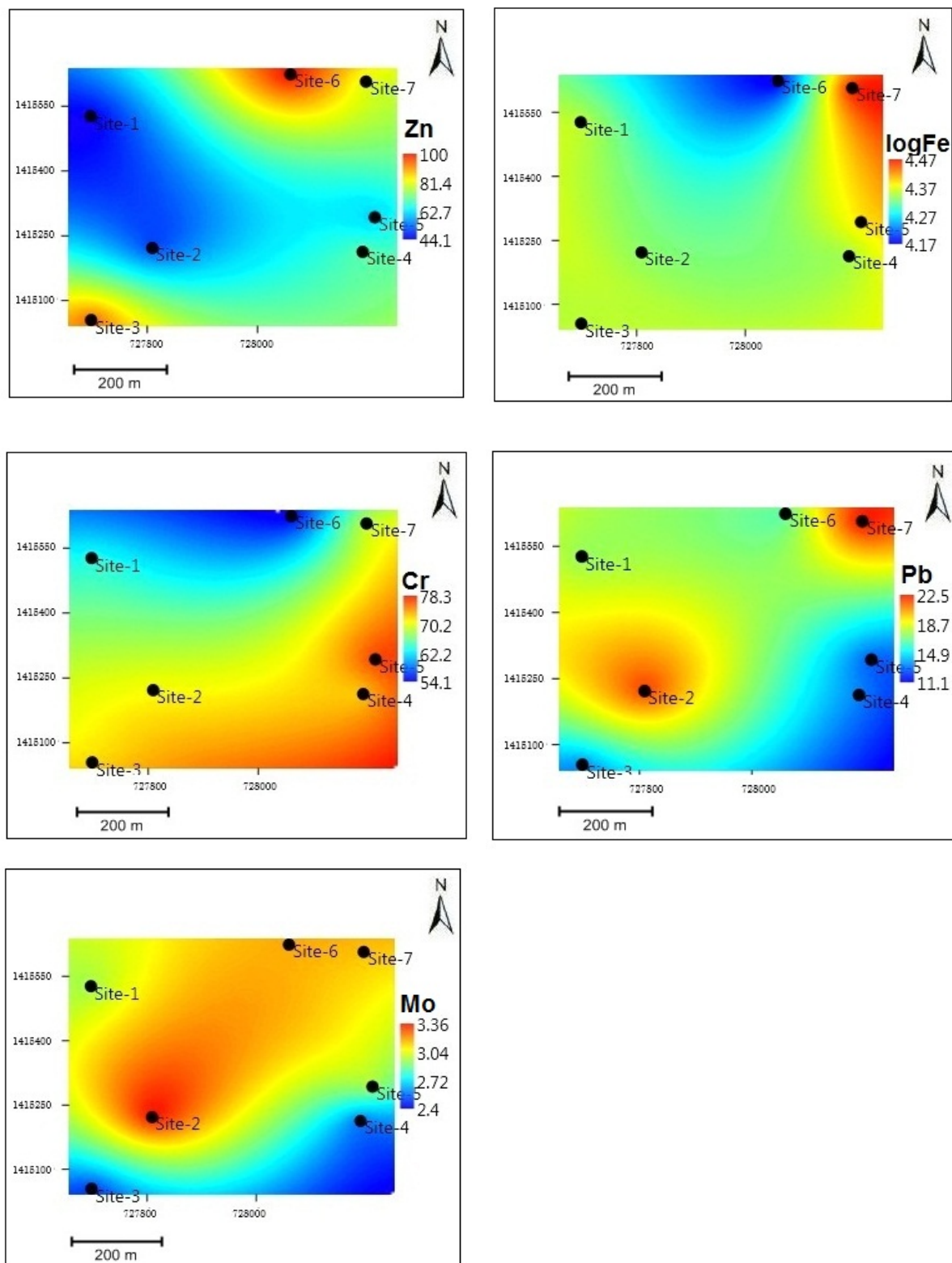
Figure 3. continued

3.3 Potential Sources of Heavy Metals

The concentrations and distribution of the investigated heavy metals can have both geogenic and anthropogenic sources. In order to assess the relationships between the metals and physico-chemical parameters (i.e., variables) and to identify their potential sources and loading pathways into the reservoir, Pearson's correlation matrix was used. Thus, a significant correlation between two variables indicates that they have common sources, mutual dependence or identical behavior during transport and resuspension in the aquatic environment (Suresh *et al*., 2011).

As expected, strong positive correlations (p <0.05) were observed between clay, TOC and CEC, suggesting that clay and TOC contributed to CEC (Table 3). Negative correlations between pH and Cr (r = -0.61), Mo (r = -0.59) and, to a lesser extent, Mn (-0.44) are consistent with the high solubility of these metals under low pH conditions. Cadmium, Cr, Cu, Co and Mn exhibited strong correlations with both clay and CEC, implying a strong affinity of these divalent cations for negatively charged aluminosilicate minerals (Aguilar et al., 2012). As a result, clay constitutes an important factor for these metals' immobility in the Soubeira reservoir. Significant relationships were also observed between TOC and Mn (r = 0.75) and TOC and Cr (r = 0.77), suggesting that TOC was a scavenger of Mn and Cr in the sediments. Because of noticeable significant positive relationships between Cr and Cd (r = 0.83), Cu and Cd (r = 0.95), it can be therefore assumed that these metals were mainly originated from common anthropogenic sources and carried by fine-grained particles into the reservoir. High Cu and Cd concentrations in sediments have been attributed to wastewater discharges and agricultural runoff (González *et al*., 2006; Aguilar *et al*., 2012; Zeng and Wu, 2013). In the Soubeira reservoir drainage basin, agriculture is the main economic activity, which generates large quantities of Wastes through the use of inorganic fertilizers. These wastes generally contain large amounts of Cd and other heavy metals.

Table 3. Pearson's correlation matrix of the Soubeira reservoir sediment samples

Variable	pH	CEC	TOC	Clay	Fe	As	Cd	Co	Cr	Cu	Hg	Mn	Mo	Pb	Zn
pH	1.00														
CEC	-0.50	1.00													
TOC	-0.72	**0.75**	1.00												
Clay	**-0.64**	**0.96**	**0.83**	1.00											
Fe	-0.21	0.28	0.42	0.26	1.00										
As	0.29	**-0.75**	-0.34	-0.64	-0.05	1.00									
Cd	-0.25	**0.79**	0.48	**0.82**	0.21	-0.65	1.00								
Co	0.10	**0.69**	0.50	0.52	0.43	-0.53	0.44	1.00							
Cr	-0.61	**0.93**	**0.77**	**0.97**	0.37	-0.56	**0.83**	0.48	1.00						
Cu	-0.08	**0.79**	0.45	**0.76**	0.37	-0.61	**0.95**	**0.64**	**0.79**	1.00					
Hg	-0.44	-0.12	0.14	-0.03	0.54	0.45	-0.28	-0.31	0.13	-0.27	1.00				
Mn	-0.41	**0.66**	**0.75**	**0.78**	-0.05	-0.28	**0.69**	0.34	**0.68**	**0.60**	-0.29	1.00			
Mo	-0.59	0.25	0.05	0.30	-0.10	-0.16	0.09	-0.37	0.40	-0.07	**0.53**	-0.09	1.00		
Pb	-0.37	0.43	0.005	0.47	-0.42	-0.42	**0.51**	-0.23	**0.51**	0.31	-0.05	0.27	0.77	1.00	
Zn	0.41	-0.51	-0.27	-0.40	-0.26	**0.86**	-0.31	-0.36	-0.35	-0.29	0.13	0.08	-0.24	-0.20	1.00

Correlation coefficients in bolds are significant at p-value < 0.05

The high correlation between As and Zn (r = 0.86) suggests that the abundance of these two metals in the Soubeira reservoir was controlled by similar geochemical processes. Significant negative correlations between CEC and As (r = -0.75) and Zn (r = -0.51) indicates that a decrease in basic cations in sediments (i.e., pH) will enhance As and Zn adsorption. However, the negative relationships between clay and As and Zn, implies that the physico-chemical conditions of the reservoir do not favor As and Zn retention and accumulation by the sediments. Regardless to the total concentrations, As and Zn are likely to be highly mobile and bioavailable within the reservoir. The range of Mo abundance in the present sediment samples is similar to those found in the world's soils, and thus it can be concluded that Mo is primarily derived from a geogenic source. The significant

positive correlation between Mo and Pb (r = 0.77), implies that Pb is also mainly of a natural source. Iron exhibited weaker relationships with other heavy metals suggesting that Fe abundance in the sediments were not controlled by a single factor. That is, Fe may be controlled by a combination of geochemical phases as well as by the regional ferruginous soil signatures. The low CV (19%) of Fe indicates the homogenous distribution of this metal, and thereby reflects its intrinsic nature within the reservoir. In contrast, Hg had the highest CV (49.2%) among the investigated heavy metals with only a moderate correlation with Fe (r = 0.54). Thus, it can be suggested that a relative high Hg concentrations were anthropogenically driven. Artisanal gold mining in the area (~1.5 km from the reservoir) could be the primarily source of Hg loadings into the reservoir. In addition to destruction of soil structure and increase in erosion rate, artisanal mining uses metallic mercury (Hg^0) to extract gold from crude ore. This activity releases large amounts of mine wastes enriched with toxic heavy metals (e.g., Hg and As), which are poorly managed and end up in the reservoir through rivers and streams. The moderate correlation between Hg and As (r = 0.45) can be explained by the fact that Hg^0 is manually added to sediments through Hg-amalgamation, whereas As is present in geological materials and dispersed into the reservoir through mining activities. As a result, the two mining-derived metals may not necessary behave in the same way in the sediments (Donkor *et al*., 2005).

3.4 Potential Ecological Risk and Adverse Effect Assessment

In the absence of toxicity study data, PERI that takes into account both total and toxic-response factors can be used to identify which heavy metals and aquatic systems need to be given a special attention (Håkanson, 1980). Contrary to single geochemical indices (e.g., geoaccumultion index and enrichment factor), PERI simultaneously evaluates the combined effects of several pollutants. Therefore, PERI was used in this study to assess the potential ecological risk of seven potentially harmful heavy metals (As, Cd, Cr, Cu, Hg, Pb and Zn) as follows:

$$C_f^i = \frac{C_i}{C_n^i} \tag{1}$$

$$E_r^i = T_r^i x C_f^i \tag{2}$$

$$RI = \Sigma E_r^i \tag{3}$$

Where C_f^i is the pollution factor of a metal i; C_i is the measured concentration of the metal i in the sediment samples; C_n^i represents the pre-industrial reference concentration of the metal in sediments. In the present study, the pre-industrial concentrations for As, Cd, Cr, Cu, Hg, Pb and Zn are 15, 0.5, 60, 30, 0.2, 25 and 80 mg/kg, respectively (Hilton *et al*., 1985). E_r^i is the potential risk of individual metals and T_r^i is the biological toxic-response factor for a metal that accounts for the toxic and sensitivity requirements taken as As = 10, Cd = 30, Cr = 2, Cu = 30, Hg = 40, Pb = 5 and Zn = 1 (Håkanson, 1980; Hilton *et al*., 1985; Wang *et al*., 2011) and RI is the sum of potential risk of the individual metals. Håkanson defined five categories for RI and four categories for potential ecological risk (Table 4).

Table 4. Ecological risk indices and corresponding risk factor for individual metals (E_r^i) and potential ecological risk index for the environment (RI) as suggested by Håkanson (1980)

E_r^i values	Grade of ecological risk for single metal	RI values	Grade of potential ecological risk for the environment
$E_r^i < 40$	low	RI < 95	low
$40 \leq E_r^i < 80$	moderate	$95 \leq RI < 190$	moderate
$80 \leq E_r^i < 160$	Considerable	$190 \leq RI < 380$	Considerable
$160 \leq E_r^i \leq 360$	High		
$E_r^i \geq 320$	very high	$RI \geq 380$	very high

Mercury had the highest E_r^i values (average = 585 ± 288) followed by Cd (56 ± 4.2), indicating high and moderate ecological risk of Hg and Cd, respectively (Table 5). Other heavy metals (As, Cu, Cr, Pb and Zn) had E_r^i less than 10, implying their low potential ecological risk. Based on the calculated RI (663 ± 291), the

Soubeira reservoir exhibited very high potential ecological risk. The inlet area (sites 5, 6 and 7), with high E_r^i and RI, are considered as hotspots of Hg and Cd pollution. In overall, PERI indicates possible toxicity of benthic organisms of the Soubeira reservoir. According to E_r^i and PERI, sites 5, 6 and 7, with the highest indices, need particular attention within the reservoir.

Table 5. Potential ecological risk indices of individual heavy metals (E_r^i) and potential ecological risk indices of the sites (RI)

Site	E_r^i							RI
	As	Cd	Cr	Cu	Hg	Pb	Zn	
Site-1	8.3	53.4	2.1	5.5	484	3.5	0.6	557
Site-2	6.7	52.2	2.4	6.9	514	4.4	0.6	587
Site-3	7.4	59.4	2.4	4.5	278	2.7	1.2	355
Site-4	7.6	55.8	2.4	6.2	302	2.7	0.9	378
Site-5	11.1	57.0	2.6	7.4	988	2.5	0.8	1069
Site-6	7.2	64.8	1.8	4.6	966	3.3	1.3	1049
Site-7	8.1	55.2	2.3	8.8	564	4.5	1.0	644
Min.	6.7	52.2	1.8	4.5	278	2.5	0.6	355
Max.	11.1	64.8	2.6	8.8	988	4.5	1.3	1069
Average	8.0	56.8	2.3	6.3	585	3.4	0.9	663
SD	1.4	4.2	0.2	1.6	288	0.8	0.3	291
CV (%)	17.9	7.4	10.8	24.8	49	24.1	29.7	44
PER grade	low	moderate	low	low	very high	low	low	very high

The extents of the adverse effects (AEI) of the seven heavy metals on the benthic biota were assessed by comparing total concentrations of individual heavy metals to their threshold effect levels (Munñoz-Barboza *et al*., 2012; Baraud *et al*., 2017) as follows:

$$AEI = \frac{[M_i]}{TEL} \tag{4}$$

Where $[M_i]$ is the concentration of the heavy metal i; TEL is the Threshold Effect Level of the metal i, a minimum concentration below which adverse biological effects are expected to occur rarely. The TEL values used in this study are: 7.2, 0.68, 52.8, 18.7, 0.174, 30.2 and 124 mg/kg for As, Cd, Cr, Cu, Hg, Pb and Zn, respectively (CCME, 2001). According to Eq. 4, if the AEI is less than 1, the concentration of a metal is not high enough to cause adverse effects to the benthic organisms. In contrast, an AEI value greater than 1, suggests that the metal could cause adverse biological effects. Except Pb and Zn, the heavy metal concentrations in the Soubeira sediment samples exceeded the TEL in the following decreasing order: Hg > Cu > As > Cd > Cr > Pb ~ Zn). With the average AEI value of 28.4±16.8, Hg is the most likely to induce negative biological effects followed by Cu, Cd and Cr (Table 6). In accordance with RI, AEI values showed that the Soubeira reservoir was highly polluted, and that it needs particular remediation efforts. Furthermore, the two assessment techniques identified Hg as the biggest pollutant in the reservoir. Likewise, the low RI and AEI values of Pb and Zn imply that the concentrations of these two metals do not pose serious threat to benthic ecosystem. However, the difference between E_r^i and AEI values is reflected on the results of As, Cd and, to a lesser degree, Cr. Thus, potential ecological risk indices showed that Cd had moderate effects and low effects for As and Cr, whereas AEI values suggested adverse biological effects for all metals except Pb and Zn. Therefore, AEI values are more stringent and conservative for monitoring heavy metal pollution of the reservoir than these of potential ecological risk index for individual metals (i.e., E_r^i).

Table 6. Adverse Effect indices of seven potentially harmful heavy metals in the Soubeira reservoir sediment samples

Site	As	Cd	Cr	Cu	Hg	Pb	Zn
Site-1	**1.7**	**1.3**	**1.2**	**1.8**	**13.9**	0.6	0.4
Site-2	**1.4**	**1.3**	**1.3**	**2.2**	**14.8**	0.7	0.4
Site-3	**1.5**	**1.5**	**1.4**	**1.4**	**8.0**	0.4	0.7
Site-4	**1.6**	**1.4**	**1.4**	**2.0**	**8.7**	0.4	0.6
Site-5	**2.3**	**1.4**	**1.5**	**2.4**	**28.4**	0.4	0.5
Site-6	**1.5**	**1.6**	<u>1.0</u>	**1.5**	**27.8**	0.5	0.8
Site-7	**1.7**	**1.4**	**1.3**	**2.8**	**16.2**	0.7	0.6
Min.	1.4	1.3	1.0	1.4	8.0	0.4	0.4
Max.	2.3	1.6	1.5	2.8	28.4	0.7	0.8
Average	1.7	1.4	1.3	2.0	16.8	0.6	0.6
SD	0.3	0.1	0.1	0.5	8.3	0.1	0.2
CV (%)	17.9	7.4	10.8	24.8	49.2	24.1	29.7

4. Conclusions

The results of this study indicated that the Soubeira reservoir was not sufficiently protected against the pollution of heavy metals, and the pollution was more pronounced around to the reservoir inlet.

Correlation analyses indicated that Cd, Cu and Cr were predominately derived from agricultural and untreated wastewater sources, and their mobility within the reservoir is likely to be controlled by clay minerals. Artisanal gold mining appeared to be the main source of As and Hg in the reservoir, whereas Fe, Mn and Zn abundances could be attributed to geogenic sources. Both RI and AEI showed that heavy metal pollution occurred in the Soubeira reservoir sediments. Mercury appeared to be the only metal posing serious ecological risk to sediment-dwelling organisms. According to AEI values, Hg, As, Cd, Cu and Cr are predicted to produce adverse biological effects. The study demonstrated that the Soubeira reservoir is exposed to high loadings of potentially harmful heavy metals, and hence urgently need a sound environmental monitoring program.

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