9th EnvIMEKO Symposium of Environmental Instrumentation and Measurements
June 2-3, 2022, Le Mans, France

GEOCHEMICAL CHARACTERIZATION OF HEAVY METALS IN THE SEDIMENTS OF THE SINÚ RIVER (COLOMBIA)

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Abstract:
The presence of heavy metals in the superficial sediments of the Sinú River in Colombia was studied by analyzing soil samples taken along the course of the river at two different depths. Significant concentrations of several heavy metals were found in the samples as a function of the sample location and depth which may be related to the presence of intensive agricultural activities and mining plants in the region surrounding the sampling area. In particular, several sites showed high concentrations of nickel, cadmium and mercury, up to five times larger than the allowable safety limits.

Keywords: geochemistry; sediments; heavy metals; Sinú River

1. INTRODUCTION

Heavy metals are among the most frequent sources of soil pollution, they can create serious damage to flora, fauna and eventually to man, accumulating in organisms and ultimately causing a serious range of diseases [1]. The presence of heavy metals in soils is justified only in part by the natural mobilization of elements [2], while anthropic activities play the most significant role in increasing heavy metal concentration in soils [3].

Unregulated intensive agricultural activities and the illegal exploitation of mineral resources cause the mobilization of highly harmful heavy metals that, once accumulated in the soil and in the groundwater, represent a serious risk for the ecosystem and the entire trophic chain [4].

In this paper we analyze the concentration of several harmful heavy metals in an area of the Department of Cordóba in Colombia located along the Sinú River, between the towns of Montería and Santa Isabel. This area is characterized by intensive agricultural activities and mining plants, most of the latter run illegally and without any control, all potential sources of heavy soil pollution.

To evaluate the pollution level by heavy metals in the area we have taken samples of sediments along the banks of the river at the surface and at a depth of 50 cm, repeating the measurements in the dry and wet season of last year. The concentration of heavy metals was determined using an inductively coupled plasma mass spectrometer.

The main goal of this study was to provide a high spatial resolution analysis of soil contamination in the study area, which might be useful to managers and stakeholders in implementing policies to reduce heavy metal pollution in the soil, ensure the quality of food crops, and protect the health and well-being of the local population.

2. STUDY AREA

The Department of Córdoba is located in the north-western part of Colombia and is crossed from north to south by one of the most important Colombian rivers, the Sinú River (Rio Sinú), which is also one of the main sources of fresh water in the Córdoba department (Fig. 1). The Sinú River originates in the Paramillo mountain range in the Department of Antioquía, in north-western Colombia, but its course occurs mainly in the Department of Córdoba. The alluvial plain of the river covers a total area of 13700 km^2 and, thanks to its continuous flooding, the lands around its course are extremely fertile and are often compared to those surrounding the Nile River.

For this reason, the 16 municipalities of the Córdoba department, irrigated by the waters of the Sinu River, benefit economically thanks to the excellent development of agriculture.

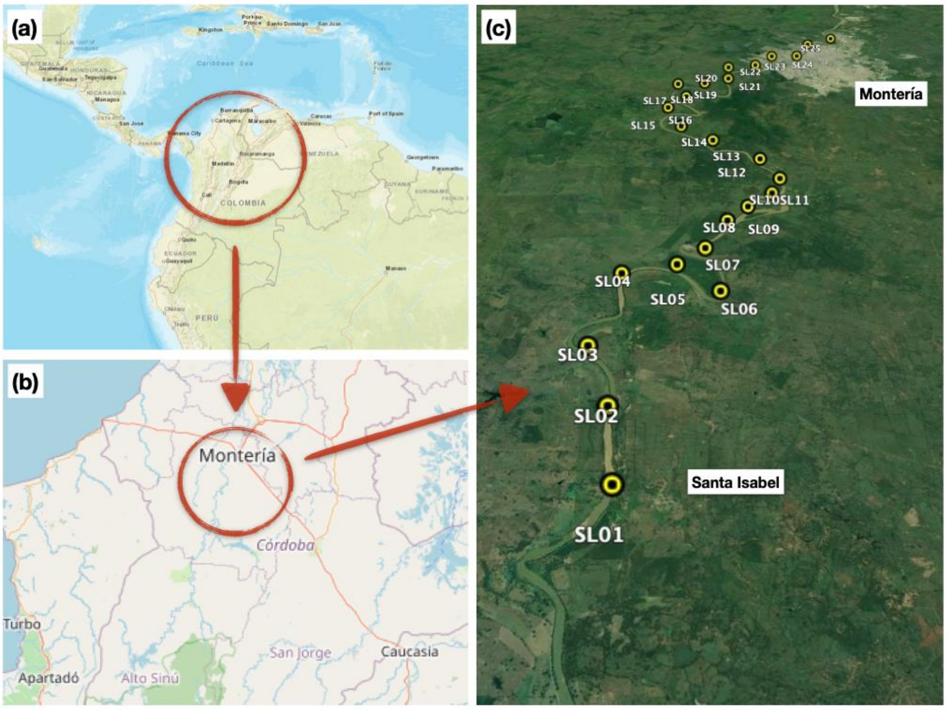

Figure 1: Study area and location of the sampling sites: (a) overall map of Colombia, (b) Córdoba department and Sinú River, (c) sampling sites along the river.

The rainfall regime of the area is basically related to the alternation of two seasons, a wet season from April to September, and a dry season from December to March. The annual precipitation varies from a minimum of 1500 mm/year in the coastal area up to 4000 mm/year and more in the southern mountainous region of the Department. The rainy days are between 50 and 100, and up to 200 in the southern end [5].

In the Department of Córdoba there are currently 106 permanent mining concessions related to extraction facilities of coal, nickel, copper, silver, gold, and platinum, for a total area of more than 124000 hectares, corresponding to 5% of the entire territory of the Department. In addition, there are 220 temporary concessions for the extraction of the same minerals. However, many illegal mining facilities can be found in the Department, and these represent the main source of heavy metal pollution, as this illegal activity generates an enormous amount of excavation residues that are dispersed into air, soil and water without any control, causing serious environment [6].

3. MATERIALS AND METHODS

Two sets of 25 sediment samples were taken in 2021 during the wet and dry seasons along the course of the Sinú River in sites between the towns of Montería and Santa Isabel. The sampling sites were spaced apart by ~0.5 km, for a total sampled length of around 12 km (Fig. 1c). The first set was composed of samples taken at the soil surface, while the other set was made up of samples taken at a depth of 0.5 m. To prevent metal contamination, no metal tools were used during sampling, storage, and transport. The samples were sealed in polyethylene bags and stored in a refrigerated container at 5°C, and then transported to the laboratory for analysis (Fig. 2).

Sediments were then homogenized and sorted using a polyethylene sieve with 60 µm mesh size. Reducing and sorting sediments to this particle size is of paramount importance because heavy metals concentrate in the silty clay fraction.

Figure 2: Sampling sediments along the Sinú River.

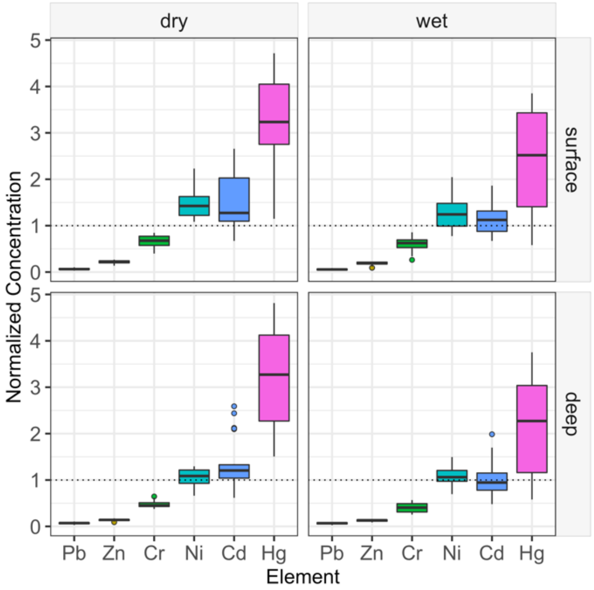

Figure 3:Distribution of concentration of heavy metals at the two sampling levels in the wet and dry seasons. The measurements are normalized to the IAEA's safety limits (dotted horizontal line) [9].

After sieving, the samples were divided into two groups, the first group was used to determine the mercury content, while the other group was used to determine the concentration of all the remaining heavy metals. In view of its high volatility, samples to be used for the determination of mercury were dried at room temperature placing them under a fume hood for 5 days [7], while the remaining samples were heated in an oven at 75°C for 4 days.

An elective method using acid attack by dissolution with aqua regia was employed for heavy metal determination [8]. After further washing with distilled water, the resulting solutions were analysed by inductively coupled plasma mass spectrometry[1].

4. RESULTS AND DISCUSSION

Table 1 shows an example of the measured concentrations at a single site for the four possible combinations of sampling level (at the surface/50 cm deep) and season (dry/wet), together with the values of the safety limits stated by the International Atomic Energy Agency (IAEA) [9]. The overall distribution of measurements in the wet and dry seasons at the two sampling levels is shown in Fig. 3, while the measurements for each location are summarized in the heatmap of Figure 4. All concentrations reported in Figures 3 and 4 are normalized to the IAEA's safety limits for each metal.

Overall, the results show that in all sampled sites the measured concentrations of Pb, Zn and Cr are always well within the allowed limits, whereas those of Ni, Cd and Hg are much higher than the safety limits (Figs. 3 and 4). Measured Ni and Cd concentration can be up to 2.5–3.0 times the maximum value allowed by IAEA, while Hg is particularly worrisome since it can reach levels that are almost 5 times the safety limits [9]. Surface samples usually show higher concentrations of heavy metals than corresponding samples taken at a depth of 50 cm (Fig. 4). The difference is stronger in the dry season, probably because the minimum amount of precipitation during the dry season reduces surface transportation and produces heavy metal accumulation zones that are not leached by rainfall and thus tend to concentrate at the surface [10]. This causes a continuous accumulation of heavy metals in areas characterized by low kinetic energy of the river, where the action of deposition of sediments prevails over erosion. During the heavy rainfall season typical of the area, soil pollutants are dispersed in the floodplains of the Sinú River and infiltrate into groundwater [11, 12, 13], causing further and more diffused harm to the neighbouring ecosystem.

Analysing the results in more detail, we note that the concentration of nickel ranged from a minimum of 21.5 mg/kg to a maximum of 72.5 mg/kg, with an average value of 48.3 mg/kg in sediments taken from the surface during the dry season and 41.7 mg/kg in sediments taken from the surface during the wet season. As for the sediments taken at 50 cm depth, the average concentration of Ni is 34.3 mg/kg in the dry season and 35.2 mg/kg in those taken during the rainy season. The largest Ni concentrations are found in the surface sediments, with a large variation between the two seasonal periods. At 50 cm below the surface the concentration of Ni is lower, with a less pronounced variability between the two seasons. In all cases, most measured Ni concentrations are above the limit for uncontaminated sediments, that for Ni is 32.5 mg/kg (Table 1).

The high concentration of Ni in these soils could be related to the presence, a few tens of kilometers from the sampling area, of the Cerro Matoso mine, which is the largest iron and nickel mine in Latin America, as well as of smaller unregulated mining plants scattered around the sampling area.

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[1] PerkinElmer NexION 5000 Multi-Quadrupole ICP Mass Spectrometer.

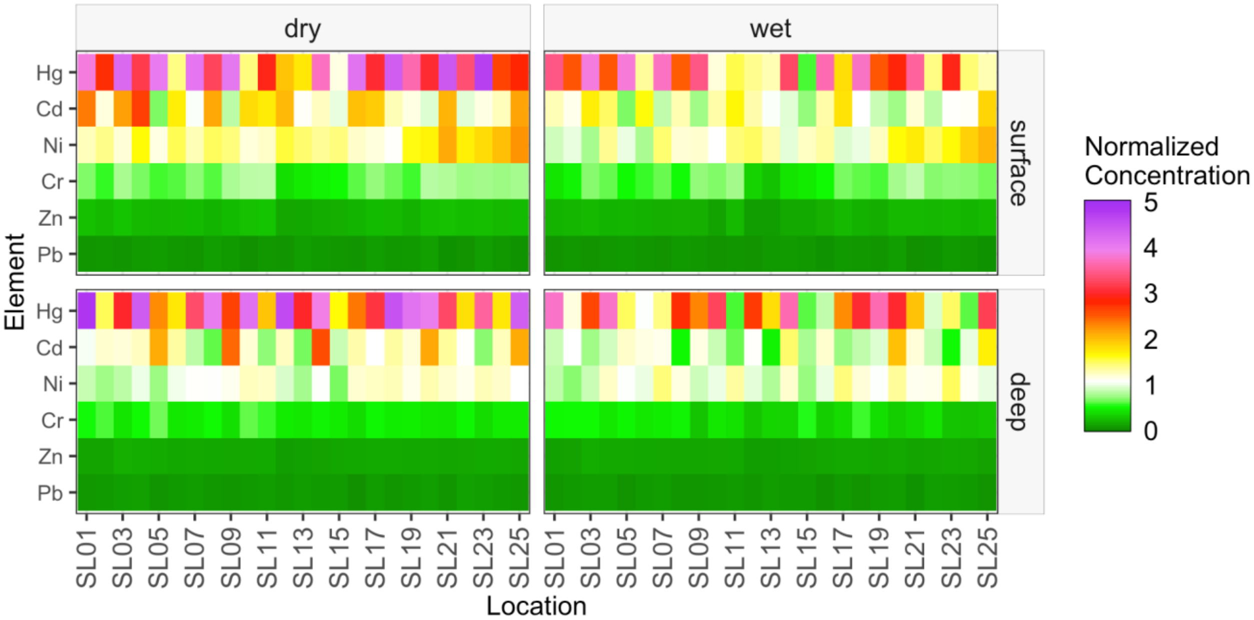

Figure 4: Heatmap showing the concentration of heavy metals at the two sampling levels in the wet and dry seasons. All the measurements are normalized to the safety limits stated by IAEA [9].

An additional possible source of Ni pollution could be related to the presence of extensive farming areas, where the use of large amounts of ultra-low-cost pesticides and fertilizers based on copper and iron sulfates, which have been shown to contain relatively large amounts of heavy metals among which Ni [14], leads to a further increase of Ni concentration in the sampled soils.

As for Cd, the highest cadmium content is 1.94 mg/kg, well above the allowed limit of 0.73 mg/kg, found in the samples taken at the surface in the dry season, while the lowest concentration of 0.35 mg/kg is recorded in the wet season 50 cm below the surface. The average concentration of Cd varies between 0.87 mg/kg and 1.12 mg/kg for the surface samples in the wet and dry seasons, respectively, while for samples taken at 50 cm, it varies between 0.73 mg/kg and 0.96 mg/kg in the wet and dry seasons, respectively. Most measured values are in most cases two or three times larger than the allowed values.

Such high concentrations of Cd can be attributed to different causes such as mining exploitation, atmospheric deposition, use of phosphate fertilizers and residual polluted sludge. Cd is characterized by its high mobility in aquatic systems where, transformed into sulfide, it may solubilize easily and remain trapped in river sediments [15]. In our sediments the measured pH ranged from 5.7 to 6.8, contributing to the mobilization of this element [16]. High concentrations of Cd dispersed in the environment are dangerous to organisms, in humans it can produce high respiratory damage, intake of Cd-contaminated water and food induces severe gastrointestinal effects [17].

Mercury contamination constitutes one of the main environmental problems due to its high toxicity and the ability by living beings to increase the concentration of this metal in their tissues, this process involves the entire trophic chain reaching up to humans [18].

Table 1: Example of measured heavy metal concentrations at one of the sampling sites as a function of sampling level (at the surface/50 cm depth) and season (dry/wet). The last line in bold reports the safety concentration limits for each metal [9]. The full dataset consists of 25 similar blocks, one for each sampling location. All reported values are in mg/kg.

Location	Level	Season	Cd	Cr	Hg	Ni	Pb	Zn
…	…	…	…	…	…	…	…	…
SL05	surface	dry	0.49	48.2	3.26	37.4	6.26	58.4
SL05	surface	wet	0.49	44.4	3.10	32.2	5.38	55.9
SL05	deep	dry	1.53	54.2	1.84	24.2	3.60	42.9
SL05	deep	wet	0.89	41.2	1.21	34.4	3.11	39.8
…	…	…	…	…	…	…	…	…
Safety limits			**0.73**	**84.0**	**0.81**	**32.5**	**74.8**	**279.0**

The total Hg concentration in the sampled sediments ranges from 0.47 to 3.82 at the surface and in the rainy and dry season, respectively, with very similar extreme values at 50 cm, where again the lower concentrations of Hg are measured in the rainy season and the higher concentrations in the dry season. More specifically, the Hg concentration at the surface ranges from 0.47 mg/kg to 3.12 mg/kg in the wet season and from 0.93 to 3.82 mg/kg in the dry season, with an average of 1.99 and 2.59 mg/kg in the wet and dry seasons, respectively.

Measurements at a depth of 50 cm below the surface show a very similar variability as they range from 0.47 mg/kg to 3.04 mg/kg in the wet season and from 1.22 to 3.90 mg/kg in the dry season, with an average of 1.75 and 2.58 mg/kg, respectively. The largest measured Hg concentrations are thus up to 5 times higher than the limit of 0.81 mg/kg. These fluctuations can be attributed to preferential deposition phenomena due to runoff and surface leaching processes by the frequent and intense rainfall.

The presence of such high concentrations of Hg is probably attributable to an anthropic contribution. In fact, the exponential growth of alluvial gold extraction plants in the neighbouring area, many of which are illegal, has had an extremely high environmental impact over time since the local population, indiscriminately uses high amounts of Hg in the process of gold amalgamation [19, 20].

The other heavy metals found in the sediments studied, namely Cr, Pb and Zn, always show concentration values well below the permissible limits [5]. Their presence is attributable to the numerous livestock farms and intensive crops present in the study area, all activities conducted with a high use of ultra-low-cost pesticides and fertilizers which are also characterized by high contents of Pb and Zn [14, 21].

5. SUMMARY

This study examined six heavy metals present in the sediments of the Sinú River, between the towns of Montería and Santa Isabel in the Cordóba Department, Colombia.

The results of the analysis show an anomalous concentration of Ni, Cd and above all Hg both in the surface samples and in samples taken at depth, while the concentration of Pb, Zn and Cr is always well below the safety limits. Surface samples show higher concentrations of metals than samples taken at 50 cm depth, in particular in the dry season, probably because the minimal amount of precipitation in the dry season produces zones of accumulation of heavy metals at the surface of the soil. During the following rainfall season the soil pollutants are dispersed in the floodplains of the Sinú River and infiltrate into groundwater, causing further harm to the neighbouring ecosystem.

Cd and Hg are a serious environmental and health risk, and they should be carefully and continuously monitored. The anomalous presence of these two heavy metals is probably attributable to anthropogenic actions connected to mining activities, while the anomalous presence of Ni could be related to the release from natural sources and intensive agricultural activities.

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