Abstract

Heavy metals currently represent a very important source of contamination, since their intake by humans and animals in many cases is the cause of serious damage to health. Soil, air, water and food are the most common pathways for heavy metals to reach organisms. Since soil is their origin, in this study we focus on soil analysis to determine the concentration of Cr, Ni, Cu, Zn, As, Hg, Cd and Pb, which are the most toxic metals. The study site is the agricultural soils of the northwestern region of the Dominican Republic where bananas and rice are the main crops grown. Chromium levels in most samples exceeded the NOAA-USEPA Probable Effects Level (PEL). Other heavy metals were within the acceptable ranges for healthy soil, according to the Food and Agriculture Organization (FAO).

Keywords

Heavy Metals, Soil Contamination, Agricultural Soils

1. Introduction

The northwestern region of the Dominican Republic economically dedicated to agricultural activities (Londoño-Franco et al., 2016) represents a great food source for the Dominican people and the border towns (Butterlini, 1955). The presence of heavy metals in agricultural soils (Romic & Romic, 2003) of heavy metals such as Cr, Ni, Cu, Zn, As, Hg, Cd and Pb could represent a health risk (Al-Taani et al., 2021). In the earth’s crust, all these metals are found in small quantities in the form of traces, except in mining areas (Rudnick & Gaos, 2003). Heavy metals are a group of chemical whose density is greater 7.0 gr·cm⁻³. Many heavy metals are also called trace element, because their concentration does not
reach 0.1% in rocks and soils (Duffus, 2002). The cultivation of bananas and rice covers almost all the areas of agricultural soils in the sedimentary plains of the Yaque of the Norte River (Fuentes-Hernández et al., 2019), which are products of erosion (Fonseca et al., 2011) of the northern slope of the central mountain range and the southern slope of the northern mountain range during the recent Quaternary and today. The texture of the soils is sand, silt and clay dragged by the Yaque of the Norte and its tributaries Bao, Guanajuma, Jánico, Amina, Mao and Jicome. This is the reason why the composition of these soils is basically the mineralogical composition of both mountain ranges, which varies along the banks of the Yaque of the Norte River and its tributaries. The geological formations of Tireo, Loma Caribe, Loma la Peguera (McDonald et al., 2010; Vyzmalová et al., 2012) and Guanajuma mainly structured by peridotites (Marchesi et al., 2016) and composed of harzburgite minerals, lherzolites, tholeiitic, komatiitic and gabbro (IGME-BRGM-Inipsa, 2010) are made up of chromium spinel (Lewis et al., 2006) and nickel (Aiglsperger et al., 2015), which contribute to the presence of these trace metals in the agricultural soils of the northwestern region of the Dominican Republic. Nickel and chromium are elements that bioaccumulate (Barea-Sepúlveda et al., 2022) in the husks of rice (Aqeel Kamran et al., 2016; Raju et al., 2016). So, the frequent intake of brown rice can represent a risk to health if it is grown in soils with a high content of these metals, which are bioavailable (Shahbaz et al., 2018).

Heavy metals can accumulate in agricultural soils, posing a health risk for soil organisms and humans, its negative effects depending on the concentrations of the metals and specific properties of the soil (Gjoka et al., 2010). Therefore, the presence of trace metals in soils is of great importance (Xuan et al., 2017). However, in appropriate concentrations, crops use them as nutrients to synthesize fruits which constitute the most important source of nutrition. Such is the case of Chromium that helps metabolize sugars, but in excess, especially Cr⁶⁺, is very harmful to health (Turner & Lewis, 2018). Other elements that in appropriate concentrations are good for nutrition are Ni and Zn, and in the same way could be fatal in high concentrations (Prieto-Méndez et al., 2009). High concentrations of heavy metals can inhibit the development of crops and their fruits when absorbed by the roots (Pérez-Olvera et al., 2008). Leachate from these soils can contaminate surface and underground aquifers (Bravo-Covarrubias et al., 2020), and make the waters toxic to plants, animals and humans, through the food chain (Martínez-Alva et al., 2020). In addition, crops that bioaccumulate (Mesa-Pérez et al., 2015) these metals would become a danger to the health of those who consume them (Vinodhini et al., 2008).

**Study Zone**

The study site is the soils of several towns that are dedicated to the cultivation of rice and bananas, especially in the provinces of Mao and Montecristi and the adjoining town of Navarrete, belonging to the province of Santiago, approximate area of 450 km² (Figure 1).
2. Materials and Methods

2.1. Sampling

Soil sampling was carried out by plots, referencing the sampling site with GPS. These points were taken randomly depending on the access facilities and the distribution of the crops. A plastic shovel was used to collect approximately 1.0 kg of soil, both at the surface level and at a depth of 30 cm. To take the sample at a depth of 30 centimeters, a hole was made with a stainless steel tool. Then they were packed in plastic bags to be transported.

2.2. Drying

The samples were dried, first at room temperature, and then to remove all humidity in an oven at a temperature between 30 - 100 degrees Celsius; for slow drying and to decrease the possibility that some elements will evaporate along with the water.

2.3. Sample Preparation

After drying, the samples were crushed in a mortar and then sieved at 75 micro-
ns. This sieve mesh was chosen because the texture of the soils in the region is composed of a significant amount of sand. About 3 g were taken, measured on a 0.1 mg precision balance. With this mass of soil, using a press (15 tons), a tablet with a diameter of 2.0 cm was made.

2.4. Methodology and Analysis

The tablet was taken and placed in an x-ray fluorescence spectrometer (Roca & Bayon, 1981; Fernández-Ruiz, 2009) brand Skyray EDX36000B. The excitation voltage of the X-ray emitting source was 40 kV and 600 μA (Marguí et al., 2011). The spectrometer was previously calibrated using standard sediment and soil samples certified to ISO/IEC 17025 and ISO Guide 34 by Sigma-Aldrich (Trace-Cert; NIST, IAEA) and BAM-CRM (SRM1944, SRM2707, SRM1646a and IAEA356). The quality of the heavy metal determinations was verified using the certified materials BCR277, SRM2710a, SRM2711a. The values of the NOAA-SQuiRTs and USEPA guide, which are for marine sediments, fresh waters and soils, coincide with the Canadian agricultural sediments and soils guide (CCME, 2014). For this reason we compare the Threshold Effects Levels (TEL) of a metal with the limits of the guide for a healthy soil in relation to this metal, they coincide in both guides. They were also compared to FAO data, for common agricultural soil concentrations (Table 1).

3. Results

Table 1. Concentration of heavy metals in agricultural soils expressed in mg.kg⁻¹ (Source: Freedman, 2018).

| Elem | Granite | Basalt | Shale | Limestone | Sandstone | Soils |
|------|---------|--------|-------|-----------|-----------|-------|
| Cd   | 0.09    | 0.13   | 0.22  | 0.03      | 0.05      | 0.35  |
| Co   | 1       | 35     | 19    | 0.1       | 0.3       | 8     |
| Cr   | 4       | 90     | 90    | 11        | 35        | 70    |
| Cu   | 13      | 90     | 39    | 5.5       | 30        | 30    |
| Ni   | 0.5     | 150    | 68    | 7         | 9         | 50    |
| Pb   | 24      | 3      | 23    | 5.7       | 10        | 35    |
| Zn   | 52      | 100    | 120   | 20        | 30        | 90    |

Table 2. Maximum, minimum and average levels of Heavy Metals in Rice cultivation areas in the municipality of Esperanza, Mao Province; Castañuela, Montecristi province. Threshold Effects Levels (TEL) and Probable Effects Levels (PEL), NOAA-USEPA.

| Element | Sed | Soil | TEL | PEL | Esperanza (54) | Castañuela (20) |
|---------|-----|------|-----|-----|----------------|-----------------|
|         | (µg/g) |       | Min | Max | Mean | Min | Max | Mean |
| Cr      | 37.3 | 64   | 52.30 | 160.0 | 430.2 | 268.5 | 278.9 | 628.2 | 378.5 |
| Ni      | 17.0 | 45   | 15.90 | 42.8 | 111.2 | 37.4 | 20.3 | 69.8 | 40.0 |
The values of Sediment (Sed) correspond to the maximum levels in sediments and those of Soil to the maximum values in agricultural soil according to the Canadian guide (CCME, 2014).

**Figure 2.** Spatial distribution of Cr (a) and Ni (b). The green color corresponds to the places where the concentration is below the Threshold Effect Level (TEL). Towards the red they correspond to the concentrations tending to the Probable Effect Level (PEL).

**Figure 3.** Comparison of Cr concentrations (right) found in soils in the northwestern region of the DR with the Probable Effect Level (160) (NOAA-USEPA). Left, Ni concentrations compared to PEL (42.8). The scatter plot represents the mean of each measurement made at the sample points. There is no correlation between the values.

### 4. Discussion

The Cr values in the municipality of Castañuela (20 samples), Monte Cristi province were higher than in the municipality of Esperanza (54 samples) (Table 2),
Table 3. Values of trace elements in soil samples by village (sample number in parentheses).

| Element | Jicome (10) | Villa Vásquez (10) | Navarrete (7) |
|---------|-------------|-------------------|--------------|
|         | Min         | Max    | Mean   | Min     | Max   | Mean   | Min   | Max   | Mean   |
| Cr      | 122.5 µg/g  | 628.5 µg/g   | 347.5 µg/g | 161.1 µg/g | 396.3 µg/g | 288.9 µg/g | 66.7 µg/g | 386.6 µg/g | 164.5 µg/g |
| Ni      | 7.8 µg/g    | 183.7 µg/g   | 62.2 µg/g | 4.3 µg/g | 85.0 µg/g | 41.2 µg/g | 51.6 µg/g | 217.2 µg/g | 114.3 µg/g |
| Cu      | 20 µg/g     | 14.4 µg/g   | 5.4 µg/g | 2.7 µg/g | 9.0 µg/g | 5.7 µg/g | 8.5 µg/g | 68.2 µg/g | 25.2 µg/g |
| Zn      | 20.4 µg/g   | 68.9 µg/g   | 37 µg/g | 23.4 µg/g | 58.1 µg/g | 39.1 µg/g | 29.6 µg/g | 58.4 µg/g | 43.3 µg/g |
| As      | 2 µg/g      | 4.1 µg/g   | 3.1 µg/g | 2.1 µg/g | 3.5 µg/g | 2.8 µg/g | 2.1 µg/g | 3.7 µg/g | 2.9 µg/g |
| Hg      |             | 3.5 µg/g   | 3.5 µg/g | 3.5 µg/g |
| Cd      | 6.3 µg/g    | 58.7 µg/g   | 34.6 µg/g | 20.0 µg/g | 57.4 µg/g | 32.1 µg/g | 24.5 µg/g | 39.3 µg/g | 31.4 µg/g |

Valverde Mao province (Figure 2(a)), exceeding the PEL (Figure 3(a)). Ni was another element that, according to the spatial distribution (Figure 2(b)), had concentrations higher than PEL in several places (Figure 3(b)). Cd and Pb exceeded the TEL on average, but did not exceed the PEL. In both places the values of the metals were similar with little difference. All the samples taken in Cástañuela were in rice cultivation; those of Esperanza were mixed between cultivation of bananas and rice. It is noted that mercury was not found above 0.3 mg/kg, which is the quantification limit of the equipment. We compare the values of the metals in the superficial samples with the deeper ones, in some cases the superficial ones contain higher values and in other cases the deeper ones. In the case of Cd, only two samples had quantifiable concentration levels with the equipment used. Hg was not determined in any of the samples.

Table 3 shows that the average Cr exceeded the PEL in the samples from the three cultivation areas. The Ni in Jicome and Navarrete exceeded the PEL. The concentrations of the other metals were still below the TEL.

5. Conclusion

The concentrations of heavy metals were found, in most cases exceeding the Probable Effect Levels (PEL) established by USEPA and CEQGs. These heavy metal concentrations are traceable to their origin as the Yaque of the Norte River eroded the mountains to form peridotite rocks composed of spinel minerals containing Chromium and Nickel, such as harzburgites, lherzolites, tholeiites, komatiites and gabbros. Therefore, these soils can be considered free of heavy metal contamination due to human activities in the area. The high concentrations of Cr and Ni, which exceed the PEL levels, are of natural origin, a product of the geochemistry of the rocks that gave rise to the soils of the Cibao valley basin in the northwest of the Dominican Republic, not due to the anthropogenic activities.
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Conflicts of Interest
The authors declare no conflicts of interest regarding the publication of this paper.

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