Copper, Nickel, Lead, and Cadmium Concentration in Soils around Industrial Areas from Latacunga, Ecuador

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Abstract. Environmental pollution has increased in recent decades as a result of various human activities and the presence of various chemical compounds, including heavy metals. The goal of this paper is to determine the concentration and distribution of copper, nickel, lead, and cadmium in soils around industrial areas from Latacunga, Ecuador. Soil samples were obtained from 19 localities: two zones with influence from the industrial sector and two recreation areas and public access. Samples obtained were pretreated and then analyzed by flame atomic absorption spectrophotometry following USEPA 3050B and USEPA 3052 methodology. Finally, a statistical analysis belonging to a randomized complete block design, an analysis of variance (ANOVA) was applied (confidence level of 95%). The results show that the concentration of the metals analyzed decreased in the order of nickel > copper > lead. Additionally, it is shown that the concentration of nickel exceeds the limits suggested by local regulators in all study zones. On the other hand, Zone 1 and Zone 2 show copper and nickel concentrations that exceed the referenced limits.

1. Introduction
The contamination of water, air, and soil has been among the main environmental problems worldwide for decades. Some instances of said contamination come from human activities and bad practices related to the improper treatment of wastes. Pollution can be happen then, due to the presence of various waste chemical compounds in environmental media, including heavy metals, causing a threat to public health and environmental safety. Heavy metals, when found in soil, can be transferred to living organisms through the food chain [1]. Heavy metals, however, are present in the earth's crust in elemental form or as part of other chemical compounds. Their concentration vary depending on the type of soil and the activity that is carried out [2] since the natural concentration of a metal in soil derives from the bedrock that originated the soil, while the amount of metal that is incorporated into the soil will depend on the degree of resistance of the mineral that constitutes it and anthropogenic actions [2].

The presence of heavy metals in soil can become a contamination problem when concentrations become representative and even excessive. Several studies regarding the presence of heavy metals in air, water, and sediments have been proposed around the globe, however, there are few studies in Ecuador regarding this matter [3][4]. The city of Latacunga, in the Andean region of Ecuador, is the capital of the province of Cotopaxi at an altitude of approx. 2,850 meters above sea level where cold weather predominates. The area is purely volcanic, and five types of soils can be distinguished i.e. entisol, histosol, inceptisol, mollisol and untransformed volcanic remains [5]. Within the city of Latacunga, there are green areas with public access and green areas in contact with wastes generated by different kind of industries. The main objective of this paper is to analyze the
concentration of copper, nickel, lead and cadmium in soil samples from green areas with public access and green areas with influence from effluents generated by a foundry, a food (flour) industry, and a textile industry in the city of Latacunga. Finally, areas with concentrations that exceed the maximum limits established in the country are determined.

2. Methodology
The city of Latacunga is located at an altitude of approx. 2,850 meters above sea level. Weather is predominately cold and low in humidity. The geographical extension covers around 138,630 hectares with diverse soil formations throughout its territory [5]. For the development of this study, three green areas with public access and two areas with direct influence of two types of industries belonging to the city center were taken into account, as well as one area with direct influence by an industry in the rural area of the city as can be seen in Figure 1.

Figure 1. Study area in the city of Latacunga. 19 sampling points located in the city center (Zone 1, Zone 2 and Zone 3) and a rural sector (Zone 4). Basemap data © Google 2019.
2.1. Sampling
Soil samples collected for this research were obtained during February 2019. Samples were obtained from a total of 19 points, establishing 6 collection areas: three of them have direct influence from the industrial sector and three are recreational areas and are of public access. At each sampling point, the approx. amount of 200 g of surface soil was collected at a depth between 10 and 20 cm with a plastic spatula after vegetable remains were removed. Each soil sample was stored in plastic containers and covered with a cloth to prevent conductivity or oxidation of the metals present in the soil. Once the samples were collected and stored with their respective labeling, they were dried in the laboratory at room temperature for a period of 96 hours and then dried in an oven at 60°C for 72 hours [6].

2.2. Analytical procedures
The nineteen soil samples were subjected to a 38 μm plastic sieve and 6 random samples (one sample for each collection area) were subjected to a 1,000 μm sieve, totaling 25 samples for chemistry and composition determination, in order to analyze the variability related to metal concentration.

The chemical treatment for the digestion process of the samples was based on USEPA 3050B [7] and USEPA 3052 standards [8]. Briefly, each sample had to be homogenized and sieved. An amount of 0.1 g of the sample was then added to 8 ml of HNO₃, 5 ml of HCl, 1 ml of HF and 5 ml of concentrated H₂BO₃. Under operating conditions in a microwave digestion equipment (ETHOS ONE), the added acids were allowed to act to subsequently obtain a solution that was diluted with distilled water to 100 ml. Finally, the resulting solution was used for the analysis by using atomic absorption spectroscopy.

The soil samples obtained from the digestion process were analyzed by using a Perkin Elmer flame atomic absorption spectrophotometer (model Aanalyst 300). Copper, nickel, lead and cadmium were determined. The equipment was calibrated with deionized water and standard solutions of 5, 15, and 30 ppm for each element analyzed in order to prepare calibration curves.

Chemical analysis was performed using deionized water, distilled water, 65% HNO₃, 37% HCl, 40% HF, and 5% H₂BO₃. The standard solutions used were typical of the atomic absorption equipment.

Instrumental analysis was carried out using a Digestion Microwave (ETHOS ONE) and a Perkin Elmer (model Aanalyst 300) flame atomic absorption spectroscopy kit.

2.3. Statistical analysis
The concentration data were processed with statistical software package Minitab. Descriptive statistics were obtained and the analysis was performed using a randomized complete block design, with a confidence level of 95% (α = 0.05).

3. Results and discussion
Soil samples information was contrasted with the maximum permissible limits established in Ecuadorian standards, where values of 0.5 mg/Kg for cadmium, 30 mg/Kg for copper, 20 mg/Kg for nickel and 25 mg/Kg for lead are mentioned [9].

3.1. Heavy metal concentration in soil samples by zone
A comparative analysis between zones was carried out with respect to the concentration of metals, where sampling points were grouped. Zone 1 refers to samples obtained at La Cocha sector (MC1, see Fig. 1), Zone 2 refers to samples collected at Ignacio Flores Nautical Park and Illuchi River banks (MC2 and MC3), Zone 3 refers to the banks of Cutuchi River around a food industry and an aluminum foundry (MC4 and MC5), and Zone 4 refers to Saquimala River banks close to a textile industry in a rural area (MR6). Regarding the concentration of copper, nickel, lead and cadmium in the study areas, the highest copper concentrations were obtained in Zone 1. Nickel concentrations were higher in Zone 1 and Zone 3. Lead concentrations were the highest in Zone 2. Cadmium concentrations in all zones were below the minimum detection value of 0.1 mg/Kg. Metal concentrations analyzed in Zone 1 decreased in the order copper > nickel > lead. In Zone 2, they decreased in the order copper > lead > nickel. In Zone 3, they decreased in the order nickel > copper > lead. In Zone 4, it followed the order nickel > copper > lead. Concentrations of heavy metals in the study areas can be seen in Figure 2.
As shown in Table 1, concentration values for copper in Zone 1 exceed the permissible reference values, but not in the rest of the zones. With respect to nickel, it was found that all the studied areas exceed the concentration values compared to the permissible reference values, while lead concentration values exceed the permissible reference values only in Zone 2. Finally, cadmium concentration values were always below the minimum detection value of 0.1 mg/Kg.

![Figure 2. Average concentration (mg/Kg) of copper, nickel, lead and cadmium in four study areas in Latacunga, Ecuador. Zone 1 refers to La Cocha sector. Zone 2 refers to Ignacio Flores Nautical Park and the banks of the Illuchi River. Zone 3 refers to the banks of Cutuchi River close to a food industry and an aluminum founry. Zone 4 refers to the banks of Saquimala River close to a textile industry, in a rural area.](image)

**Table 1.** Heavy metal concentration values and permissible levels in the city of Latacunga

| Metal | Zone | Permissible reference (mg/Kg) | Concentration (mg/Kg) | Standard deviation |
|-------|------|-------------------------------|-----------------------|-------------------|
|       |      | Minimum                      | Maximum               | Average           |                   |
| Cu    | 1    | 29.6                          | 39.0                  | 34.07             | 4.72              |
| Ni    | 1    | 22.4                          | 29.3                  | 25.70             | 3.46              |
| Pb    | 1    | 8.5                           | 14.6                  | 11.43             | 3.06              |
| Cu    | 2    | 19.9                          | 24.6                  | 22.22             | 1.64              |
| Ni    | 2    | 13.4                          | 24.6                  | 20.00             | 4.05              |
| Pb    | 2    | 11.0                          | 32.6                  | 21.45             | 7.42              |
| Cu    | 3    | 13.2                          | 15.0                  | 14.10             | 0.76              |
| Ni    | 3    | 17.7                          | 30.0                  | 23.25             | 5.38              |
| Pb    | 3    | 8.8                           | 10.6                  | 9.60              | 0.70              |
| Cu    | 4    | 13.7                          | 14.7                  | 14.20             | 0.48              |
| Ni    | 4    | 19.4                          | 24.5                  | 22.48             | 2.17              |
| Pb    | 4    | 4.9                           | 9.8                   | 8.28              | 2.27              |
3.2. Spatial distribution of copper, nickel and lead

Figure 3 shows the spatial distribution of each metal analyzed in the 4 study areas. Zone 1 has the highest copper and nickel concentration values compared to the other studied areas. Zone 2 has a high copper concentration with respect to Zone 3 and Zone 4 and higher lead concentration values with respect to the other study zones. All the zones have similar nickel concentration values. This way, the concentration of copper by zones decreases in order of Zone 1 > Zone 2 > Zone 4 > Zone 3, the concentration of nickel decreases in order of Zone 1 > Zone 3 > Zone 4 > Zone 2 and the concentration of lead falls in order of Zone 2 > Zone 1 > Zone 3 > Zone 4.

After analysis of variance applied to the concentration values of copper, nickel and lead for each of the study areas, the following results were obtained: an F value of 78.44 was obtained for the copper concentration with a p-value of 0.000 (95% confidence level); therefore it is concluded that the copper concentration values are different in each of the sampled areas. For nickel, an F value of 1.35 with a p value of 0.296 (95% confidence level) were obtained, therefore, there is no significant difference between the concentrations of nickel in the sampled areas. Finally, the analysis applied to lead concentration values resulted in an F value of 9.49 and a p value of 0.001 (95% confidence level) resulting in a significant difference between the lead concentrations in the different sampled areas.

Figure 3. Spatial distribution of copper, nickel and lead in the study area: a) Zone 1, b) Zone 2, c) Zone 3, d) Zone 4. Basemap data © Google 2019.
3.3. Analysis of the concentration of copper, nickel and lead for two particle sizes

The analysis of the concentration of copper, nickel and lead for different particle sizes was performed by analyzing 6 pairs of samples, each pair of samples belonging to the same sample point and the analyzed particle sizes were 38 µm and 1,000 µm as seen in Figure 4.

The analysis of variance of the copper concentration in the different points of soil samples was proposed in order to check if the copper concentration is the same in all the sample points. When obtaining a calculated F value of 13.10 and a p-value of 0.007 (95% confidence level) for the analyzed samples, it is concluded that the copper concentrations of each sample obtained are different from each other. In the paired t test applied to the copper concentration data obtained from the analysis of samples of particles of 38 µm and 1,000 µm, a p-value of 0.245 was obtained (confidence level of 95%), therefore it is concluded that there is no significant difference between the copper concentration data obtained from the same sample point but analyzed with two different particle sizes (38 µm and 1,000 µm).

Regarding the analysis of variance carried out for the nickel concentration in the soil samples, it was concluded that nickel concentration values in each analyzed sample do not have a significant difference between their values, this as a result of a calculated F value of 4.28 and a P value of 0.068 (95% confidence level). The nickel concentration data obtained for the two particle sizes (38 µm and 1,000 µm) were analyzed by applying the paired t test, obtaining a p-value of 0.214 (95% confidence level), therefore it is concluded that there is no significant difference between the nickel concentration data obtained from the same sample point but analyzed in two particle sizes (38 µm and 1,000 µm).

Regarding the results obtained as a consequence of the application of the analysis of variance, it was determined that the concentration indices of each sample point are different from each other, because the calculated F value of 12.29 and a P value of 0.008 (95% confidence level). The paired t test applied to the data of lead concentration obtained from the analysis in samples of particles of 38 µm and 1,000 µm yielded a p-value of 0.029 (95% confidence level), therefore it is concluded that there is a significant difference between the lead concentration data obtained from the same sample point but analyzed with two different particle sizes (38 µm and 1,000 µm).

4. Conclusions

Zone 1 (La Cocha sector - green area with public access) shows higher concentration values to those established in local regulations due to the presence of copper; Zone 1 and Zone 2 (Ignacio Flores Nautical Park and Illuchi river bank - green areas with public access) present higher concentration values than those established by authorities for lead; all the studied areas present higher concentration values for nickel; finally, no studied area presents Cadmium concentration values exceeding permissible references since every reading was below detection limits.

Despite the fact that Zone 2 does not exceed the maximum permissible limits, it is the zone that has the highest concentration values for copper and lead with respect to Zones 3 and 4. The industries taken into account for this research located in Zone 3 and Zone 4 do not represent a determining factor in soil contamination due to the presence of copper and lead.

Figure 4. Comparison of the results of the concentration of copper, nickel and lead for the two sizes of particles analyzed

There is a significant difference between the concentrations of the sample points of copper and lead, while nickel does not show a significant difference. Therefore, nickel shows a homogeneous distribution, while copper and lead have a heterogeneous distribution in all study areas.
The data obtained in the comparison of concentrations of heavy metals according to particle size showed that the concentration of copper is greater in the smaller particles (38 μm), while the concentration of nickel and lead is greater in the larger particles (1,000 μm). The paired t test showed that there is a significant difference for the lead concentration data, while for the copper and nickel concentration data it was concluded that there is no significant difference with a confidence level of 95% (α = 0.05).

Soil contamination due to the presence of nickel in all study areas is related to activities of each industry, since the textile company, the flour processing company and the foundry company use this heavy metal in their production processes. The main affection to human health due to the presence of nickel in the human body is the spread of allergies, in extreme cases it produces stomach damage, adverse effects on the blood and the kidney and in case of extreme inhalation kidney [10].

The main goal of this paper was to identify the nature of nickel, lead, and copper concentrations in soils around Latacunga city. Monitoring soil quality around industries is a job that local authorities must continue and research workers must collaborate with this tasks.

5. References

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