

New method to estimate total elements of chromium (VI), nickel and iron to analyze their mobility and spatial distribution from an open dump

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Abstract. Open dumps are a global problem due to their scant planning studies. In Ecuador, many of the dumps are of this type, operating for several years, as in the case of the open dump of Portoviejo, which is in its technical closure stage. The current study determined the physical-chemical characterization of the soils around the dump, and the concentration in aqueous extracts of Chromium (Cr (VI)), Nickel (Ni) and Iron (Fe). Therefore, a methodology for the estimation of total, soluble and fixed elements based on the theory of maximums and minimum through leaching curves have been proposed. The results have been compared with the permissible concentration limits of the Ecuadorian Regulation where Ni presents serious enrichment. Finally, the spatial distribution of the soluble elements have been performed in order to relate to the processes of mobility and availability in the soil, this let know that soils with possible contamination problems are oriented to the southern part of the dump towards the city of Portoviejo and could possibly be causing pollution in that area.

1. Introduction

In the current study, a soil examination has been conducted in order to determine the mobility and availability of three typical elements found in an open dump. Thus, the open-air dump of Portoviejo was studied, in western Ecuador. The area comprises of approximately 16 hectares and being the origin of contamination in water, soil and air of that sector [1].

Garbage dumps have been considered to be a global problem over the recent years. The International Solid Waste Association [2] recommended that the closure of open dump should be considered as a health emergency, due to the corresponding generation of pollution.

Eighty percent of the dumps of the different cities of Ecuador dispose their waste in open dumps, streams and banks of bodies of water, while the residual twenty percent dispose their waste in manual, mechanized and pooled sanitary landfills. The open dump in the city of Portoviejo has been in operation for more than 40 years and is currently in the technical closure stage, for which plans have been drawn up for the Procedure for Operation, Control and Maintenance for the final disposal of the common waste [3].

Two soil profiles were performed by the Ecuadorian Space Institute at approximate distances of



1.87 km and 1.94 km from the dump, the physicochemical characteristics consist of a textural class of clayey type, with a pH 7.5 and an electrical conductivity (EC) of 0.45 dS m^{-1} for the first soil site and a clay-loam type texture, with a pH of 8 and an EC of 0.59 dS m^{-1} for the second site, respectively [4]. In addition these two soil profiles give information about the soil type, where have been determined as Fluventic Haplustepts and Vertic Haplustepts soils [4]. Based on the geological map of Ecuador Map [5], the soil formation of the studied area is Onzole, which contains clays and siltstones, the upper levels are becoming sandy and there are sandstones at the top of the formation [6].

Analysis of the concentration of different heavy metals, indicate only the content of such elements in the soils, but lacking to provide information about their mobility or availability, which are fundamental data to determine the degree of contamination [7]. Cr (VI), Ni and Fe have been selected to determinate possible soil contamination due to in the Ecuadorian Regulations establish quality soil criteria in function of the presence of some elements, among them, these three mentioned. Furthermore, according with the type of waste is deposited in open dump of Portoviejo, which one of their principal economic activities is the manufacturing industry [8]. Cr (VI) is common to find in dyes, paints and metallurgical waste, and the hexavalent state is the most common form found in contaminated [9]. Ni and Fe are generated by industrial activities [10].

The pH of the soil and the soluble and available fractions of a metal in differ similarly for each element. Acid conditions favor the maintenance of the soluble forms of the compounds of these metals thus, providing a high potential for metal leaching [11]. The process of displacement of soluble or dispersible substances is named leaching [12]. This process has been able to cause to some layers of the soils to lose their vital compounds and, in turn to generate toxicity [12]. The reference [13] mentions that soluble salts in soils may be determined or estimated from aqueous extracts of soil samples.

To obtain the total, soluble and fixed elements in this study, a methodology has been proposed under the theory of maximum and minimum. The first derivative is found and its roots are calculated, in addition to analyze the behavior of the derivative to the left and right of said point [14]. On the other hand, the criterion of the second calculates the sign taken by the roots of the first derivative and the following is checked if $f''(a) < 0$ the function has a relative maximum and if $f''(a) > 0$ a relative minimum [15]. This way for determining these elements is a proposal of this study due to in Ecuador, the process of measuring the total elements which depend on acid digestion is complicated where the use of these acids is restricted by the Ecuadorian government for being a precursor of narcotic substances.

Therefore, the main aim of this study has been to physically and chemically characterize the soils of an open-air dump, to extract three soil water ratios to elaborate leaching curves of the concentrations of Cr (VI), Ni and Fe according to the different extracts of 20 sampled soils of Portoviejo's dump. Additionally, functions have been obtained where the maximum and minimum theory is applied as a proposal to elaborate leaching curves of the concentrations according to the different extracts of the sampled soils. Furthermore, the behavior of the elements has been tried to determinate, with the purpose to estimate the total, soluble and fixed concentrations of metals. Hereby, based on the asymptotic curves, the analysis of the availability and mobility of such elements have been performed, in order to compare with their spatial distribution.

2. Methodology

2.1. Study area and sampling and methods

The study area is- the western coastal region of mainland Ecuador, within the province of Manabi (figure 1). Sampling methodology has been performed based on [16] as such sampling design, together with the design of the network of control of piezometric designs as well as analytical and water quality, allowed to obtain the objectives set in relation to the characterization and mobility of the contamination, with the greatest reliability, speed, minimum effort and cost [16].

Twenty samples have been taken in December 2017 during low precipitation, with a mean monthly

value of 25 mm [17]. Nonetheless, rainfall and humidity play a minor role in this study, since extracts of soil moisture have been handled in the laboratory.

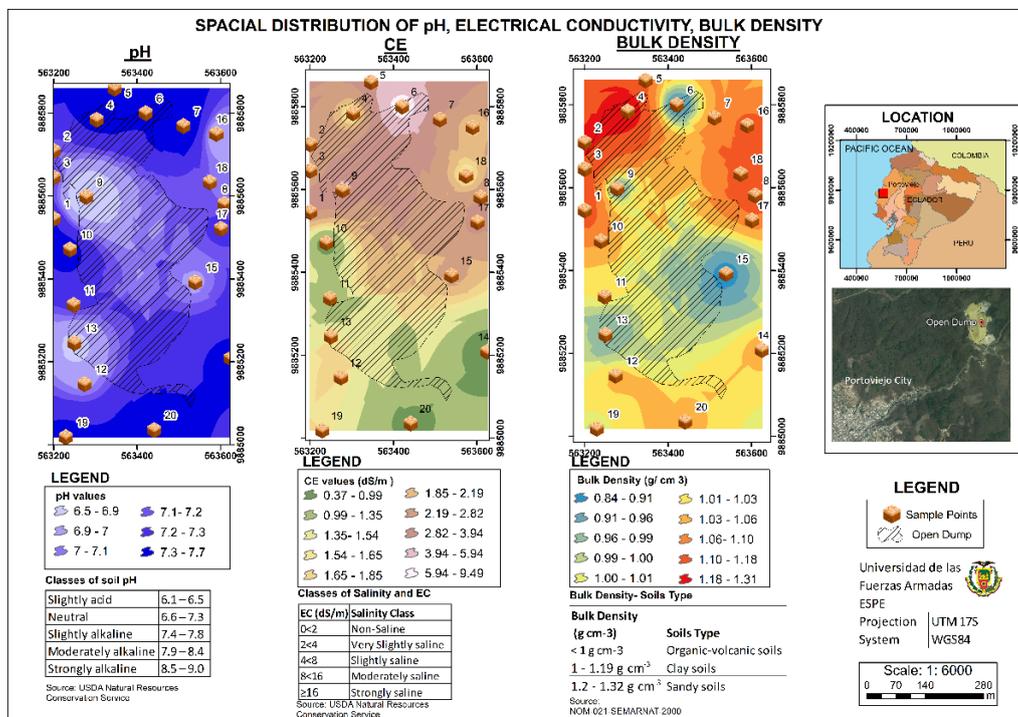


Figure 1. Spatial distribution of physical-chemical parameters (pH, EC, Bulk density).

Soluble salts of soils have been able to be determined or estimated from extracts of soil samples [13]. The preparation of soil samples has been performed based in [18]. Therefore, the twenty extracts have been conducted in scales of 1: 1, 1: 5 and 1: 10, in order to understand the mobility of polluting elements [19]. These extracts have been performed through soil-water relationships. The extracts have been handled with distilled water in order to clean the soil and determine the elements in the aqueous solutions [20]. The used methods and references in order to determine the physical-chemical parameters, and the measurement of heavy metals (Cr (VI), Ni, and Fe) in each of the three obtained extracts have been listed in table 1.

Table 1. Methods for determination of physical-chemical parameters and measurement of metals.

Parameter/ Metal	Method	Reference
pH	pH-Meter Brand: HANNA	APHA-4500 HB [21]
Electrical Conductivity (EC)	Device for measure EC, Brand HANNA	APHA-2510.B [21]
Real Density	Pycnometer	[18]
Bulk Density	Test Tube	[22]
Cr (VI), Ni and Fe	Spectrophotometer Brand: HANNA	[23]

The pH measurements have been calibrated using the buffer solutions of 4 and 7 as established in [21] based on the Method 4500-H + B. The electrical conductivity and its calibration has been based on the conductivity buffer solution and the methodology APHA-2510.B proposed in [21]. Finally, the procedure specified by [18] and [22] has been followed for the apparent and real density respectively.

The metals have been individually determined and calibrated following the equipment manual [23].

2.2. Elaboration of the spatial distribution of physical-chemical parameters

The Universal Kriging (UK) interpolation method has been employed for the spatial distribution of pH, electrical conductivity and real density. Based on comparative studies performed by [24] where UK has been evaluated as well as the methods Ordinary Kriging (OK), Spline, IDW, it has been generally concluded that it is the most optimal method to represent soil properties, has been the UK. Hereby, the mean error (ME) has been analyzed, where OK and UK have been the most optimal, followed by the mean square error (RMSE), which consists of precision measurements of the interpolation. These need to have values close to 1, as highlighted only within the UK. Also, the UK takes into consideration an exponential semivariogram, supporting the conclusion that UK is the most accurate method for the interpolation of pH values, electrical conductivity and bulk density [24].

2.3. Elaboration of the spatial distribution of the soluble elements of Cr (VI), Ni and Fe

The efficiency of an interpolation method to map the distribution of metals (contaminants) in the soil depends on certain factors, such as the number of samples and their location. A further factors that most affects effectiveness has been the amount of samples, since a large number of such will certainly generate more optimal results, in spite of economic issues of the sampling process and the access to the study area [25].

Due to the fact, that not all the samples provided the concentration of the total elements, therefore it has been taken into consideration the soluble elements for the spatial distribution. The Weighted Reverse Distance interpolation (IDW) has been applied using the ArcGis software, which uses a specific number of nearest points, being subsequently weighted according to their distance [26]. In [27], the distribution of heavy metals generally fits this interpolation, as if the content of heavy metals has been relatively high in an area, the soil and surrounding water will also gradually have high concentrations.

2.4. Leaching curves and proposal way for determination of total, soluble and fixed elements

For the analysis of the leaching of the determined elements (Cr (VI), Ni, Fe), the corresponding leaching curves of the concentration of the metals according to the different extracts have been performed. The trend lines of each curve have adjusted with a polynomial function of second order in all cases with a correlation coefficient of 1 for each one.

The determination of these elements has been conducted based on the theory of maximum and minimum as a proposal of the current study through the criteria of the first and second derivatives. From each leaching curve, those that behave asymptotically have been determined since the concentration threshold has been able to be taken as a function of the extracts. The first and second derivatives have been applied to the equations of these curves, and under such criterion the maximums and minimums have been obtained, where only the maximums have been taken into consideration for the estimation of the totals. The totals represent the maximum point, while the soluble elements have been those that approximate the saturation extract 1:1. The saturation extract has been defined as the solution extracted from the soil after saturation with water, in order to fit it at a point close to its field capacity since it is related to the maximum amount of moisture that the soil may resist. That explains that this saturation extract approached the extract of 1:1 [28]. Finally, the fixed elements have been those that resulted from the difference between the total elements and the soluble ones.

3. Results

3.1. Physical-chemical parameters

3.1.1. Hydrogen potential (pH). In the study area the values of the twenty samples of the 1: 1, 1: 5 and 1:10 extracts varied between a range of 6 - 7.5 pH units (figure 1). The metals are sparingly soluble in

alkaline conditions, the solubilities of the metals have been higher when they have been in slightly acidic conditions and increased drastically when the pH remained at 3.3, as mentioned in [29]. These results may be contrasted with those of [30], where it has been concluded that if the pH of the soil decreases, the availability and mobility of the metal ions increases due to the chemical form in which these metal ions are present in the solutions of the floor. Our results indicate that most of the samples have a moderately alkaline pH (figure 1), which reveals that solubility is scarce, in addition to availability and mobility.

3.1.2. Electrical conductivity. The values of electrical conductivity for soils of the study area vary in a range of 0.36-9.45 dSm⁻¹ (figure 1). According to the Mexican norm [18] as well as the USDA [31] it has been established that these are soils from negligible to moderate salinity [18]. If the soils have conductivity higher than 4 dS m⁻¹, they are considered unproductive [32]. The variability of the EC has been considerable, especially in the extract 1: 1 of sample 17, where an extreme value of 9.5 dS m⁻¹ change has been established, being moderately saline. Therefore, the maximum value to be 21 times is more than the background values presented by the profiles. If the concentration is three times higher than the background value, immediate attention will be given and the remediation of the soil will be forced until the present concentration is less than or equal to 1.5 than the background value [33].

3.1.3. Bulk density. The soils that are in a bulk density range less than 1 g cm⁻³ are named organic and volcanic, between 1 to 1.19 g cm⁻³ as clay, from 1.2 to 1.32 g cm⁻³ as frank and higher than 1.32 g cm⁻³ as sandy [18]. Therefore, our samples present compositions from organic and volcanic to sandy soils. The high bulk density is an indicator of low soil porosity and soil compaction [34] (figure 1).

3.2. Leaching curves and estimation of total, soluble and fixed elements

The leaching curves that document asymptotic behavior, allow observing the threshold where the concentration of the element begins to decrease by the washing to which it has been subjected (figure 2(a)-(c)).

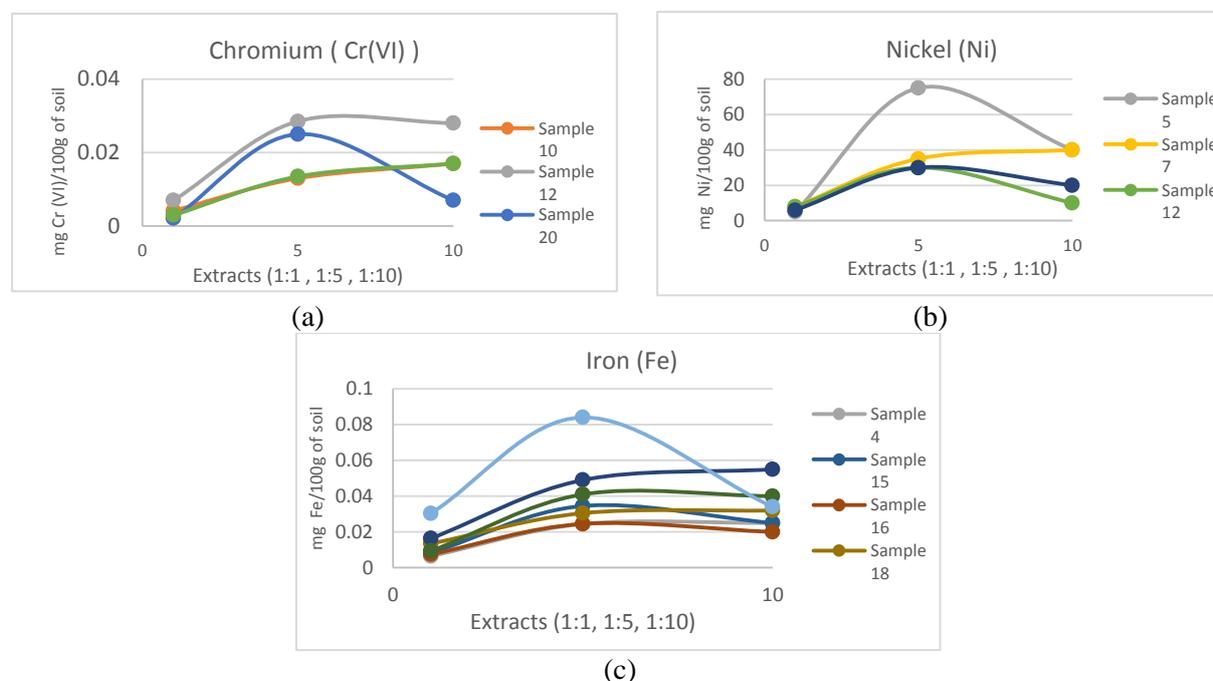


Figure 2. Leaching curves with corresponding equations that document asymptotic behavior: (a) Cr (VI), (b) Ni and (c) Fe.

The total elements have been possible to be estimated from the curves that illustrated asymptotic behavior. The importance of estimating these elements is that they help to understand the behavior of the metal in the soil. Furthermore, the total elements allow establishing a comparison with the permissible limits of the environmental regulations.

3.3. Comparison with Ecuadorian Environmental Regulations.

Due to the fact that the total elements of Cr (VI), Ni and Fe of all of the samples have not been determined, it might be considered, that of the curves that documented an increasing behavior, these could be generating some type of alteration, if they are situated outside of the permissible limits. Therefore, the concentrations of the 1:10 extract of the samples have been evaluated in order to determine if this exceeds the norm even being undetected though the threshold, concluding that it may be a soil with issues of contamination. A comparison may be established with the quality standard of the water resource, as soil parameters may also be determined through the water and this certainly reduces time and costs in terms of soil analysis [35].

The Ecuadorian regulations for soil resources [33] establish permissible limits for Cr and Ni, on the base of soil quality and the intended use. Thirty percent of the samples exceeded the permissible limits according to the quality criteria of land use. The twenty soil samples exceeded the permissible limits for Ni, causing severe problems in the soils. In case of Fe, twenty percent of the samples have been outside the permissible limit for the water resource [36].

Studies consider Ni as a toxic element outside the permitted range. Its sources of enrichment have been several in a dump, due to the deposition of urban and industrial waste. Under acidic conditions, Ni becomes more mobile and may be leached to groundwater, causing contamination to aqueous sources [9].

3.4. Spatial distribution of soluble elements of Cr (VI), Ni, Fe

Figure 3 illustrates the spatial distribution of the soluble elements, which have been the most harmful in terms of toxicity as they are the ones that have the ability to migrate to other media and integrate more easily with a transfer into a living organism [10].

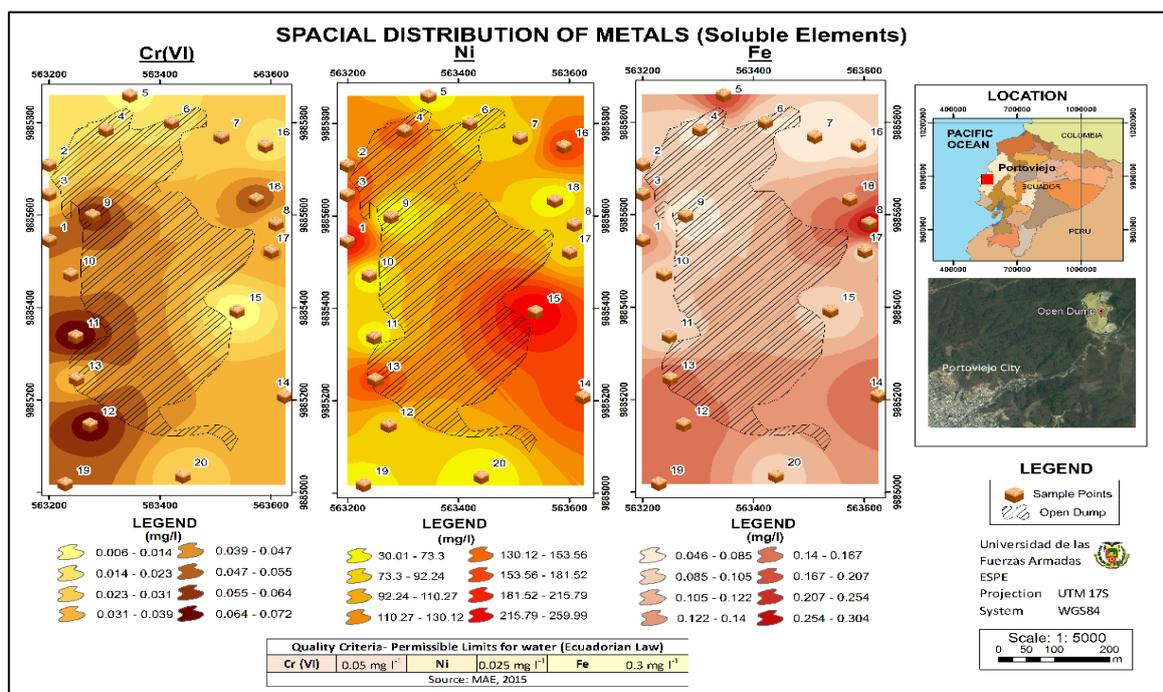


Figure 3. Spatial Distribution of Soluble elements of Cr (VI), Ni and Fe.

For a better understanding about the availability of these elements, the leaching curves facilitate the process of interaction with the soil and water, explaining why not all the samples have been able to estimate their threshold. The physical-chemical characteristics of the soil represent a key data for an availability study. The pH varies between slightly acidic and slightly alkaline. Metals tend to be more available in acidic conditions, except for Cr which is more mobile at alkaline pH [10]. According to the EC, the soils are modernly saline. The increase in salinity is able to increase the mobilization of metals [39]. Therefore, due to the present salinity, this process is expected to exist in the dump grounds.

4. Conclusions

Referring to physical and chemical characterization, the samples presented a range of 6 - 7.5 pH units, which reveals that exist a variation from acid to low alkaline soils. According to the electrical conductivity values vary from 0.37 to 9.49 dS m⁻¹, which indicates that they are non-saline to moderately saline soils and finally the determined apparent density of each sample, results in the presence of volcanic-organic, sandy and clayey soils. Through the aqueous extracts, the leaching curves were determined for the concentration of Cr (VI), Ni and Fe of all the samples, where most of them showed a growing behavior and the threshold of the total concentration could not be determined. The proposal for the estimation of total, soluble and fixed elements has been made for those curves that showed asymptotic behavior. According the comparison with the Ecuadorian Regulations, 30% of the samples exceeded the limits allowed for Cr (VI), Fe with 20% of the samples and for Ni all the soils presented their values over the permissible limit. Finally, the spatial distribution of the soluble elements of these metals, showed that in general the highest concentrations are found south of the dump, where a few kilometers away is the city of Portoviejo, which could possibly be affected by the mobility and surface runoff of the metals to there.

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