# ENVIRONMENTAL IMPACT OF NICKEL INDUSTRIES IN CUBA. A CASE OF STUDY FROM MOA MINING DISTRICT

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## ABSTRACT

*The analysis of mineralogical, major, minor and trace elements in surface and ground water, metallurgical wastes and lateritic soil to evaluate the main environmental impact of nickel industry in the Moa district (Cuba) are presented here. Several techniques have been employed in order to obtain the physical, chemical and geochemical characteristics of soil and wastes. The mineralogical study was carried out by means of XR diffraction technique. Chemistry of samples was determined by inductively coupled argon plasma emission spectrometry (ICP-AES) and ICP-MS. The hydrogeochemical behaviour and migration of selected heavy metals (Ni, Cr, Co, Fe, Mn and Sr) present in mine waste and lateritic profiles, that have been detected in surface and ground water, was obtained with batch tests. Batch tests have revealed the potential capacity of mining wastes to transfer heavy metals to the environment. The waste from acid leaching process represents the major environmental risk for natural ecosystem.*

## INTRODUCTION

Since 1943 Holguín area (Mayari, and Moa) has been one of the most important active Ni, Co and Cr mining district and constitutes one of the most important Ni-ore deposits of the world. Ni reserves up to 800 Million Tons have been calculated from both mining drilling studies and mining data and 3000 Million Tons have been estimated (UNI, 1994).

However, as a consequence of mining activities some negative environmental effects have been produced: deforestation of 1200 ha of tropical forests, surface and ground water pollution, air pollution (gases and solids), slope instability, changes of water table and recharge variation, Moa bay pollution and landscape degradation. One of the most important problems is the presence of heavy metals and sulphate both in the alluvial aquifer and in the surface water of the Moa river basin.

The main aim of this work is to show the impact of nickel mining in the Moa region and to present the preliminary results on the behaviour and migration of Ni, Cr, Co, Mn and Fe detected in surface and ground water, and contained in mine wastes and lateritic profiles.

## SITE DESCRIPTION

The Cuban nickel and cobalt industry is located in the Northeast area of the Holguín province (Figure 1). Average annual climatic parameters (1973-1995 period) are: 1800 mm of rainfall, 24.5 °C of temperature, 1600 mm of evaporation and a mean relative humidity of 86 %.

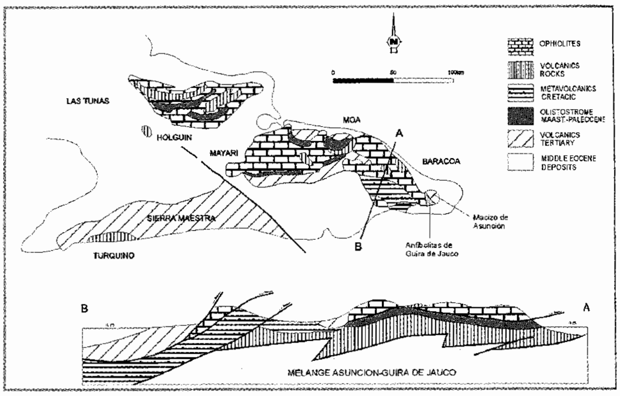

Figure 2. Map showing the Mayari-Baracoa massif (adapted from Iturralde and Vinent, 1996).

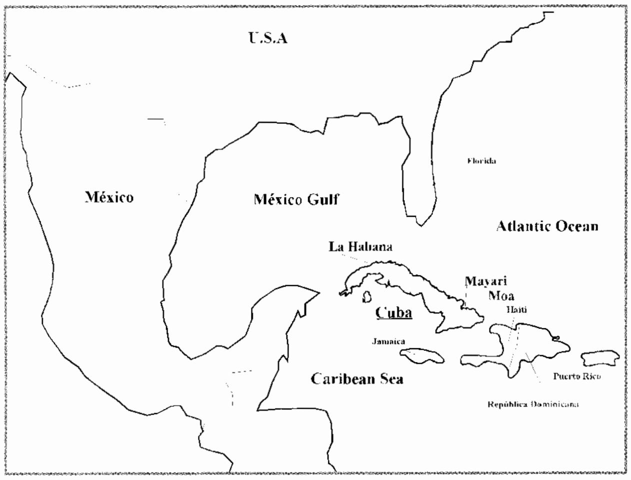

Figure 1. Location of the study area.

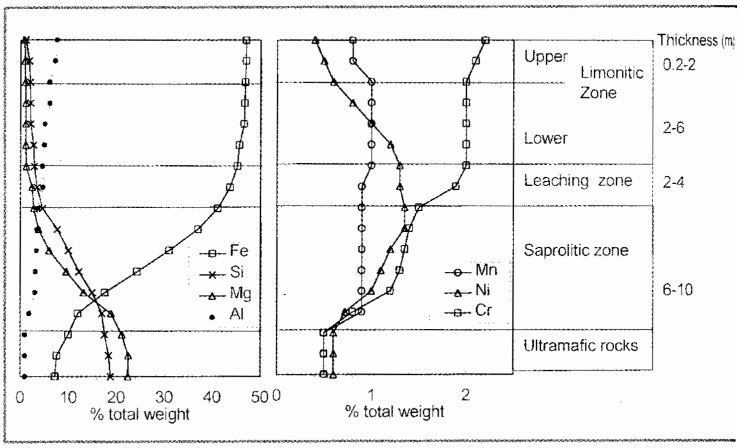

Figure 3. Diagram showing the vertical distribution of Fe, Ni, Cr, Mg, Si and Al in a lateritic profile in Moa deposits (adapted from Vera, 1975).

## GEOLOGY

The Northern part of the Cuban archipelago is composed of ultrabasic rocks named Cuban Ophiolitic Belt. The belt outcrops extend along more than 1000 km and it is thought to belong to the Upper Jurassic-Lower Cretaceous in age (Iturralde-Vinent, 1996). The Eastern most part of the Cuban Ophiolitic Belt, 170 km long and 10-20 km wide, is known as the Mayarí - Baracoa area.

According to Iturralde-Vinent (1996), within the ophiolitic sequence it can be distinguished (Figure 2):

- serpentinized interlayer harzburgites (with minor lherzolites, dunites and wehrlites);
- interlayer harzburgites (with minor dunites) and gabbros, olivine gabbros and troctolites;
- isotropic gabbros, microgabbros, dolerites and diabase dykes; and
- pillowed basalt flows interbedded with limestones and radiolarites.

As a consequence of the climatic characteristics and weathering over ultramafic rocks, lateritic crusts enriched in heavy metals (Ni, Cr, Co and Fe) are present over ultramafic rocks in this area. Figure 3 shows the vertical distribution of some selected metals (Fe, Ni, Cr, Mn, Al) and Si in the Moa lateritic deposits. Vertical concentration depends on the degree of the lateritic weathering development. The enrichment in Fe, Cr, Al in the limonitic horizon is due to the leaching of Si and Mg. The Cr content decreases with depth.

## MINERAL EXTRACTION FROM LATERITES

The lateritic rocks, rich in Ni and Co, are treated using two different metallurgical processes 1) Ammonium Carbonate Leaching (ACL) with oil addition and 2) Sulphuric Acid Leaching (SAL). These materials are dried at high temperatures (ACL = 1100 °C and SAL = 600 °C) in order to obtain nickel and cobalt oxides (ACL) and sulphides (SAL). These processes generate a great volume of subproducts currently eliminated as wastes (Table 1 and Figure 4).

| Contaminants | SAL | ACL |
|---|---|---|
| Solid wastes (T/day) | 4000 | 1200 |
| Liquid wastes (m$^3$/day) | 12000 | |
| Dust emission to the atmosphere (T/day) | | 10 |
| Gases $SO_2$ (T/day) | 16.3 | 17 |
| $SO_3$ (T/day) | 2.0 | |

Table 1. Volume of generated wastes (UNI, 1994).

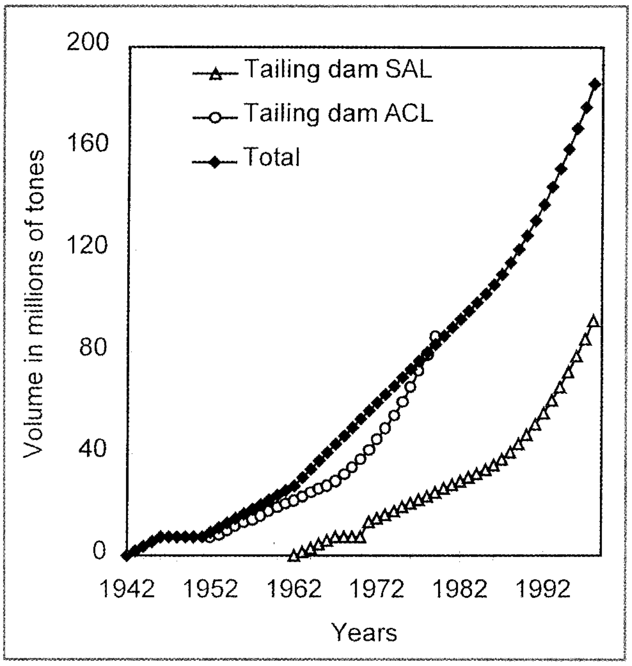

Figure 4. Volume of mine wastes in 1943-1998 period.

After the treatment, mineral residues are transported in a slurry form to the tailing dams located at Levisa bay and over the Moa river terraces (Figure 5). The water content of the tailings varies in time, depth and within the different areas of the dams, due to the climatic characteristics of the area and to the fact that the discharge of the residue is produced in a very small zone within the dam. Drying of macro cracks, 20 - 80 cm deep and more than 5 cm wide, have been observed in the surface of the mine tailing deposits.

Since 1943 residues and waste of mining have been continuously increasing. At present, there are 5 tailing dams, (3 of them out of activity), occupying an area of 10 km$^2$, where 180 millions tons of solids approximately are stored (Figure 4 and 5). The tailing thickness range varies from 6 to 27 m and they are subjected to oxidising conditions and rainfall leaching (Figure 4).

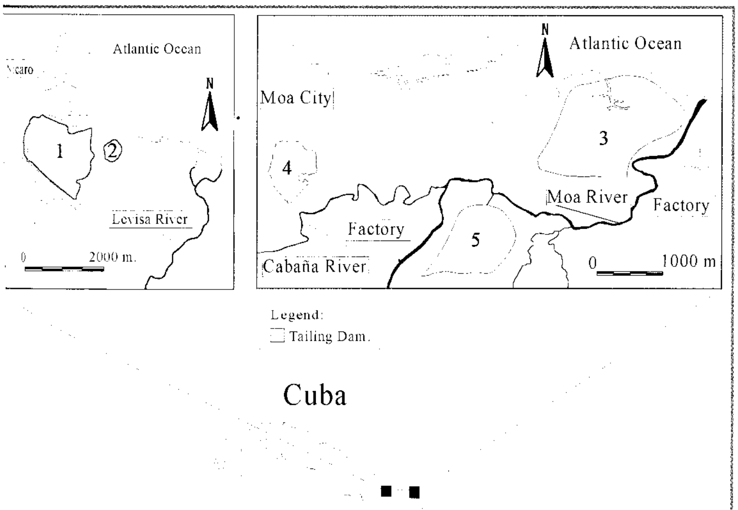

Figure 5. Map showing the location of the tailing dams in Moa and Mayari. Holguín. Cuba (1,2 and 3 are ACL and 4 and 5 SAL).

| | | Ni | Mn | Fe | Cr |
|---|---|---|---|---|---|
| Ground water *** | Maximum | 0.086* | 8.30* | 5.10* | 1.62* |
| | Minimum | 0.01 | 2.10* | 0.02 | 0.01 |
| Surface water | Maximum | 2.52* | 3.60* | 2.36* | 0.02 |
| | Minimum | 0.005 | 0.02 | 0.07 | 0.001 |
| Spring | Maximum | 0.006 | 2.00 | 2.00 | |
| | Minimum | 0.005 | 0.004 | 0.007 | |
| Sediment in Moa bay ** | Maximum | 8000 | 241.0 | 2040 | |
| | Minimum | 8.30 | 40.00 | 0.50 | |

(* Concentration superior to drinking water standards).
Table 2. Heavy metals detected in sediments(mg/kg), surface and ground water (mg/L) in Moa area (** González and Ramírez, 1995; *** Rodríguez and Candela, 1998).

The geochemical background of metals within this region shown by the concentration in surface and ground water is high, as a result of the weathering of the lateritic rocks.

## SAMPLING AND METHODOLOGY

To characterise the quality of water, a sampling survey was performed during October.-November of 1996. Analysed water samples refer to spring (4 samples) and surface water from different rivers (22 samples). All samples were collected and stored at 4 ºC following standard methods described elsewhere and acidificated with $HNO_3$ to preserve metals. No field analysis measurements were accomplished.

Water analysis by standard procedures consisted on the determination of major ions content (Na, K, Ca, Mg, $HCO_3$, Cl, $SO_4$ and $NO_3$), turbidity, conductivity, pH and hardness. Likewise, Ni, Mn, Cr, Fe, Cu and Co in water were analysed.

Ten representative samples of metallurgical waste were taken from two tailing dams located on the Moa River terraces, and three samples of lateritic soil profiles were selected according to the weathering zonation defined by laterites (Friedrich, *et al.*, 1987). The mineralogical study was carried out by means of the XR diffraction technique (SIEMENS D-500, Cu K$\alpha$= 1.5418 $\alpha$ a 40 kV y 30 mA).

Grain size distribution was obtained using the laser method with the Malvern Mastersizer/E equipment (range 0.5 - 600 µm).The pH was determined using a distilled water with (water/soil) ratio of 1:2.5 and CEC according to the Gillman methods for acid soils (Pague, *et al.*, 1990). Chemistry of samples was determined by inductively coupled argon plasma emission spectrometry (ICP-AES) and ICP-MS. Prior to the analysis, samples were digested in PFA bombs (250 mm) using acid attack ($HNO_3$, $HClO_4$, HF). Solutions were dried by leaching at 180 ºC, and finally, they were diluted to a fixed volume, obtaining a final clear solution.

To obtain the leached fractions from waste and lateritic profile through a batch test, 0.2 g of air dried samples (minor 0.5 mm in grain size) were shacked during 24 h in teflon bottles (250 ml) using Milli-Q water at different water/rock ratio. Extracts for the analysis were obtained by filtering (0.46 µm Millipore filters).

## RESULTS AND DISCUSSION

According to the obtained results, fresh water in the Moa region has a remarkably low salinity (minor of 150 mg/L). The chemical composition both in ground and surface water shows that the dissolution and leaching of silicate minerals is a very slow process that does not produce significant variations of the water chemistry. This was clearly observed in the studied area, where the ground and surface water silica concentration is uniform in different points (Table 3).

When looking at the spatial distribution of chemical compounds from the Stiff diagrams (Figure 6), an important water quality change in several rivers can be observed from the S-N line to coast. Chemical composition of water along the stream changes from magnesium bicarbonate at the head waters to magnesium sulphate in the river mouth (6, 7 and 8 sampling points). Also, the influence of erosion and water mining drainage is shown in Figure 6 where heavy metal concentration has been plotted. High concentration of heavy metals in the water of some sampling points is directly related to the presence of the mining factories and the tailing dams (point 6, 7 and 8) and point 9 is due to the pouring waters from the mine (Figure 7 and Table 3). Point 6 and 8 present an acid pH caused by the liquid waste disposal.

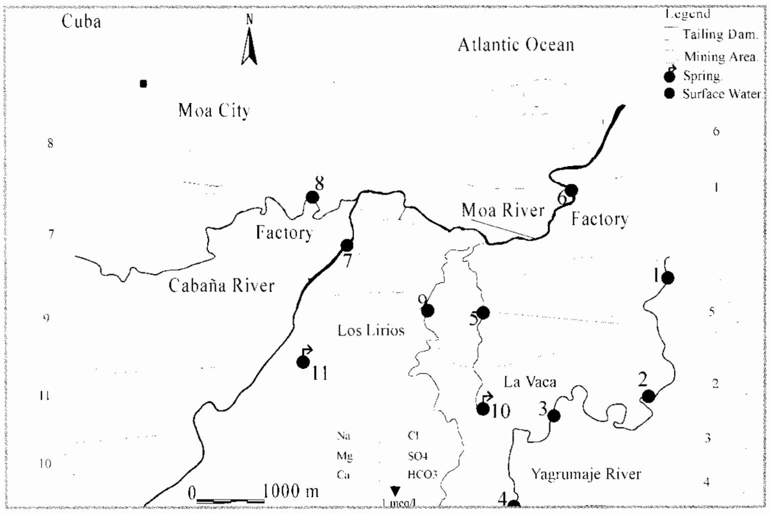

Figure 6. Stiff diagrams of the surface water and spring.

The main physical and chemical characteristics of the sample wastes (SAL and CAL) and lateritic profile (OI, OE and SL) are detailed in Table 4. The residues and geological materials are characterised by a sandy, silty and clayey grain size distribution, with a predominance of the silt fraction and acid pH. The existence of an acid pH in the lateritic profile can be attributed to the intense weathering generated by the climatic conditions and to the local sulphur dioxide emissions produced by the metallurgical industry (Table 1). Differences between the pH values found in the analysed wastes depend on the extraction treatment used. The CEC is a typical value for the (oxy)hidroxy iron, Mg, Al and Cr, beings lightly lower in wastes than in laterites.

For the ACL process, oil addition constitutes an essential part of the treatment; consequently, the waste acquires both black colour and a noticeable content of organic matter (OM) (Table 4).

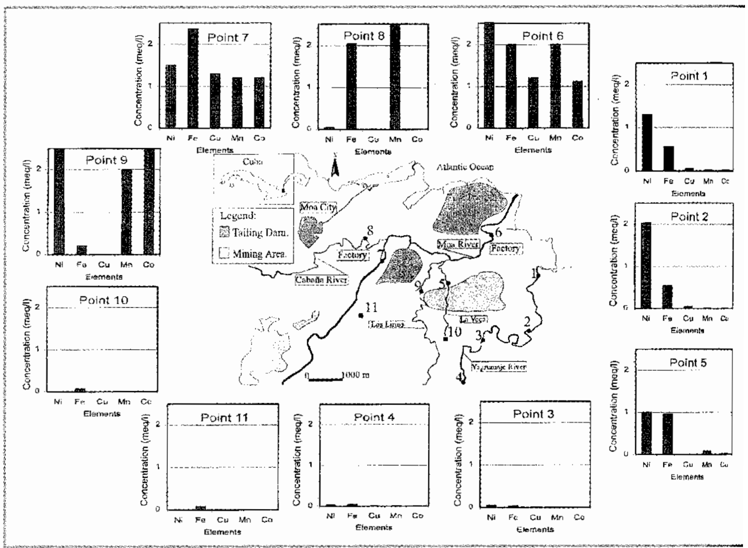

Figure 7. Heavy metal concentration in surface waters and spring.

| Samples | SAL | CAL | OI | OE | SL |
|---|---|---|---|---|---|
| pH | 4.1 | 6.5 | 5.7 | 6.6 | 6.4 |
| CEC (meq/100g) | 6.5 | 7.2 | 7.4 | 7.3 | 8.4 |
| OM(%) | - | J-1.6 | | | |
| % sand | 14 | 10 | 15 | 4 | 3 |
| % silt | 70 | 70 | 83 | 86 | 88 |
| % clay | 16 | 20 | 2 | 10 | 9 |
| Medium diameter of the particles $D_{50\,(\mu m)}$ | 20 | 10 | 60 | 16 | 20 |
| Colour | Red | Black | Red ochre | Wine red | Yellow |

(OI :upper limonitic zone; OE: lateritic leaching zone and SL; saprolitic zone)
Table 4. Characteristics of different samples.

Table 5 shows the mineralogical composition of the samples studied. During the metallurgical treatment, silicate minerals disappear and an increment of the useful metal oxides is produced. The main minerals are Fe (oxy)hydroxides, primarily magnetite and hematite. Secondary minerals are magnesioferrite, quartz and gibbsite. Clay minerals were not detected.

| Minerals | Formula | SAL | ACL | OI |
|---|---|---|---|---|
| Magnetite | $Fe^{2+}Fe_2^{3+}O_4$ | X̲ | X̲ | X |
| Maghemite | $\gamma Fe^{3+}O_3$ | | | X |
| Hematite | $Fe^{2+}O_3$ | X̲ | X̲ | X |
| Goethite and Hydrogoethite | FeOOH, FeOOH n OH | | | X |
| Antigorite | $Mg_6(Si_4O_{10})(OH)$ | | | |
| Forsterite | $Mg_2SiO_4$ | | | |
| Lizardite | $Mg_3(SiAL)_2O_5OH_4$ | | | |
| Quarz | $SiO_2$ | X | X | X |
| Chlorite | $H_4Mg_3Si_2O_9$ | | | |
| Gibbsite | $Al(OH)_3$ | X | X | |
| Other of cromoespinels Group | | X | X | |

Table 5. Mineralogical composition (X̲ essential, X accessory).

| Point | pH | EC | Turbidity | OM | $SiO_4H_4$ | Cl | $SO_4$ | $HCO_3$ | $NO_3$ | Na | Mg | Ca | K | Ni | Fe | Cu | Mn | Co |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 6.8 | 95.1 | 32 | 4 | 12.68 | 15.31 | 5.03 | 34.17 | 4.43 | 8.3 | 15.79 | 2.02 | 2 | 1.3 | 0.56 | 0.05 | 0.029 | 0.03 |
| 2 | 7 | 92.4 | 31 | 3.4 | 12.36 | 14.91 | 10.78 | 33.74 | 3.12 | 16.01 | 13.4 | 2.00 | 1.2 | 2.03 | 0.54 | 0.051 | 0.009 | 0.003 |
| 3 | 6.8 | 91.7 | 3 | 3.0 | 12.3 | 14.90 | 5.57 | 35.21 | 3.2 | 18.02 | 13.6 | 1.95 | 1 | 0.053 | 0.04 | 0.006 | 0.008 | 0.003 |
| 4 | 6.8 | 113.2 | 6 | 4.2 | 7.81 | 18.13 | 1.02 | 41.49 | 3.1 | 15.6 | 9.8 | 2.65 | 2 | 0.03 | 0.04 | 0.005 | 0.006 | 0.005 |
| 5 | 6.8 | 96.2 | 3 | 11.6 | 8.42 | 13.29 | 2.6 | 44.21 | 11.2 | 14.8 | 13.5 | 3.25 | 2 | 1 | 0.96 | 0.004 | 0.08 | 0.02 |
| 6 | 2.8 | 98.5 | 18 | 0.7 | 7.98 | 29.8 | 46.21 | 36.58 | 0.23 | 7.9 | 19.2 | 3..21 | 1.2 | 2.52 | 2 | 1.2 | 2 | 1.11 |
| 7 | 6.5 | 118.2 | 26 | 0.7 | 6.42 | 16.92 | 65.12 | 38.21 | 1.25 | 8.2 | 18.5 | 3.12 | 1.65 | 1.5 | 2.36 | 1.3 | 1.2 | 1.2 |
| 8 | 2.2 | 116.3 | 31 | 0.2 | 10.9 | 28.36 | 66.23 | 39.41 | 0.85 | 8.5 | 19.3 | 2.94 | 1 | 0.04 | 2.04 | 0.004 | 3.6 | 0.011 |
| 9 | 6.6 | 111.1 | 8 | 0.7 | 7.3 | 16.12 | 5.40 | 38.42 | 0.12 | 8.21 | 18.32 | 20.85 | 1.65 | 3.5 | 0.21 | 0.002 | 2.004 | 3.2 |
| 10 | 6.5 | 50.8 | 0 | 0.0 | 8.3 | 16.2 | 1.41 | 35.50 | 11.20 | 6.20 | 9.21 | 2.80 | 1.10 | 0.005 | 0.07 | 0.002 | 0.004 | 0.004 |
| 11 | 6.2 | 51.3 | 0 | 0.0 | 8.3 | 14.2 | 1.50 | 36.61 | 10.07 | 7.01 | 8.90 | 3.11 | 1.00 | 0.005 | 0.07 | 0.002 | 0.004 | 0.004 |

Table 3. Concentration of chloride, sulphate, bicarbonate, nitrate, Na, Mg, Ca, K, Sr and $SiO_4H_4$ (all in mg/L), pH, electrical conductivity (EC, µS) Turbidity (ppm $SiO_2$)

The samples of the lateritic profile (OI, OE and SL) and of the wastes (SAL and ACL) are mainly composed of iron and heavy metals. The main constituent is Fe, secondary elements are Cr, Mn, Sr and Ni, and Co, Zn and Cu are the accesories (Table 6).

The leaching behaviour of the different heavy metals was studied through batch tests at different water/rock ratio. The batch tests reveal that all the samples have the capacity of leaching considerable volumes of heavy metals in a soluble way (Table 7 and Figure 8). However, for chromium, the leaching concentration during the batch test is lower than the value detected in the aquifer (Table 1), this effect can be due to the possible formation of soluble organo-metalic compounds with a long residence time.

From the analysis of samples obtained from batch tests, leaching of other potentially toxic elements has also been observed. Compounds such as Ba, B, and Sr, not previously detected in surface and ground water should be taken into account for future studies.

The leaching behaviour of the different metals depends on the solvent availability. To evaluate this possibility, several water/rocks phases were prepared for batch tests. When W/R increases, the leaching of soluble metals also increases (Table 7 and Figure 8).

The pH has an important role in the leaching properties of the metals in the surface and ground water. The SAL samples, with a very acid pH, present the highest metal leaching values (Table 7 and Figure 8). For all samples, the pH tends to increase until a dynamic equilibrium is reached after 24 hours (Table 8).

| Elements | SAL | ACL | OI | OE | SL |
|---|---|---|---|---|---|
| Cu | 0.86 | 0.12 | 0.02 | 0.06 | 0.03 |
| Cr | 24.79 | 19.72 | 0.17 | 21.07 | 27.91 |
| Co | 1.31 | 1.15 | 0.05 | 0.59 | 0.21 |
| Ni | 7.23 | 6.47 | 4.51 | 9.85 | 2.59 |
| Fe | 430 | 450 | 530 | 453 | 190 |
| Mn | 18 | 19 | 16 | 18 | 8 |
| Zn | 0.67 | 0.45 | 0.03 | 0.33 | 0.26 |
| Sr | 18 | 16 | 22 | 14 | 6 |

Table 6. Heavy metal concentration in waste and lateritic profiles (g/kg of soil).

|  | SAL |  |  | ACL |  |  | OI |  | OE |  | SL |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ratio | l:5 | l:20 | l:250 | l:5 | l:20 | l:250 | l:20 | l:250 | l:20 | l:250 | l:20 | l:250 |
| Cu | 0.08 | 0.48 | 8.52 | 0.17 | 0.84 | 28.08 | 10.39 | 45.00 | 3.73 | 49.82 | 5.71 | 42.3 |
| Cr | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 | 0.26 | 3.14 | 0.00 | 0.03 | 0.00 | 0.01 |
| Co | 0.11 | 0.86 | 1.30 | 0.00 | 0.07 | 0.35 | 0.60 | 8.88 | 0.02 | 0.69 | 0.12 | 1.31 |
| Ni | 0.04 | 0.23 | 0.52 | 0.00 | 0.04 | 0.37 | 0.03 | 0.41 | 0.01 | 0.19 | 0.06 | 0.89 |
| Fe | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 |
| Mn | 0.32 | 2.17 | 2.04 | 0.02 | 0.07 | 0.36 | 0.01 | 0.10 | 0.00 | 0.06 | 0.01 | 0.14 |
| Zn | 0.10 | 1.75 | 7.41 | 0.09 | 0.49 | 4.27 | 3.87 | 6.20 | 0.47 | 8.06 | 0.55 | 6.10 |
| Sr | 0.00 | 0.02 | 0.94 | 0.00 | 0.01 | 0.55 | 0.00 | 0.04 | 0.00 | 0.51 | 0.02 | 1.20 |

Table7. Concentration of leached metals relative to the total metal concentration in solid phase for different ratios (all concentrations are expressed in % of the total).

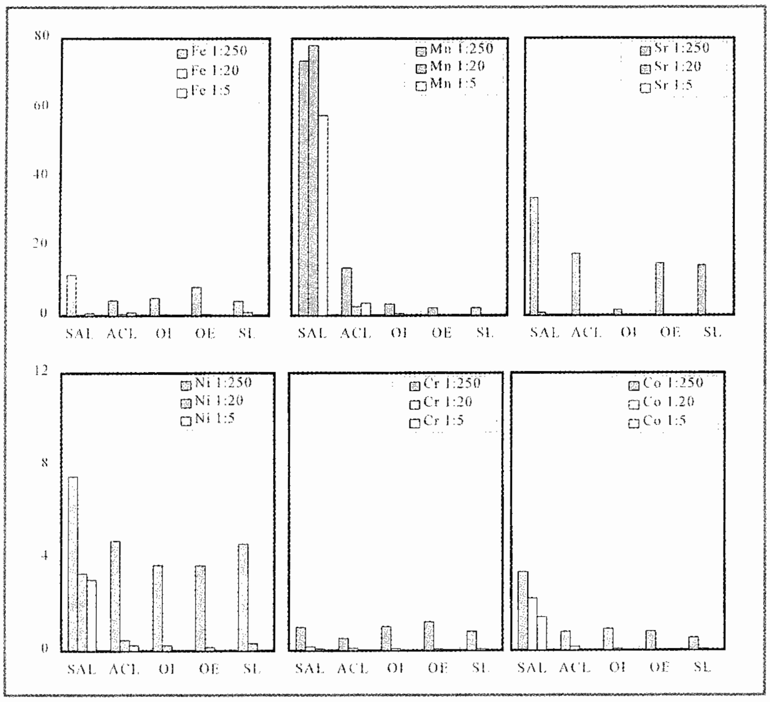

Figure 8. Extraction of Ni, Co, Cr, Mn, Sr and Fe for different ratios 1:5, 1:20 and 1:250. (OI: upper limonitic zone; OE: leaching zone and SL: saprolitic zone).

## ACKNOWLEDGEMENTS

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| | SAL | | ACL | | OI | | OE | | SL | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ratio | 1:20 | 1:250 | 1:20 | 1:250 | 1:20 | 1:250 | 1:20 | 1:250 | 1:20 | 1:250 |
| pH start | 4.61 | 4.52 | 7.80 | 7.72 | 5.37 | 5.31 | 5.73 | 5.85 | 7.86 | 7.90 |
| pH final | 7.02 | 6.85 | 7.52 | 7.60 | 7.64 | 7.60 | 7.48 | 7.55 | 7.39 | 7.63 |

Table 8. Startand final pH of the batch tests.

## CONCLUSION

The geochemical background of heavy metals in surface and ground water in the area is high, as a result of the weathering of lateritic rocks, and of the leaching of metallurgical wastes.

According to the data and experimental results, it could be expected that contamination of the surface and ground water would increase in time and it is also possible that new contaminants (B, Br and Sr) detected in the analysis of samples obtained in batch tests, would appear.

Environmental conditions prevailing in the Moa area: concentration in a reduced geographic site of extractive activities; leaching of contaminant residues; high rainfall in acid conditions favouring the contaminants transfer, represent a very high potential risk to the environment.

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