Assessment of Soil Solution Chemicals after Tannery Effluents Disposal

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Abstract: Knowledge about soil solution chemicals is important for assessing their mobility, availability, migration to groundwater and toxicity to plants. The objective of this study was to apply factor analysis to data obtained on soil solution chemicals during a one-year monitoring program in a controlled experiment with tannery effluents disposed on the soil surface, to extract information on their relationship and identify the main contaminants. Seventeen chemical parameters were monitored at six different depths on soil profile, focusing on metals and nitrate in soil solution. Four Factors accounted for 79.20% of the total variance, of which the most important were: Factor 1 (48.35%) showed significant loadings for Mn$^{2+}$, Na$^{+}$, K$^{+}$, Ca$^{2+}$, Mg$^{2+}$, Cl$^{-}$, Pb$^{2+}$ and electric conductivity, strongly influenced by high load effluent disposal; Factor 2 (12.21%) was related with SO$_4^{2-}$, Factor 3 (10.16%) associated with Cu$^{2+}$ and Zn$^{2+}$ and Factor 4 (8.49%) associated with nitrogen mineralization dynamics after high disposal.

Key words: Soil solution, groundwater, tannery effluents, factor analysis

INTRODUCTION

Industrial activities are capable of generating soil and groundwater pollution as a result of the emission of liquid effluents or waste disposal practices. The tanning industry is considered an activity with elevated potential for environmental pollution all over the world. Tanning processes use substantial amounts of chromium salts and other heavy metals, sulfide and organic compounds. Brazilian bovine hide tanneries usually consume 20 to 40 m$^3$ of water per ton of processed hide. According to IBGE, it is estimated that about 35 million hides from chrome processing were tanned in 2005, generating 24 to 49 million m$^3$ of wastewater and 0.6 to 1.2 million tons of sludge.

A great deal of these effluents has been continuously discharged in soils in the northeast region of the State of São Paulo (SE, Brazil), affecting the soil and groundwater quality, but the effects of these practices are not yet well known. These soils are mineral soils formed under tropical climates subjected to intense weathering. They have a sandy clay loam to sandy loam texture, low activity clay, mainly kaolinite and low organic matter content.

It is known that heavy metals added to soils are rapidly and specifically adsorbed by the solid fraction. However their availability, potential toxicity and mobility within the soil profile will depend upon the binding forms with clays, organic matter and hydrous oxides, oxides and oxyhydroxides; the interactions of their associations with time; the saturation of specific sites of adsorption; the crystallinity and morphology of absorbent surfaces; pH variation and physicochemical characteristics.

Several studies have shown that the availability of Cr(III) in the soil solution is limited by the formation of hydroxides as Cr(OH)$_3$ and Cr$_2$O$_3$(H$_2$O), at pHs between 6 and 12 or by co-precipitation with Fe, forming (Cr$_x$Fe$_{1-x}$)(OH)$_3$, (Cr$_x$Fe$_{1-x}$)OOH, Fe$_x$Cr$_{2}$O$_3$.[16, 17] Another mechanism controlling Cr availability is the adsorption on the surface of Fe, Mn and Al oxides and oxy-hydroxides and clay-minerals, at pH < 6 and adsorption onto organic matter. The Cr(III) oxidation seems to be mainly controlled by the...
sorption on Mn-oxides surfaces followed by the electron transfer and desorption of Cr(VI) and Mn\(^{2+}\)[21, 23] and by MnO\(_2\) amount[24]. Tzou et al.[25] showed that chromium oxidation by Mn-oxides was rapid at acidic conditions and kinetically slow at high pH, inhibited by organic ligands.

Conservative solutes move with soil water and in response to solute concentration gradients[26] and are influenced by soil hydraulic[27] and heterogeneity[28]. These studies require monitoring of a wide range of physical, chemical and biological data. Multivariate analysis is a mathematical tool that can be employed to study the interrelationship among wide data sets by reducing the dimensionality of the data variables[29-31].

Our interest in this work focuses on metal and nitrate levels in soil solution at different depths in an acid soil (Typic Haplustox) with tannery effluents disposal. The data obtained during a one-year monitoring program in a controlled experiment were subjected to factor analysis, to extract information on the relationship between soil solution chemicals and to identify the principal contaminants.

**MATERIALS AND METHODS**

The experiment took place in a 9m\(^2\)-experimental plot, located in Monte Aprazível (NW of the State of São Paulo, Brazil, 20\(^\circ\) 46′S, 49\(^\circ\) 42′W), in the Aw climate zone, according to the Köppen classification. During the experiment (1996-1997) the annual average temperature was 25 °C and the annual average precipitation was 1400 mm. The driest period was observed between the months of July and August/97 (0 mm). The period with most rainfall was from November/96 to March/97 with precipitations from 118 mm to 321 mm.

In the experimental plot, 6 pressure-vacuum lysimeters with ceramic porous cups were installed at 0.5 m intervals to 3.0 m of depth to sample soil solution according to ASTM procedures[32]. The sampling was done applying a continuous suction of 20-40 to 60 kPa. From every sample, a subsample was kept in its natural pH and used for determination of anions (NO\(_3\), SO\(_4\)\(^{2-}\), Cl and PO\(_4\)\(^{3-}\)) by liquid chromatography. A second subsample was acidified to pH 2 with nitric acid for metal analysis (Cr\(_{\text{total}}\), Fe\(_{\text{total}}\), Mn\(^{2+}\), Al\(^{3+}\), Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\), Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\) and Mg\(^{2+}\)) by atomic absorption spectrophotometry. A third subsample was acidified to pH 2 with sulphuric acid for Na\(^{+}\) and K\(^{+}\) analysis by flame atomic absorption spectroscopy. Analytical data was controlled by calibration done with standard solutions in the appropriate matrix and analyzed at the beginning of series and after 10 samples series. Besides the check samples, regularly repeated analyses of the same samples were done. Electric conductivity (EC) and pH measurements were performed in situ (Table 2).

The soil samples were stored at 4°C, dried at 25°C, homogenized, quartered and sieved at 2 mm. They were analyzed for the determination of pH (electrode, 0.01molL\(^{-1}\) CaCl\(_2\)), organic matter, exchangeable ions and cation exchange capacity (cation exchange resin, 1N NaHCO\(_3\), pH 8.5)[34], texture[35] and chemical composition (X-ray fluorescence) (Table 3).

**Statistical analysis:** The correlation coefficients were calculated for the 17 variables values that presented more than 6 valid cases, accepted to factor analysis. Factor analysis was performed from the correlation matrix to extract principal factors with eigenvalues greater than 1 and detect the relationship between the variables. The selected factors were subjected to normalized varimax rotation in order to define a clear pattern of loadings[36]. Analysis of variance was employed on the factor scores to evaluate the effects of effluent load and different depths on the extracted factors. The statistical analyses were carried out in Statistica software package[37].

**RESULTS AND DISCUSSION**

The effluents discharged into the soil presented high variability of the chemical and physical characteristics due to different quantities of processed
The pH values of the soil solution (mean: 7.03) can reflect non-equilibrium condition between soil and soil solution chemistry due to abundant rainfall (summer) that change the moisture content regulating the availability of the elements. Also, the sampling procedures of the soil solution, duration and degree of sampler vacuum, may change pH values.

After the first disposal (700L), the pH decreased in the subsurface (0.5 m) attributed to nitrogen transformations, which affect the acid-base chemistry of the soil and the soil solution. These conditions increased the solubility of Al$^{3+}$ and Mn$^{2+}$. Chromium was not observed in soil solution, probably due to the occurrence of reducing agents, such as ferrous iron and organic matter and sorption onto iron oxi-hydroxides that might contribute to the retention of chromium in trivalent state.

With the second disposal, it was observed that ion concentration increased up to approximately 2.0 m in depth indicating movement of Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, NO$_3^-$ and Mn$^{2+}$. In spite of the great amount disposed (1,700 L), the concentration of Cr$_{total}$ was below the detection limit of the analytical method. In some samples, iron concentration was below the detection limit, indicating that it may have contributed to retention of chromium in the trivalent state probably through co-precipitation reactions, reducing the chance of toxicity for plants and downward migration in the soil profile.

The correlation coefficient matrix is shown in Table 4. The highest correlation ($r=0.93$; $p<0.01$) occurred between Ca$^{2+}$ and Mg$^{2+}$ and Mn$^{2+}$ versus Ca$^{2+}$ and Mg$^{2+}$ ($r=0.85$, p<0.01). Strong and negative correlations were obtained for pH versus Mn$^{2+}$ ($r=-0.77$, p<0.01). The Mn$^{2+}$ presented low concentrations in effluents, but the increase of its availability in soil solution (Table 2), might be related to Mn-oxide reduction caused by Cr(III) and pH decrease. The availability of Al$^{3+}$ was attributed to pH decrease (pH<5.0), according to McBride and to higher potential acidity of these acid soil. Pb$^{2+}$ also present a significant but lower correlation with pH($-0.48$), pointing to heavy metal mobilization and acidification processes. The positive correlation of NO$_3^-$ with Ca$^{2+}$, Mg$^{2+}$, Mn$^{2+}$ and Cl$^-$ (r=0.40 p<0.01) can be the result of a similar solubility and mobility through the unsaturated zone.

**R-mode factor analysis:** Eigenvalues indicated that the first four Factors accounted for 79.20% of the total variance, where all these eigenvalues are greater than one (Table 5). The first Factor accounted for 48.35% of the total variance and presented high loadings (>0.7) for EC, Mn$^{2+}$, Pb$^{2+}$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ and Cl$^-$. This Factor, called “salinity”, emphasizes the important role of Na$^+$, Mg$^{2+}$, K$^+$, Ca$^{2+}$, Cl$^-$, Mn$^{2+}$ and Pb$^{2+}$ in the composition of soil solution, related to the effect of high load effluent disposal, with high salinity.
### Table 2: Soil solution quality attributes at different depths before and after effluent disposal

| Date  | Effluent depth (L) | EC (dS/m) | pH | Cr (mg/L) | Fe (mg/L) | Zn (mg/L) | Ni (mg/L) | Mn (mg/L) | Na (mg/L) | K (mg/L) | Ca (mg/L) | Mg (mg/L) | NO3 (mg/L) | SO4 (mg/L) | Cl (mg/L) |
|-------|-------------------|-----------|----|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|------------|-----------|---------|
| fev96 | 0.5               | 8.1       | 0.23| 11.3      | BDL       | 8.10      | 11.3      | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |
| fev96 | 1.0               | 7.6       | 0.16| 7.0       | BDL       | 5.15      | 7.0       | 5.15      | 2.65      | 2.65     | 2.10      | 0.57      | BDL        | BDL       | 4.7     |
| fev96 | 1.5               | 7.7       | 0.29| 9.0       | 3.40      | 9.70      | 3.40      | 9.70      | 5.05      | 5.05     | 5.05      | 7.55      | BDL        | BDL       | 11.3    |
| fev96 | 2.0               | 6.9       | 0.31| 10.0      | 12.0      | 16.15     | 12.0      | 16.15     | 8.35      | 8.35     | 8.35      | 4.20      | BDL        | BDL       | 20.5    |
| fev96 | 2.5               | 6.7       | 0.23| 11.5      | 12.0      | 11.25     | 12.0      | 11.25     | 6.50      | 6.50     | 6.50      | 4.40      | BDL        | BDL       | 6.4     |
| fev96 | 3.0               | 6.6       | 0.20| 11.1      | 2.62      | 3.8       | 2.62      | 3.8       | 7.65      | 7.65     | 7.65      | 4.20      | BDL        | BDL       | 4.1     |
| mar96 | 0.5               | 7.2       | 0.21| 11.3      | 0.10      | 22.5      | 0.10      | 22.5      | 3.95      | 3.95     | 3.95      | 2.00      | BDL        | BDL       | 18.9    |
| mar96 | 1.0               | 7.1       | 0.14| 7.0       | 0.21      | 20.0      | 0.21      | 20.0      | 7.90      | 7.90     | 7.90      | 4.20      | BDL        | BDL       | 7.0     |
| mar96 | 1.5               | 6.8       | 0.27| 9.0       | 0.32      | 14.0      | 0.32      | 14.0      | 13.05     | 13.05    | 13.05     | 9.30      | BDL        | BDL       | 11.0    |
| mar96 | 2.0               | 6.5       | 0.39| 0.22      | 0.08      | 12.0      | 0.08      | 12.0      | 12.00     | 12.00    | 12.00     | 145.0     | BDL        | BDL       | 6.0     |
| mar96 | 2.5               | 6.6       | 0.21| 0.23      | 0.11      | 11.5      | 0.11      | 11.5      | 11.30     | 11.30    | 11.30     | 57.00     | BDL        | BDL       | 4.0     |
| mar96 | 3.0               | 6.6       | 0.17| 0.12      | 0.07      | 0.11      | 0.07      | 0.11      | 10.25     | 10.25    | 10.25     | 51.00     | BDL        | BDL       | 4.0     |
| feb96  | 0                 | 1.5       | 6.8  | 9.0       | 17.0      | 10.50     | 17.0      | 10.50     | 6.15      | 6.15     | 6.15      | 9.80      | BDL        | BDL       | 3.0     |
| feb96  | 0                 | 3.0       | 6.6  | 9.0       | 16.0      | 10.50     | 16.0      | 10.50     | 5.95      | 5.95     | 5.95      | 9.40      | BDL        | BDL       | 3.0     |
| feb96  | 3.0               | 6.7       | 0.21| 11.1      | 2.62      | 3.8       | 2.62      | 3.8       | 7.65      | 7.65     | 7.65      | 4.20      | BDL        | BDL       | 4.1     |
| afb96  | 0                 | 0.5       | 8.1  | 0.23      | BDL       | 8.10      | BDL       | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |
| afb96  | 0                 | 0.0       | 8.1  | 0.23      | BDL       | 8.10      | BDL       | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |
| afb96  | 0                 | 0.1       | 8.1  | 0.23      | BDL       | 8.10      | BDL       | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |
| afb96  | 0                 | 0.2       | 8.1  | 0.23      | BDL       | 8.10      | BDL       | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |
| afb96  | 0                 | 0.3       | 8.1  | 0.23      | BDL       | 8.10      | BDL       | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |
| afb96  | 0                 | 0.4       | 8.1  | 0.23      | BDL       | 8.10      | BDL       | 8.10      | 3.85      | 3.8      | 3.8       | 2.25      | BDL        | BDL       | 17.0    |

*Note: EC = Electrical Conductivity, Cr = Chromium, Fe = Iron, Zn = Zinc, Ni = Nickel, Mn = Manganese, Na = Sodium, K = Potassium, Ca = Calcium, Mg = Magnesium, NO3 = Nitrate, SO4 = Sulfate, Cl = Chloride.*
Table 2:continued

| Parameter | Depth (m) | pH | EC (dSm⁻¹) | Cr (mg L⁻¹) | Fe (mg L⁻¹) | Mn (mg L⁻¹) | Al (mg L⁻¹) | Zn (mg L⁻¹) | Cu (mg L⁻¹) | Ni (mg L⁻¹) | Pb (mg L⁻¹) | Na⁺ (mg L⁻¹) | K⁺ (mg L⁻¹) | Ca²⁺ (mg L⁻¹) | Mg²⁺ (mg L⁻¹) | NO₃⁻ (mg L⁻¹) | SO₄²⁻ (mg L⁻¹) |
|-----------|----------|----|------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|--------------|----------------|----------------|----------------|----------------|
| mar97     | 1.5      | 2.25 | 0.10 | 0.23 | BDL | 0.11 | BDL | BDL | 428.8 | 20.1 | 11.40 | 7.80 | 484.0 | 263 | 222.5 |
| mar97     | 2.0      | 2.0 | 9.23 | 0.12 | 7.12 | 0.64 | 0.04 | 0.12 | 46 | 1306.2 | 111.1 | 122.50 | 61.00 | 1364.0 | BDL | 2090.0 |
| mar97     | 2.5      | 4.0 | 3.11 | BDL | 0.15 | 0.80 | BDL | 0.04 | 0.12 | 488.7 | 20.0 | 15.10 | 13.50 | 499.4 | BDL | 445.0 |
| mar97     | 3.0      | 5.3 | 5.59 | BDL | 0.17 | 0.98 | 0.49 | BDL | 0.06 | 0.19 | 817.6 | 30.2 | 50.75 | 70.00 | 609.4 | BDL | 1230.0 |

EC: electrical conductivity, BDL: below detection limit; n.a: not analysed

Table 3: Physical and chemical characteristics of reference soil

| Parameter | Depth (m) | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|-----------|----------|-----|-----|-----|-----|-----|-----|
| pH        |          | 4.2 | 4.2 | 4.1 | 4.2 | 4.1 | 4.1 |
| Organic matter (%) | | 1.0 | 1.0 | 0.7 | 0.7 | 0.7 | 0.7 |

Exchangeable (mmol dm⁻³)

| Parameter | Depth (m) | Clay | Silt | Sand |
|-----------|----------|------|------|------|
| K⁺        |          | 7    | 3    | 5    |
| Ca²⁺      |          | 3    | 2    | 6    |
| Mg²⁺      |          | 6    | 2    | 3    |
| SiO₂      |          | 79.60| 79.40| 80.70|
| TiO₂      |          | 2.80 | 2.90 | 2.76 |

BDL: below detection limit; CEC: cation exchange capacity (sum of K, Ca, Mg, H+Al), SB: percent base saturation (sum of K, Ca, Mg / CEC) * 100

The analysis shows that application of tannery effluents increases Mn²⁺, Pb²⁺ solubility and availability in soil solution.

Factor 2 accounted for 12.21% of the total variance related to SO₄²⁻. It is likely that the availability of sulphate depends on higher concentrations in the effluents.

The third Factor with 10.16% of the total variance including Zn²⁺ and Cu²⁺, indicating a behavior similar in the soil, not correlated to soil solution pH (Table 4), possibly due to adsorption reactions with inorganic and organic colloids [42].

Nitrate in high concentrations in soil solution is a contaminant that can leach and contribute to degrade groundwater quality. Therefore, NO₃⁻ was only included at Factor 4 (8.49%). Nitrification, a process that includes microbial activity, presents different dynamics than usual ionic processes and can explain this factor, representative of this delayed process.

The factor analysis using the three first Factors was suitable for explaining the variance of 12 of the 14 variables (Table 5) and it was shown to be an interesting tool to verify the results.

One concludes that high disposal caused significant alteration of soil solution and that clay content could enhance an accumulation of leached cationic species by clay surface adsorption at approximately 2.0 m depth. This depth showed the lower base saturation (Table 3), which contributes to cation exchange and enhances their accumulation.
Table 4: Correlation coefficients of the 17 physico-chemical variables of soil solution. The symbol * show statistical significance at 0.01 level

| pH | EC | Cre | Fcre | Mn²⁺ | Al³⁺ | Zn²⁺ | Cu²⁺ | Ni²⁺ | Pb²⁺ | Na⁺ | K⁺ | Ca²⁺ | Mg²⁺ | NO₃⁻ | SO₄²⁻ | Cl⁻ |
|----|----|-----|------|-------|------|-------|------|------|------|-----|----|------|------|------|-------|-----|
|    | 1  | 1   | 1    | 1     | 1    | 1     | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| EC | -0.70* | 1    | 1    | 1     | 1    | 1     | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Cre| 0.05 | 0.07 | 1    | 1     | 1    | 1     | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Fcre| 0.16 | -0.10 | 0.30* | 1    | 1    | 1     | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Mn²⁺| -0.77* | 0.79* | 0.11 | 0.04 | 1   | 1    | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Al³⁺| -0.71* | 0.69* | 0.05 | -0.04 | 0.62* | 1    | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Zn²⁺| -0.20 | 0.31* | 0.22 | 0.10 | 0.41 | 0.34 | 1    | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Cu²⁺| -0.06 | 0.13 | -0.13 | -0.09 | 0.09 | 0.16 | 0.37* | 1    | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Ni²⁺| -0.64* | 0.74* | 0.13 | -0.03 | 0.76* | 0.72* | 0.40* | 0.17 | 1    | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Pb²⁺| -0.48* | 0.46* | -0.08 | 0.06 | 0.53* | 0.59* | 0.27 | 0.10 | 0.69* | 1   | 1  | 1    | 1    | 1    | 1    | 1   |
| Na⁺| -0.69* | 0.83* | 0.02 | -0.12 | 0.78* | 0.63* | 0.31* | 0.10 | 0.79* | 0.48* | 1 | 1    | 1    | 1    | 1    | 1   |
| K⁺| -0.29* | 0.63* | -0.33* | -0.07 | 0.49* | 0.49* | 0.14 | 0.13 | 0.62* | 0.44* | 0.59* | 1 | 1    | 1    | 1    | 1    | 1   |
| Ca²⁺| -0.59* | 0.78* | 0.18 | 0.03 | 0.85* | 0.63* | 0.45* | 0.07 | 0.79* | 0.66* | 0.71* | 0.64* | 1 | 1    | 1    | 1    | 1   |
| Mg²⁺| -0.66* | 0.80* | 0.07 | 0.05 | 0.85* | 0.62* | 0.46* | 0.13 | 0.79* | 0.66* | 0.72* | 0.60* | 0.93* | 1 | 1    | 1    | 1   |
| NO₃⁻| -0.30* | 0.47* | 0.20 | 0.21 | 0.41* | 0.15 | 0.11 | -0.29* | 0.28* | 0.17 | 0.35* | 0.24 | 0.43* | 0.41* | 1 | 1   |
| SO₄²⁻| 0.06 | 0.11 | 0.13 | 0.05 | 0.08 | -0.10 | 0.20 | 0.01 | 0.05 | -0.06 | 0.22 | -0.04 | 0.05 | -0.04 | 0.00 | 1   |
| Cl⁻| -0.61* | 0.83* | 0.09 | 0.08 | 0.75* | 0.66* | 0.29* | 0.08 | 0.79* | 0.51* | 0.78* | 0.71* | 0.80* | 0.81* | 0.41* | 0.01 | 1   |

The higher decrease of clay contents and the increase of exchangeable-Mg²⁺ at 3.0 m depth suggest the occurrence of saprolite. Therefore, the cation exchange capability at this depth does not represent the real soil exchange capacity.

**CONCLUSION**

The elaboration of data indicated that the impact of tannery effluents on acid soils is notable because of a general increase of heavy metals availability, with the exception of total Cr and Fe, due to the change in soil pH after disposal.

The factor analysis allowed selecting four factors: salinity, SO₄²⁻, Zn²⁺ and Cu²⁺ and NO₃⁻. It is relevant to consider also the active role played by organic matter in the soil and active biotic components at different depths, the latter being directly involved in some enzymatic soil processes such as oxidation/reduction and nitrification activity.

We must take into account that Mn²⁺ was released in soil solution related to Mn-oxide reduction caused by Cr(III) input and pH decrease. On the other hand, chromium, the main heavy metal in the effluents, was not detected in the available forms, probably due to coprecipitation reactions of Cr and Fe and to sorption onto oxides, oxi-hydroxides and hydroxides. It is remarkable the importance of these mineral soil constituents for a reduction of Cr availability and downward migration in the soil profile.

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