GROUNDWATER AND HUMAN DEVELOPMENT
Bocanegra, E - Martínez, D - Massone, H (Eds.) 2002 - ISBN 987-544-063-9

EVALUATION OF HEAVY METAL AVAILABILITY IN SOILS, SEDIMENTS, AND SUPERFICIAL AND GROUNDWATER OF THE ANTA STREAM

Nascimento, S.C. [*+]; *Hypolito, R* [*+], *and Silva, C.T.J.* [*]
* *Institute of Geociências Universidade of São Paulo. São Paulo, SP. Brazil*
+ *Corresponding authors. E-mail address: raphael.hypolito@br2001.com.br*
silvia_cremonez@hotmail.com.br

Abstract. Date concerning the environmental effect of chemical clearly indicate that human activities have accelerated the dispersion of metal and metalloids in the environment and have changed global chemical cycles. The determination and monitoring of specific chemical forms of heavy metals in environmental samples such as the air bone particulates, water, biological material, soils and sediment plows are extremely important. Most of the previous studies have been limited only to the determination of the total concentration of metals. Nevertheless, total concentration donate do not provide suitable information about bioavailability of potential toxic elements, and speciation is now recognize to be the necessary tool to obtain this information. The aim of this work was to determines heavy metal concentrations and availability of polluting metal ions originated from the variety of sources and their dispersion in soils, sediments, and superficial and groundwater samples of seven selected areas along the Anta's Stream. - Northeast of S. J. of Rio Preto - São Paulo - Brazil in one drainage slope of Rio Preto River, inserted in Turvo/Grande watershed. So far, this study is based on the identification and quantification of chemical species and fractionation of metals using different reagents or extracts (sequential extraction), evaluation of ecotoxicological risks to fish, and potential connection to the food chain of human beings.
Keywords: heavy metals, soils, water.

INTRODUCTION

Data concerning on environmental effects of pollutants indicate that anthropic activities have increased in an astonishing way, in the dispersion of metallic ions in the atmosphere and it has consequently changed the global geochemical cycles.

The metals deposited in soils, can be in the form of solutions or incorporated to exchangeable ions on the soil surfaces, being eliminated slowly by leaching, absorption by vegetables etc..

In aquatic ecosystems the contamination for metals can be directly related to the presence of, pollutants in the water or through erosive processes in polluted soils.

There are a lot of works related to the sources of emission and to the chemical behavior and mechanisms of mobilization of metallic ions in water, biological materials, soils and sediments mentioning: SOLOMONS *e.t alii* 1995; KABATA-PENDIAS & PENDIAS, 1995; MESTER *et. alii* 1998; MOISENKO *et. all.* 1999; TOLALIOGLU *et. alii* 2000; MASINI *et. alii* 2002 etc..

The present work evaluated the fraction of heavy metals that could be available for the biota through the sequential extraction of metals, its occurrence, physical-chemistries viabilities, mobilization and the ions transport of Cu^{+2}, Cr^{+3}, Pb^{+2}, Mn^{+2} and Zn^{+2}, originated from different sources of soil/sediments in the Anta Stream (Sao José do Rio Presto - SP).

São José do Rio Preto is located on the northeast of São Paulo State-Brazil, its geographical position is 28 48 ' south and 49 22' west. The Anta Stream is in the northwest of the city; it is located approximately 3 km away from the urban zone (Industrial District II). This district does not have water and sewage systems and it presents, besides several urban recent nuclei, factories, a Landfill that receives urban industrial and hospital wastes and bone flour and tallow factory, which discards their effluents directly in the Anta Stream bed.

MATERIAL AND METHODS

The extraction techniques usually involve competition between the extractor and several components of the soil, through the interference of pre-existent balances, pH changes, action of masses law, introduction of stronger ligants, potential redox changes etc. (TESSIER *et. alii* 1979).

Several extraction procedures have been proposed. The main idea is to extract the metals sequentially by increasing the reactivity of the extractant solution (LAKE, 1987). A lot of studies have been developed with this purpose and seeking to evaluate the amount of available metals in different soils for sequential extraction. This technique is the one witch is given us the most informative results and also being the most accurate on chemical form contained in metallic ions (MILLÁN, *et. alii,* 2000, TOKALIOGLU *et. alii*, 2000).

Several methods of sequential extractions have been proposed for the division of metals in soils, however, there are not any defined patterns, and, for that, there is a very strong variability among the several processes proposed in relation to the nature of the used extractors, their concentrations, time of extraction, relationships extractor/solid phase etc..

This work used the standard methodology adapted by HYPOLITO in preparation, witch consists of five different phases of metal/soil association: a) Solvated Ions; b) Exchangeable Metallic Ions; c) Metallic Ions Carbonates Bounded; d) Metallic Ions Bound to of Fe and Mn Compost and e) Ions Bound to Organic Matter.

Samples of soils and sediments were used (fraction 2,00 mm 1,0000 to 3,0000 g) tap adding to tubes of 125 mL, and centrifuged. After each extraction stage the supernadant was removed, filtered and acidified with HNO_3 (pH <2) for analyses of Flame Atomic Absorption Spectrometry.

Seven sites were chosen, classified from 1 to 7, for soils/sediments sampling. Site 1 refers to riverhead of the Anta Stream; site 2 place is near to the bone flour and tallow Factory, site 3 was an old and inadequate waste deposit; site 4 is the place where the leachate in thrown; site 5 corresponds to a place out of the urban zone; site 6 is near to the estuary of the Anta Stream in the Rio Preto River and the site 7 is a place in the Rio Preto River.

For soil sampling, wells were installed. The number of soil samples varied depending on its characteristics such as color, texture etc..

The bottom sediment samples of the Anta Stream were collected according to the methodology described by CARVALHO, 1994 and APHA, 1995.

The soil/sediment samples were dried, quartered and then separated in fractions smaller than 2mm. All samples were submitted to Laboratory analysis and the Cu^{+2}, Cr^{+3}, Pb^{+2}, Mn^{+2} and Zn^{+2} ions were chemically analyzed as were.

Aiming to know the nature of soil colloidal particles, soil pH was determined (H_2O and KCl), following standard methods of the Agronomic Institute of Campinas (1986), modified by HYPOLITO and cation exchange capacity (CTC). The samples were also submitted to mineralogical analysis by X-ray diffraction.

RESULTS AND DISCUSSION

The soil/sediment samples were analyzed chemical and mineralogically.

The soils samples in the sites PM 1 to Site 4 and the sediments samples of the Anta Stream in the sites 1 to 7, showed granulometric homogeneity, with prevalence of the sandy fraction, being classified as sand and loamy sands.

The values of pH were always positive (Tables 1 and 2), indicating the presence of negative charge in the colloidal superficial particles, that are able to adsorb ions with positive charge.

Mineralogical analyses confirmed that the low values of CTC obtained (Table 3) were due to the presence of kaolinite.

It is interesting to notice that there is also the possibility of the adsorption phenomenon in oxides of iron and manganese. This fact was evidenced by the presence of oxides of iron and manganese covering grains of quartz, that are prevalent in the local soil composition, and, detected through the X-ray diffraction

Table 1: pH of soil samples of e Anta Stream boundaries.

Samples	Depth. (m)	pH (H_2O)	pH (KCl)	ΔpH
PM1 I	0.70	8.13	5.56	+2.57
PM1 II	1.30	6.70	6.69	+0.01
PM2 I	0.87	5.10	4.41	+0.69
PM2 II	2.25	5.97	4.92	+1.05
PM2 III	2.80	5.56	5.00	+0.56
PM 3 I	0.30	6.18	3.75	+2.43
PM3 II	0.80	7.00	6.62	+0.38
PM3 III	1.00	5.87	5.65	+0.22
Site 4 I	After leachate throwing	7.58	7.29	+0.29
Site 4 II	1.00	6.71	6.34	+0.37
Site 4 III	2.00	6.97	6.60	+0.37
Site4 IV	3.00	6.70	6.52	+0.18

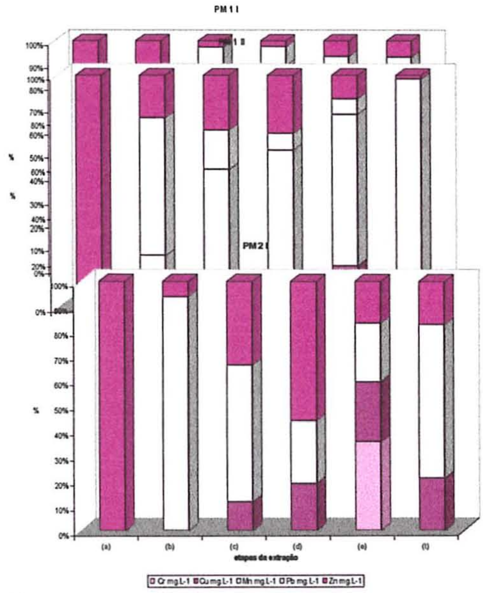
Table 2: pH (H_2O and KCl) of bottom sediment samples of the Anta Stream.

Samples	pH (H_2O)	pH (KCl)	ΔpH
1	6.04	5.45	+0.59
2	5.03	4.06	+0.97
3	7.65	6.62	+1.03
4	5.11	2.08	+3.03
5	6.22	5.74	+0.48

Table 3: Values of CTC (cmolc.kg-1)

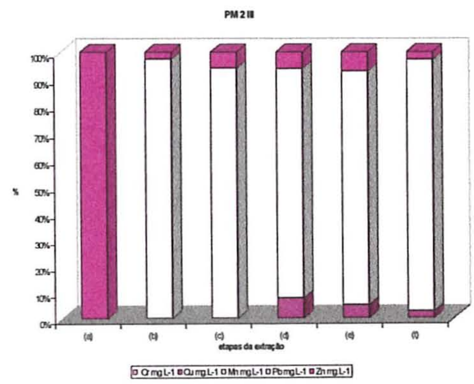
Samples	CTC
PM 1	4.46
PM 3 I	29.76
PM 3 II	25.20
PM 3 III	25.82
4 I	35.15
4 III	38.51

The sequential extraction results are shown in graphics of the elements values in the different stages of the extraction (Figures

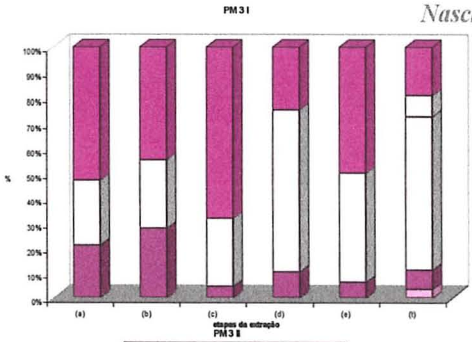


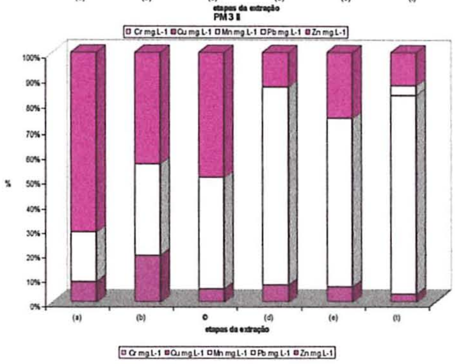
1 and 2).

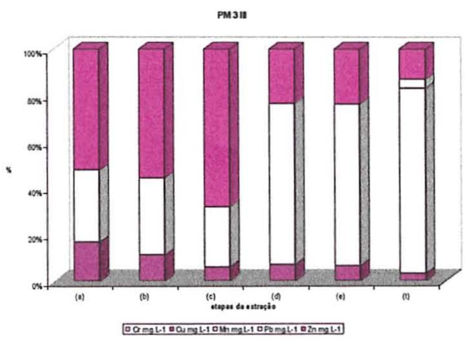
The results of the extractions presented are indicated by the letters a -e, and the resulting values of the total extraction with

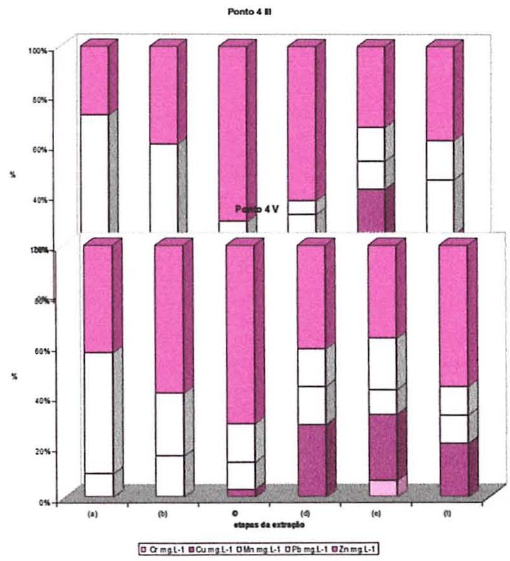


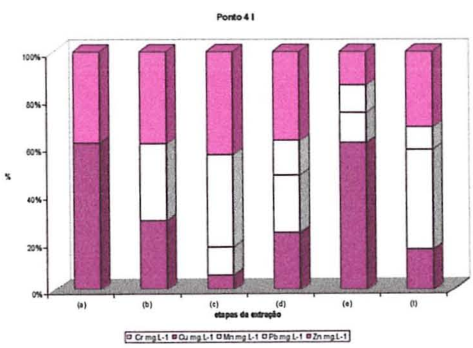
HCl (6M) are represented by the letter t.

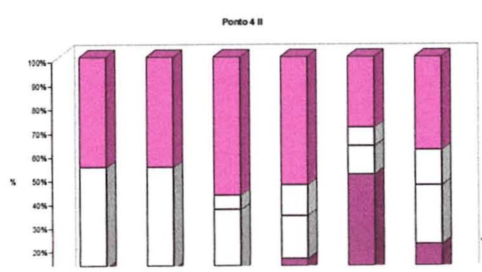

PM3 I
etapas da extração
Cr mg L-1 Cu mg L-1 Mn mg L-1 Pb mg L-1 Zn mg L-1


PM3 II
etapas da extração
Cr mg L-1 Cu mg L-1 Mn mg L-1 Pb mg L-1 Zn mg L-1


PM3 III
etapas da extração
Cr mg L-1 Cu mg L-1 Mn mg L-1 Pb mg L-1 Zn mg L-1


Ponto 4 III
Ponto 4 V
etapas da extração
Cr mg L-1 Cu mg L-1 Mn mg L-1 Pb mg L-1 Zn mg L-1

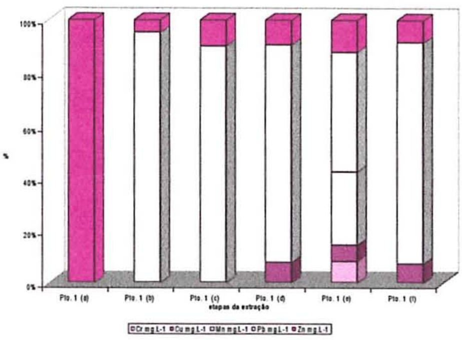

Ponto 4 I
etapas da extração
Cr mg L-1 Cu mg L-1 Mn mg L-1 Pb mg L-1 Zn mg L-1


Ponto 4 II

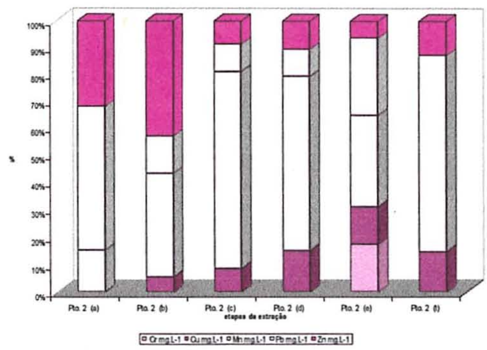
% Zn	% Mn	% Cu	%Cr	% Pb

Figure 1: Percentages of ions Cu^{+2}, Cr^{+3}, Pb^{+2}, Mn^{+2} e Zn^{+2} of boundaries soils samples of Anta Stream, getting of sequential extraction.

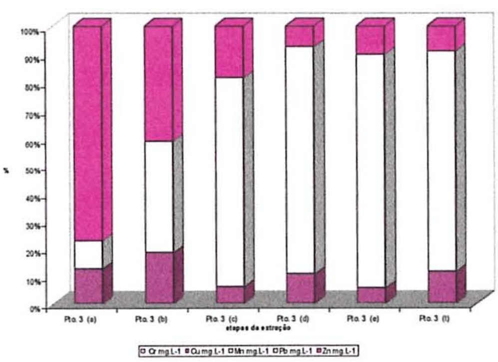
Site 1



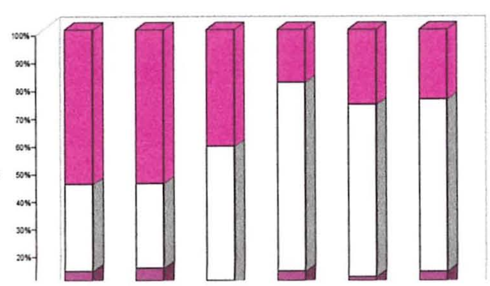
Site 2



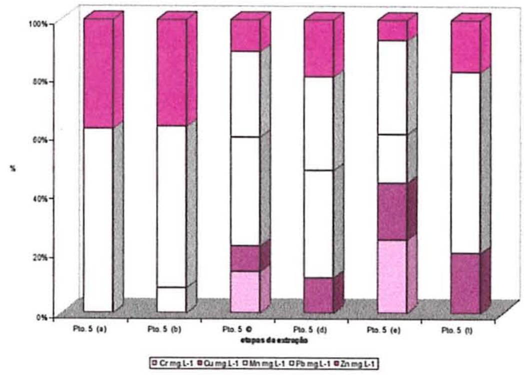
Site 3



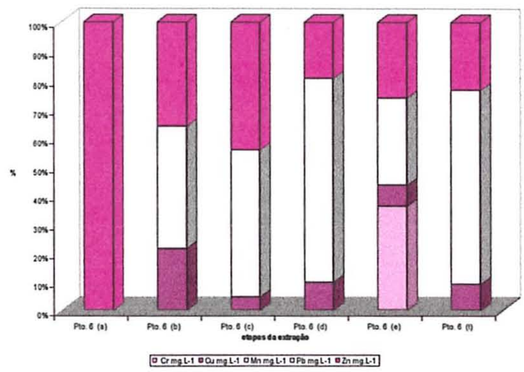
Site 4



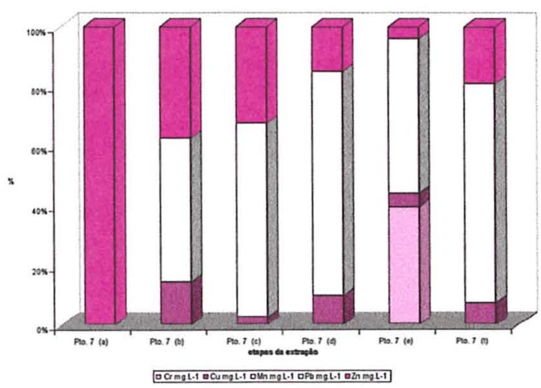
Site 5



Site 6



Site 7



%Zn	% Mn	% Cu	% Cr	% Pb

Figure 2: Percentages of ions Cu^{+2}, Cr^{+3}, Pb^{+2}, Mn^{+2} e Zn^{+2} of bottom sediments samples of Anta Stream, getting of sequential extraction.

The way that the ions behave, was generally the same to soils and bottom sediments of the Anta Stream.

A expected, the present ions in intergranular solution contain a large amount of soluble elements also for Zn, Mn and Cu.

To the exchangeable ions and those bound to the carbonates, the largest availability was, also for Zn, Cu and Mn.

To cations bound to Fe/Mn and Organic Matter, for being dependent of the conditions of pH/Eh, possess high concentrations of Cu, Zn and Mn and expressive values of Pb and Cr.

Bioindicators

Metals deposited in the aquatic environment can accumulate in the food chain causing ecological damages and maybe even human health.

A lot of species of fish are considered top of the food and therefore, the concentration of metals in fish can act as environmental indicator (BERVOETS, 2001).

The accumulation of metals in fish can occur through direct absorption for the ingestion of materials bound to sediments, which are an important reservatory of metals and other pollutants and also through the feeding of bentonics invertebrates (SOLOMONS & FORSTNER, 1984).

Total absence of aquatic life was verified at the Anta Stream. This can happen in spite of the physical-chemical conditions of the waters: pH_{mean} 6,9, OD_{mean} 4,33 $mg.L^{-1}$, $Temperature_{mean}$ $27,9^{0}$ C, and low concentrations of metallic ions.

The presence of heavy metals in the water, can contaminate the aquatic environment even in low concentrations due to cumulative effects (CHEN, 1999; BERVOEIS, 2001; WIDIANARKO, 2000; KARADEDE, 2000).

The experiments in Anta Stream showed that an assimilation of metallic ions in the animal tissue have occurred, in spite of the little time of exhibition.

CONCLUSION

The origin of the pollutant sources of the micro watershed of the Anta Stream, as well as the behavior of the ions bound to soils and bottom sediments is very complex and hard to be understood.

Even the global vision of the micro watershed is hard to be understood once there are sites buried wastes, disposed in different periods of time, randomly distributed for over 10 years that coexist with non polluted sites.

It is also hard to be understood because of the presence, of industries, such as the bone flour and tallow factory that have great portion of atmospheric pollution. Indeed, there is a Landfill, that throws effluents in the Stream and in its boundaries.

The soil that was studied possess relatively high permeability due to its texture with prevalence of the sandy fraction - class sand and sand loamy - with granulation medium to fine, characteristic of the Bauru aquifer.

According to the topography, direction of flow of the groundwater etc. (BOIAN, 1995) the industry discarded pollutants leachates and the ones generated by the gradual decomposition of the inadequate landfill, produce plume of contamination that goes to the Anta Stream.

The fraction clay of the soil possess properties that helps the adsorption of metallic ions, and this fact was confirmed by the values of Δ pH that were always positive (TAN, 1982.)

The way that the ionic behaves in the studied area is intimately related to the pH, Eh, to the nature of the colloidal particles (negatively charged), to the presence of oxyhydroxides of iron and manganese and also to the presence of organic matter in some very high points.

The influence of the kaolinite in the adsorption phenomena was not so significant due to its low CTC. The phenomenon of adsorption is quite significant in the sites with high values of organic matter.

The fixation and availability mechanisms of the metallic ions studied can be understood through sequential extractions.

The ions bounded to the soil of the Anta Stream banks boundaries, as well as those bound to the bottom sediments, presented the same behavior.

Zn was found in all the phases, what made it possible for us to realize that it is the most available cation in the soil, available in all the interstitial solutions.

The Cu is in almost all the fractions, however, it is always in smaller amounts that Mn. It is, in some points, dissolved and in the exchangeable form, thus its availability depends on the presence of other dissolved ions that are capable of moving.

Pb and Cr, were less present in the soil, bounded to the fractions of iron /manganese oxyhydroxides and to the organic matter.

The analysis of these metallic ions in the soil associated to the leachate discard, from the focus to the boundaries of the Anta Stream, showed an uniform distribution of the ions Zn, Cu, Mn

Pb is most bounded to carbonates and distributed in all the phases near to the boundaries (Site 4 V), indicating its migration and accumulation in that direction.

Cr is bounded to the organic matter in the Sites 4 II and 4 V, sites that corresponds to the Stream boundaries.

The bottom sediments of the Anta Stream had the same action observed in the soil. It should be evidenced that Cr appears in larger amounts in the bottom sediments than in the soils and it is especially bounded to the organic matter.

The ions that can be considered labels and due to that mobilized to the waters of the saturated zones, by the action of rains, and by the influence of the ionic strength are: Zn=Mn>Cu >> Pb >> Cr.

Mn is the cation that was more associated to carbonates. Its behavior is intimately bounded to the pH variations and Eh. It can become sufficiently mobile in pHs low enough to dissolve carbonates (pH <6,4) and in pH bound to redox oxygen potential witch can be easily obtain by the present organic matter.

The behavior of the Cu can be compared to the one of Zn, but only in lower concentrations.

Pb is adsorbed to the oxide-hydroxides of iron / manganese and also precipitated in the carbonate form. Its association to the organic matter is also significant: when it is fixed, when adsorbed and available, in the form of complex ions.

Finally Cr, which behavior along with the organic matter should be emphasizes is in appropriate reducer conditions to its presence in the precipitate form like Cr (III).

Fish medium analytic values, in the different sites along the Anta Stream, allow us to assure that the presence of heavy metals should be one of the main factors that impede the aquatic life in the studied ecosystem.

The main causes of contamination observed are those related to the great amount of waste buried in the boundaries of the Stream, with intermittent flows of pollutants, and those generated by the discharge of the industries.

The studied area is extremely hot, with long dry periods, with the ionic flow more concentrate in that time.

Once the mitigation measure we suggest the improvement of the process of treatment of the effluents generated in the Landfill.

For the fixation of the metallic ions, mainly those associated to the old waste deposits, it would be good a chemical action through the control of the pH by the addition of correctives as limestone, for example.

Finally, it is convenient wells settlement to generate the possibility of constant monitoring of the superficial and groundwater.

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