José Ângelo Sebastião Araujo dos Anjos
Luis Enrique Sánchez

Environmental & Medical Geology of the State of Bahia

Environmental Impact Assessment (EIA)

Volume III
Assessment of the Physical Environment of the Plumbum Mining and Metallurgy Co. in Santo Amaro - Bahia, Brazil

Environmental Series

Salvador
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This work is dedicated to the memory of Professor Maria da Glória da Silva

In the journey of life, we meet many people along the way. Very few of them stay for our eternity. Professor Maria da Glória was unique in this respect. By leading a life marked by gratefulness, appreciation, and competence, she became a model for a new generation of black women.

José Ângelo Sebastião Araujo dos Anjos

Maria da Glória in a Training School run by the Federal University of Bahia (1969)

The Maria da Glória Fellowship Badge

The Maria da Glória Fellowship started from a meeting of four black female students from the Geology School of the Federal University of Bahia (UFBA). Though coming from different backgrounds, they shared a common purpose - create a support network to help black students thrive. The Fellowship got inspiration from the life and work of Professor Maria da Glória, as she was one of the first black female professors at UFBA's Geosciences Institute. In view of these facts, we sought information about Professor Maria da Gloria's academic life, considering that none of the students who idealized the fellowship had the honor of living with her. With the discoveries, gathered information, testimonies and access to important works, the bond with Glória's legacy became more intense, as well as the pride of bearing the name of a woman who soared with great intelligence, love , appreciation for others, joy, dedication and competence for what she did.

Through the lenses and significance of her legacy we understand that there should always be a place for the new "Marias da Glória" in the research and academic departments of Higher Education Institutions. We are led to conclude that a supportive and cooperative network makes all the difference, just like Professor Glória made a great difference in the lives of those who had the honor and privilege to learn from her and witness her professional competence.

Those who pass by us, do not go alone, and do not leave us alone; they leave a bit of themselves, and take a little bit of us There are those who take a lot, but there are those who take nothing. This is the greatest responsibility of our lives, and proof that two souls do not meet only by chance.

Saint Exupéry, *The Little Prince*.

Preface

At the time Prof. Dr. José Ângelo Sebastião Araújo dos Anjos was a graduate student, this choice of research topic was guided by his deep interest in applying knowledge to improve the environment. Ângelo envisioned not only "Purifying the Subaé River" (as Caetano Veloso's song goes), but all of Santo Amaro da Purificação, and - why not? - the whole Recôncavo Bay area.

Of course, it wasn't, as it is not, a task for a single individual, but every long journey has its first step. If the path is based on solid knowledge, so much the better. Pollution of water and soil, by lead and other metals, arising from the metallurgy that operated between 1960 and 1993, by its very nature a complex and multidisciplinary issue, became even more difficult with the closure of the factory. The industry area was abandoned, the slag and the contaminated soil remained.

In the second half of the 1990s, contaminated areas were recognized as a serious environmental problem in Brazil, with the first studies started shortly before. Soil contamination with lead was known to be a serious problem, but very little studied.

With the decisive support of the São Paulo State Research Foundation (Fapesp), Ângelo planned and executed his master and doctoral degrees at the Polytechnic School of the University of São Paulo. He made partnerships with other institutions, especially with the Federal University of Bahia, and attracted other researchers. His interest and dedication continue to this day. His teaching career naturally led him to deepen his research, mentoring his own students not only in Santo Amaro da Purificação, but also in the area of the former lead mine in Boquira.

The present digital publication of the studies carried out at that time represents an important initiative that not only documents his pioneering work, but also facilitates access to the information and knowledge on the subject.

Luis Enrique Sánchez

PART I

STRATEGIES FOR THE REMEDIATION OF A SITE CONTAMINATED WITH HEAVY METALS: A CASE STUDY

Sumário

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PRESENTATION

The dissertation entitled "Strategies for remediation of a site contaminated with heavy metals: a case study" (1998), and the doctoral thesis "Evaluation of the efficiency of a wetland in the control of pollution by heavy metals: the case of the Plumbum Co. in Santo Amaro da Purificação/BA" (2003), developed at the Polytechnic School of the University of São Paulo (EPUSP) and supervised by Prof. Dr. Luiz Enrique Sánchez represent a milestone in research on the remediation of contaminated areas in Brazil.

Considering that only in 1999, in a pioneering way, the Environmental Sanitation Technology Company (CETESB), in partnership with the German Institute for Technical Cooperation (*Deutsche Gesellschaft Fur Technische Zusammenarbeit*) launched the "Manual for the Management of Contaminated Areas" as a product of the Soil and Groundwater Recovery Project in industrial waste disposal areas in the state of São Paulo. In that same year, Bojan Schianetz, in partnership with the Paraná State Federation of Industries (FIEP), and associated entities like the CIEP/SESI/SENAI/EIL of Curitiba, published the book "Environmental liabilities: Historical survey. Hazard assessment, and recovery actions" (1999), effectively contributing to studies focusing on preventing the emergence of new environmental liabilities in the country.

In the state of Bahia, studies on the environmental contamination produced by a lead metallurgy in the town of Santo Amaro, in the Recôncavo Bay, dates back to the 1980s. The most significant of these studies were conducted in the 1980s and early 1990 by the Recôncavo Bay Research Group from the Federal University of Bahia (UFBA), led by Drs. Fernando Carvalho and Tania Tavares. The study aimed at identifying the levels of lead and cadmium contamination in hundreds of samples of collected in urban soil, in addition to blood and hair of hundreds of children living in a radius of one kilometer from the metallurgy, producing the first and only study on contamination and health of children under 10 (ten) years of age in the area.

Continuing this line of study, EPUSP, in partnership with the Center for Environmental Resources of the State of Bahia (CRA) and the Center for Research and Development of the State of Bahia (CEPED), contributed to the development of the study carried out by the geologist José Ângelo Sebastião Araujo dos Anjos. This systematized study following the premises of the "Environmental and Medical Geology" represented the first study on the physical environment within the industrial area of the Plumbum Lead Metallurgy, in Santo Amaro/BA. The studies were carried out on the primary and secondary sources of contamination, in addition to the existing contamination routes, as follows: the primary contamination source (slag); secondary sources of contamination (soil and sediment); and the contamination routes (surface water; and groundwater); in addition to proposals for control measures and remediation technologies for the area.

Based on this set of information, and with the participation of a new partner, the Polytechnic School of the Federal University of Bahia (EPUFB), and funding from a Federal Agency program called “Purification Project”, it was possible to conduct a large study within the facilities of the metallurgy, and the use of remediation technologies including a study on the efficiency of wetlands in controlling pollution by heavy metals. The study had the peculiarity of evaluating the process of environmental contamination in the area, taking the Plumbum metallurgy slag basin as its primary source, in three different moments:

a) before the remedial actions produced by the company;
b) during the remediation stage; and
c) after remediation.

Thus, for better content adequacy, the compendium was divided in two parts: the first one is aimed at characterizing the sources and routes of contamination and evaluating the behavior of the main physicochemical processes in the retention and availability of metals. The second diagnosis emphasizes the control of the environmental contamination in a wetland, through the monitoring of surface waters and assessment of the potential availability of metals to the environment. It is important to emphasize the innovative character of the work when evaluating in a pioneering way the potential availability of heavy metals in the Plumbum Co. physical environment, and thus indicating the real values disposed to the environment, through chemical analyzes by sequential extraction, a critical approach for future proposals of environmental recovery of the area.

José Ângelo Sebastião Araújo dos Anjos

Abstract

This work investigated the contamination with heavy metals - lead (Pb) and cadmium (Cd) - in a pilot area, located in the deposition site of the slag produced by the smelting of lead ore, carried out by Plumbum Mining and Metallurgy Co. in the town of Santo Amaro da Purificação, State of Bahia, Brazil, during the period from 1960 to 1993. The investigation of the site involved strategies for the application of standardized procedures (NBRs. 7181/84; 6.010/87; 10.004/97; 10.005/87; 10.006/87; 10,007/87), and was followed by quantitative chemical analyses for soil, surface water and groundwater. The study concluded that: slag is a hazardous waste and in fact represents the only source of pollution at the company's site; surface waters are contaminated with Pb and Cd in the area called "swamp zone"; the soils present high concentrations of Pb and Cd in the areas where slag deposition occurs, and groundwater presents concentrations of Pb and Cd above current limits, in the downstream area near the slag dam. The high hydrogenic potential, the high concentration of organic matter, the cation exchange capacity in the soil, the type of mineral clay (mostly montmorillonite) and the clayish to very clayish soil texture favored the retention processes of metals in the soil, due to active chemical processes like precipitation, adsorption and complexation. The high concentration levels of metals found in the wetland (associated with the other indicators used in the study) suggest that this zone acts in the control and retention of metals, being efficient in reducing water pollution.

Keywords: contamination, slag, cadmium, lead

INTRODUCTION

1.1 Choice of theme

Sites contaminated with industrial toxic waste, mine waste, transport infrastructure, thermoelectric plants and nuclear installations are characterized as one of the most serious socio-environmental and economic problems at the end of the millennium and have led government agencies and private sectors to apply millions of dollars, almost always non-refundable, as remedial measures.

The industrialization process introduced since the last century has notably increased the contamination of these areas. However, contamination on a smaller scale come from civilizations from the time before Christ (BC), such as the lead and silver mines in southern Spain', exploited by the Romans[1] in the height of their empire.

In Brazil, particularly in the State of Bahia, this process started early in the 1930's with the discovery of oil in the Recôncavo Bay. This event establishes the limit of occupation of the areas of agropastoral and agro-industrial vocation of the Recôncavo Bay, by the implantation of a set of prospection and extraction techniques, in addition to its industrialization, with the installation of the first refinery in Brazil. Then, in the 60s, the Aratu Industrial Complex (CIA) was implemented and later, in the 70s, the Camaçari Petrochemical Complex (COPEC).

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[1] Researchers have found lead trapped between sheets of Greenland ice, from atmospheric pollution, more than 300m deep. Studies on the isotopic composition of lead found in ice determined that it was found in the Spanish region of the Rio Tinto, a region that was explored by the Phoenicians of Carthage before the arrival of the Romans. According to studies, the annual production reached 100,000 tons of Pb and the technique used to purify the ore caused 10 to 15% of the Pb present in the rock to end up in the atmosphere (MARTINHO, 1997).

Most probably, many of these industries have their sites contaminated with toxic residues and, through anthropic actions, have modified the balance of the active processes, while the metals contained in the residues have been made available, causing their bioaccumulation in the food chain and damage to humans (physical deformations and even death). These contaminated sites are a consequence of the deposition or dumping of contaminated industrial waste in inappropriate areas or the emission of particulate matter.

The contamination is related mostly to a lack of specific public policies, such as laws, norms, and incentives for the development of control techniques or remediation technologies and determination of "background" for shut down or functioning areas. In addition, a lack of structure and technical training of the agencies that promote environmental management policies, as well as the ability of entrepreneurs to anticipate the government, executing corrective procedures already adopted in developed countries.

In this sense, the American Congress was a pioneer in regulating, in 1980, after the *Love Canal*[2] episode, the Comprehensive Environmental Response and Liability Act (CERCLA), popularly known as "the Superfund'[3], which established investigation standards and the liability of agents that contributed to the contamination of an area.

Nearly two decades have passed after the first law was passed and many areas continue to be contaminated. However, it was not until 1993 that the Environmental Sanitation Technology Company (CETESB),

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[2] 2 In the 1940s, around 19,000t of chemical waste, packed in steel barrels, were deposited in an abandoned canal called "Love Canal". In 1953, the landfill was covered and a school and later residences were built on it. The anomalous occurrence of rains raised the level of groundwater and transformed the area into a wetland, contaminated with chemical residues leaked from steel barrels. Investigations carried out at the site revealed the presence of 248 different chemical substances, 11 of which were proven to be carcinogenic. The waste contaminated children and neighborhood residents, resulting in a legal dispute that initially awarded New York State $98 million in 1994; other legal proceedings are still in progress and so far the area has not been completely recovered (SÁNCHEZ, 1998).

[3] First law dealing with contaminated areas, especially soils, and created a fund to finance the cleaning of contaminated sites. The literature uses "CERCLA" as a synonym for Superfund.

representing the Government of the State of São Paulo in agreement with the *Deutsche Gesellschaft fur Technische Zusammenarbeit Gmbh* (GTZ)[4], began the Technical Cooperation project called " Contaminated Areas". This project, in its preliminary stage, has already characterized the existence of 2,300 potential areas in the metropolitan region of São Paulo.

The State of Bahia does not develop any specific program for the remediation of contaminated sites. However, some studies, such as the Registry of Potentially Polluting Industrial Activities (CRA, 1984), the Environmental Quality Diagnosis in the Recôncavo Bay and its Surrounding (CEI, 1984), and the proposal for water quality standards for the Subaé River Basin (BAHIA, 1995b) presented surveys and propositions to minimize the effects of industrial contamination.

The studies indicated that the Recôncavo Bay and its surroundings were contaminated with heavy metals, due to the inadequate disposal of effluents and urban and industrial waste (AZCONA et al., 1996).

Among the sites with a high degree of environmental compromise, there is the estuary of the Subaé River, in the town of Santo Amaro da Purificação, where the Plumbum Mining and Metallurgy Co. was located.

The company, shut down in 1993, produced and randomly deposited 490,000t of slag contaminated with heavy metals - especially lead (Pb) and cadmium (Cd) - used by the population of Santo Amaro to pave gardens, patios of houses, squares and school areas, and is still used today by the City Hall for paving streets and landfills. The company admits to having released 400t of Cd to the atmosphere during the period from 1960 to 1977, besides a monthly average of 1.152t of SO2 , during the 33 years of production

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[4] Company that contracted the German company Kratzig Engineering to carry out the Technical Cooperation project jointly with CETESR. This project aimed at minimizing the risk of contamination to the population and the environment through a "set of corrective measures that allow the most appropriate intervention" (GLOEDEN et al., 1977).

(CRA, 1992). However, according to the same author, the amount of lead and cadmium particulate matter released into the atmosphere is difficult to measure, as Plumbum did not use any measurement of its emissions.

In view of the high level of environmental degradation in the Subaé River Basin, one of the main sources of pollution, the State Administration developed a recovery plan, called Pró-Subaé, as part of a depollution Project, in partnership with the World Bank (BAHIA, 1995a). This plan is intended to solve the undue discharge of sanitary and industrial sewage in the area, with the construction of a sanitary sewage system and landfills for domestic solid waste.

However, notwithstanding the great potential for contamination in this basin, there was no proposal for the creation of specific environmental management instruments, of a corrective and/or preventive nature, that could investigate, evaluate and recover shut down or functioning sites contaminated with toxic waste .

1.2 The Plumbum case

The Brazilian Lead Co. (COBRAC), with French and national capital, originally belonging to the multinational group Penarroya, began operations in Santo Amaro da Purificação, BA, in 1960, as a plant to produce lead ingots. In 1989, Cobrac was incorporated into the Plumbum Mining and Metallurgy Co., belonging to the Trevo Group.

Since the beginning, the operations of the metallurgy motivated a series of complaints from the surrounding rural population[5]. The

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[5] The first study carried out on the contamination of the area was contracted by ranchers and developed by Dr. Hans F.K. Dittimar. This study held COBRAC responsible for the contamination of soil, air and water and for the death of cattle, and the deactivation of the industry was then requested, based on the violation of the Decree nº 50.877 of June 29, 1961, referring to the pollution of water courses . The problem was solved with the acquisition by COBRAC of all the land and compensation for the dead animals (OLIVEIRA, 1977).

dissatisfaction stemmed from the first signs of contamination, evidenced by the death of cattle and horses in the areas adjacent to the enterprise.

The continuity of this process of environmental degradation contributed to the contamination with heavy metals (Pb and Cd), of the water, soil, flora and fauna (OLIVEIRA, 1977; CRA, 1992; PAREDES et al., 1995; SANTOS, 1995 and TAVARES, 1990 and 1997), as well as the populations, especially children (TAVARES, 1990 and SILVANY-NETO et al., 1996).

The main sources of contamination identified in COBRAC, during the inspection of the Environmental Resources Center (CRA) in 1992 at the request of the Public Ministry, were:

a) particulate matter expelled through the chimney;
b) liquid effluents discharged directly into the Subaé River or by overflowing the tailings basin;
c) drainage water from the slag storage area, and especially;
d) slag, previously considered innocuous by the entrepreneur and used by the population and the local administration for the most diverse purposes.

Once the contamination was recognized, the Special Secretariat for the Environment (SEMA), in agreement with the Center for Research and Economic Development of the State of Bahia (CEPED) - at that time responsible for environmental policies - and the Federal University of Bahia (UFBA) carried out research on the contamination of the Bay, which served as a basis for, in the first instance, an opinion against the expansion of COBRAC and the demand for preventive measures.

Research carried out by UFBA University before (1980) and after the corrective measures (1985 and 1992) and the expansion license[6] issued by the environmental agency, showed that Cd levels in soil and water were reduced in a much greater proportion than that of Pb, as well as the levels of Cd and Pb in infant blood. However, new cases of intoxication risks continued to emerge, indicating that such measures were not enough.

Possibly, the new cases were related to the distribution of slag throughout the municipality, acting as a dispersed source of pollution and providing, initially, the development of mechanisms for retaining metals in the soils and, later, making them available in the system.

During the period 1994/95, shortly after the decommissioning of the enterprise, CRA, on its own initiative or in conjunction with Plumbum, carried out leaching and solubilization tests on the slag to confirm its degree of toxicity. Most of the results obtained by CEPED and CETESB revealed levels of Pb and Cd that classified the slag as class 1 - Hazardous waste, according to the NBR 10.004- Solid Waste: Classification (ABNT) (SANTOS, 1995).

The characterization of the contamination led the CRA, in 1994, to require Plumbum to implement an adequate disposal plan for slag and water monitoring. However, non-compliance with these requirements, justified by the company to lack of resources[7], led to the abandonment of the areas where

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[6] The expansion license was conceived by the State Environmental Protection Council (CEPRAM), ·following studies on contamination at the Plumbum metallurgical plant developed by UFBA. The studies authorizing the Expansion License replaced and discarded the initial opinion produced by the environmental agency (CEPED), upon issuing Resolution No. 54 and 10.8.80.

[7] According to the 1996 Mineral Summary, "The Plumbum Mining and Metallurgy Co. belonging to the Trevo Group is planning to implement a metallurgical project worth US$ 60 million, involving a state-of-the-art production system. In addition, it is in the process of starting operations for the exploration of lead, zinc and silver ores, in Torocapa, Bolivia, to where it will transfer all the equipment installed at the mine in Boquira-BA".

the slag was deposited and to the continuous process of contamination of the physical environment, the biota, public areas and the local communities.

1.3 Earlier studies in the area

The contamination of the area was initially studied by a multidisciplinary group of professors from UFBA University. As found in the surveys, mangroves and fishermen from the Subaé River estuary, animals that graze in the slag deposition areas, vegetables produced on the outskirts of the city, soil around the enterprise and blood samples from children aged up to 10 years living in a radius of 900m from the metallurgy chimney presented Pb and Cd values well above the limits established by current regulations (TAVARES, 1990).

Studies conducted in the Subaé River Basin identified that the contamination listed above comes from:

- the installation of the metallurgy in the area where low-speed winds and constant thermal inversions predominate, what makes dispersion difficult and favors the precipitation of particulates in the urban area;
- the proximity of the metallurgy to the bed and flooding areas of the Subaé River;
- the overflow of the tailings basin in periods of high rainfall;
- the low flow rate of the Subaé River, making it difficult to dilute and disperse untreated liquid effluents;
- the inadequate disposal of the slag in landfills, and its reuse for the construction of roads and residential areas, significantly increasing the contamination of soil, surface water, groundwater and the populations living in the vicinity;
- the high concentration of metals in the mangroves of the Subaé River estuary, contaminating shellfish that serve as a food in the region;

- the particulates expelled by the metallurgy chimney, contaminating edible vegetables, surface water, soil and the populations surrounding the metallurgy;

In 1996, the UFBA team presented the results of a study in the Bay area confirming the contamination of the Subaé River estuary by lead[8] (TAVARES, 1996). The study also revealed the existence of cadmium enrichment in the sediment north of the BTS, but not characterized as contamination.

The confirmation of contamination with Pb from Plumbum is unequivocal. Sequenced studies have confirmed this degradation, but without specifying the sources of contamination, not even the mechanisms that have caused the pollution and its availability in the system.

1.4 The study area

A significant number of factors were taken into consideration in the decision to develop the study in this area, especially the following:

a) the slag in the area represents the only unresearched source of pollution, from the point of view of its behavior in soil and water contamination;
b) the slag is the main source of pollution remaining after the deactivation of the metallurgical complex;

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[8] The study concluded that only 12% of sediments and shellfish are below the Pb levels established by the US coastal monitoring program. The fish is unfit for consumption but it continues to be consumed by the small fishing community, sold in grocery stores and street markets around the Recôncavo Bay area. According to the study, this contamination will be confirmed if an adult eats 200g of shellfish from the sampled locations, children being in a very delicate situation, since the studies established half the value for ingestion. It also showed that to the north of the bay, in the area of influence of the Landulfo Alves Refinery, there is another anomaly of lead contamination, resulting from the addition of tetraethyl lead to gasoline by Petrobras in the past. For cadmium, only 21% of the sampled points detected values higher than the reference standard used by coastal monitoring in the USA.

c) the amount of assets to be protected is quite significant (soils, the Subaé river and its estuary);
d) the factory was shut down but no control measures have been adopted;
e) a napkin manufacturer is in the process of starting its operations on the premises of the former company, without the assessment of the existing contamination;
f) the Resolution No. 812/93, of the State Environmental Protection Agency (CEPRAM), which issued the Plumbum Operation License, "recommends that State authorities look for economically viable technological alternatives for the recovery of the slag to mitigate the identified problems";
g) no remediation project was presented for the areas contaminated with heavy metals, within the scope of the Environmental Sanitation Program for Salvador and cities around the Bay area (Pró-Subaé);
h) Plumbum is classified by the non-governmental body - Environmental Recovery Group (GERMEN) - which evaluates the environmental performance of projects in the state, as the second most degrading project in the state of Bahia;
i) the studies conducted in the area can be used by CRA in initiatives to recover the area and by the Public Ministry, in the continuation of the civil liability process brought against Plumbum; and
j) the concrete possibility to propose measures to remediate the area;

The case of the Plumbum Co. represents a classic example of a site neglected by the entrepreneur, presenting a large environmental liability not yet quantified and with actions developed by public agencies in a palliative and disjointed way, mostly related to a lack of specific public policies[9].

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[9] SÁNCHEZ (1997, 1998) presents an extensive approach on typologies of policies for the management of contaminated sites, developed in North America and Europe. The following policies were raised:

CHAPTER 2: OBJECTIVES

The general objective of this work is to investigate the contamination with heavy metals from slag and propose control measures in a pilot area, located in the slag deposition site produced by The Plumbum Mining and Metallurgy Co., in Santo Amaro da Purificação-BA, with the following specific objectives:

a) characterization of the slag as a source of pollution according to standardized sampling and chemical analysis (leaching and solubilization) for Pb and Cd;

b) characterization of surface and groundwater pollution through standardized sampling and quantitative analyzes for total metal for Pb and Cd;

c) characterization of soil contamination through standardized sampling and quantitative analyzes for total metal for Pb and Cd;

d) preliminary evaluation of the main geochemical processes - precipitation and solubilization, adsorption and complexation - responsible for the retention or mobility of heavy metals, through the following physical-chemical parameters: hydrogenionic potential (pH); cation exchange capacity (CTC); percentage of organic matter; soil texture and type of clay; and

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negligence, an approach to policy that does not develop any control mechanism or wait for the problem to manifest itself; the reactive approach, characterized when there are suspicions of health risks or application of the existing legal framework; the corrective, when there are studies to apply the multifunctionality of the soil, inventories of potentially contaminated sites and forecast of public agencies for the remediation of the sites; preventive, when there is a plan to shut down contaminated areas through viable instruments, and proactive, when there is effective management for all stages of an enterprise's life.

e) proposal of a remediation and monitoring technique capable of controlling the pollution.

2.1 Scope of the work

To describe the work carried out in the area and present the results, this dissertation consists of the following chapters:

Chapter 3 briefly deals with the characteristics of the physical environment, location, hydrography, climate, geology, geomorphology and soils, in addition to anthropic actions that occur in the studied area.

Chapter 4 presents a brief report on the history of the Plumbum Co., including the main procedures for the issuance of the environmental licensing, the measures adopted during the deactivation phase and the new reuse activities carried out on the former company premises.

Chapter 5 briefly presents the main physical and chemical properties of Pb and Cd, the analytical methods used for chemical analysis, the sources of human exposure and the effects of these contaminants on humans.

Chapter 6 highlights the method for the recovery of degraded areas by the disposal of industrial waste, through the application of standardized procedures, which initially involved the characterization of the source of pollution and the identification of its contamination with Pb and Cd, followed by the characterization of the contaminated soil, groundwater and surface water in the pilot area, including a preliminary assessment of the main chemical and physical processes responsible for the retention, attenuation or mobility of heavy metals.

Chapter 7 presents a basic proposal for implementing the remediation plan, indicating the measures and control technique that best fit the effective technique, easily accessible, economically viable and suitable for the tropical environment.

Chapter 8 is reserved for the final considerations of the dissertation and the proposition of studies and measures that better explain aspects not addressed in this dissertation or that require a more specific approach.

CHAPTER 3 - CHARACTERIZATION OF THE AREA

"It is so large that, for antonomasia and excellence, it rises with the common name and, appropriating itself, is called Bahia, and with good reason, because it holds a greater bay, more islands and rivers within it than many are discovered in the world" .

SALVADOR (1627) apud OLIVEIRA (1997)

"in all recesses of the Recôncavo Bay...lots of seafood of all kinds...especially very large oysters"

NEWS FROM BRAZIL (1587) apud OLIVEIRA (1997)

"the Recôncavo Bay... where a lot of sugar, tobacco, and piassava fiber are highly cultivated and produced "

HARTT (1870) apud OLIVEIRA (1997)

Man, by instinct, looks for fertile land for his home that will provide him with sustenance and shelter. This was the case with the lowlands around the Recôncavo Bay, where the Subaé River Basin is located, with a mild temperature, productive and little uneven soils and a very humid and fishy estuarine-lagoon environment.

This scenario has been changing since the initial occupation by the Tupinambá indigenous tribes, then by the Portuguese, and later by the blacks brought from Africa for forced labor, in the longest and most important socioeconomic-cultural cycle developed in the area, the sugarcane culture.

(FONSECA, 1997).

3.1 Physical characterization

3.1.1 Location

The Plumbum Plant is located northwest of the urban area of the town of Santo Amaro da Purificação (Figure 3-1), 300m from the right bank of the Subaé River, the main river in the Subaé River basin, in the Recôncavo Bay of Bahia. It is 75km away from Salvador through highways BA-096 and BR-324, in coordinates 12° 33' south and 38° 42' west.

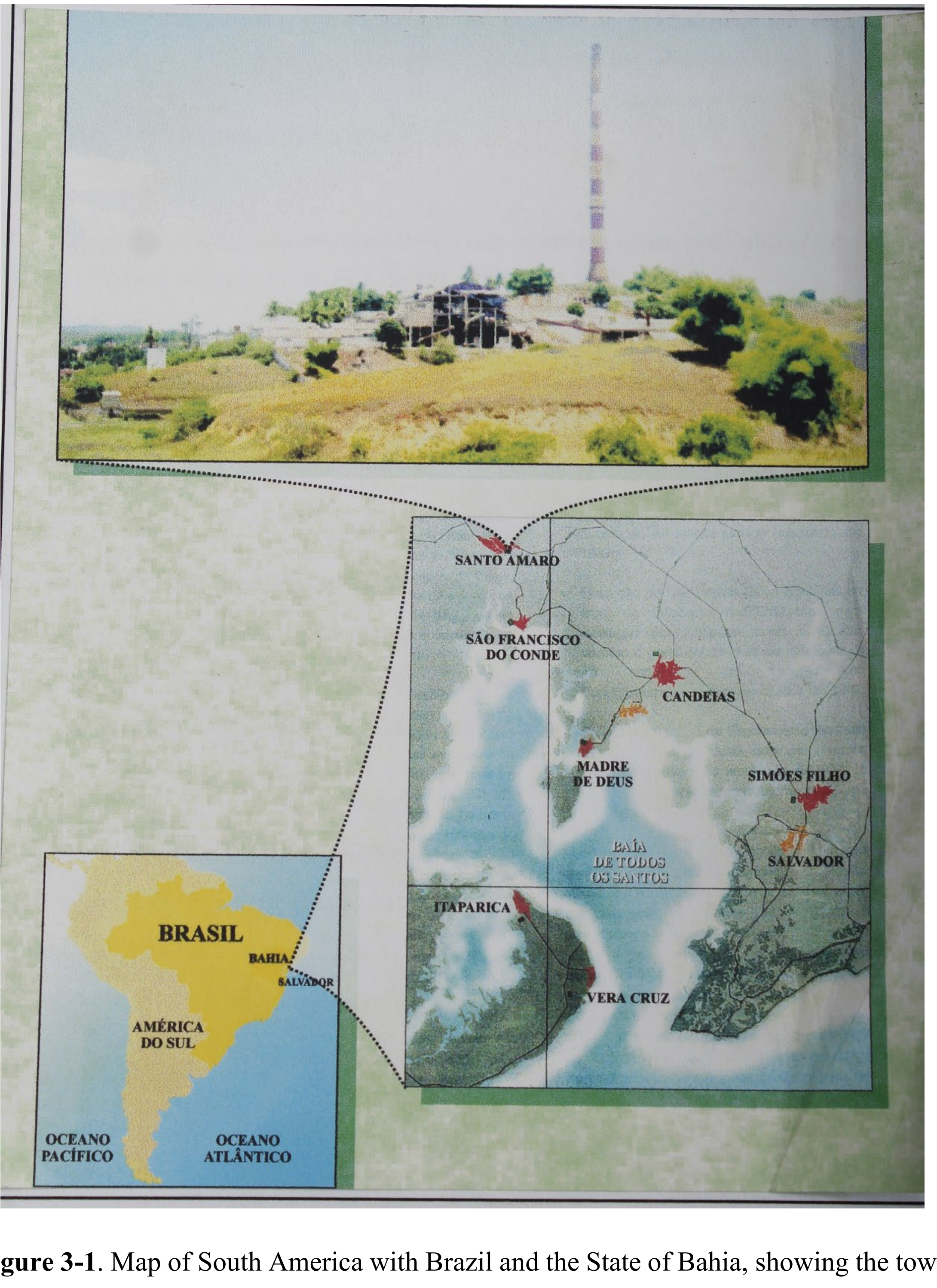

Figure 3-1. Map of South America with Brazil and the State of Bahia, showing the town of Santo Amaro da Purificação to the north of the Recôncavo Bay, and, in detail, the installations of the Plumbum Mining and Metallurgy Co.

3.1.2 Hydrography

The Subaé River basin (Figure 3-2) has a drainage area of 580 km^2 and a length of 46 km. Its main tributary is the Sergi River, whose mouth is north of the BTS, forming the island of Caraíba in its estuary.

The Subaé River has a flow rate around 1,273 m^3/s, at the point right of intersection with its effluent, the Sergi River, north of Santo Amaro (BAHIA, 1996).

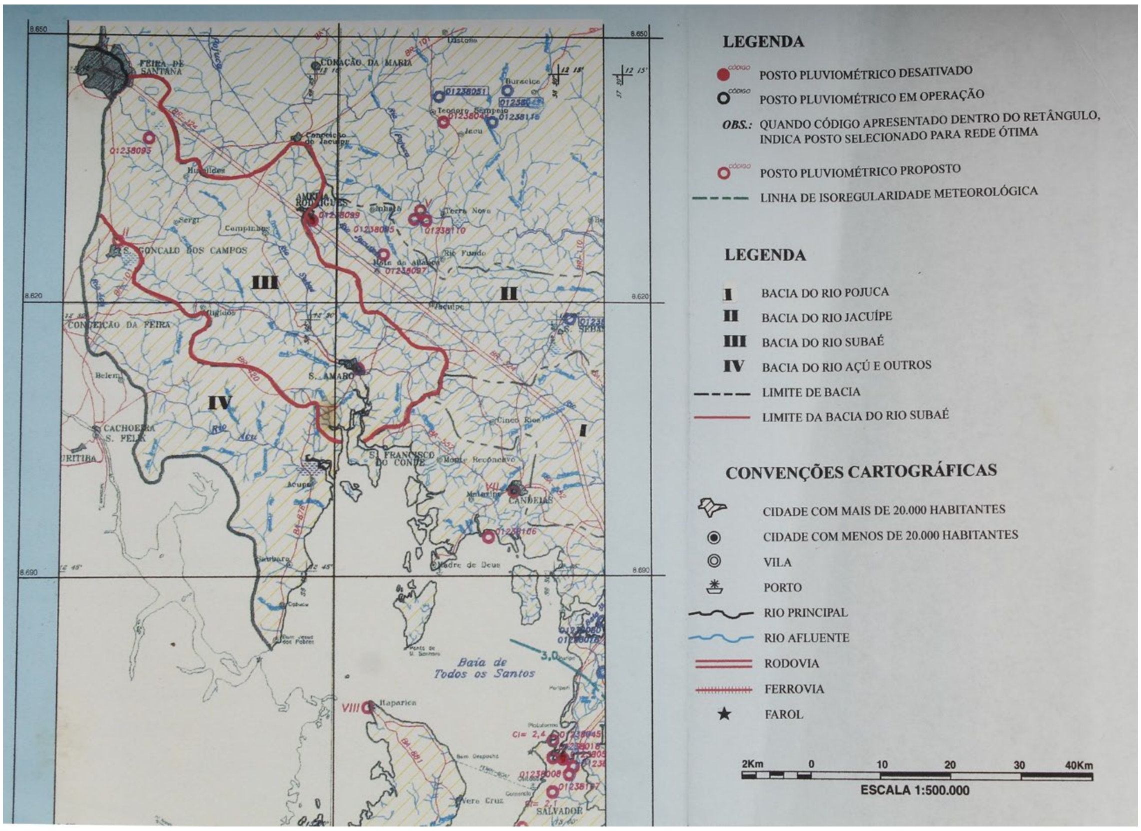

Figure 3-2. Map of the Subaé River Basin with its main tributaries. Adapted from BAHIA (1996).

The framework for the waters of the Subaé River and its tributaries was established in 1995, with the stretch between its source, in the municipality of Feira de Santana, and the estuarine zone (south of the town of Santo Amaro) classified as class 2, and the estuarine zone close to its mouth in the Bay in class 7[10] (BAHIA, 1995b).

The quality of the water is compromised especially downstream of Santo Amaro, where it receives a large contribution of organic loads from the paper industries and all domestic waste and sanitary sewage from the town of Santo Amaro, turning it critical until its mouth.

3.1.3 Climate

The area presents a humid to sub-humid and dry to sub-humid climate, with rainfall of less than 100mm but greater than 60mm in the dry months, an average annual temperature of 25.4°C, with an average maximum of 31°C and average of minimum of 21.9°C, with the rainy season from April to June. Annual rainfall varies from 1,000 to 1,700 mm and the rivers are perennial.

Studies on average precipitation during the months of the year, based on data collected from 1961 to 1963, show the months of May and December with the highest and lowest average precipitation, respectively (BAHIA, 1996).

3.1.4 Geology and geomorphology

"Until about 180 million years ago, South America and Africa formed a single continental mass, as the Atlantic Ocean did not yet exist. In one area, between the current coasts of the continents, a narrow, elongated depression was formed, between Pernambuco and Rio de Janeiro: the Afro-Brazilian Depression. Within this depression, a rift was then developed,

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[10] Class 2 and 7 are, respectively, classified as fresh water and brackish water, the former intended for domestic supply, after conventional treatment, for the protection of aquatic communities, and primary contact recreation (water skiing, swimming and diving), the second is intended for primary contact recreation, the protection of aquatic communities, and the natural and/or intensive breeding (aquaculture) of species intended for human consumption (CONAMA, 1986).

which later gave rise to the Atlantic Ocean. In the region of Salvador, we have a branch of this rift, forming the Recôncavo-Tucano-Jotabá depression.

LEITE (1997)

Geologically, the area is inscribed in the NE feature of the São Francisco craton, in the Recôncavo sedimentary Basin, of Meso-Cenozoic age, delimited by a subparallel system of normal faults (rift) presenting predominantly silty dark gray and greenish shales, and fine and clay sandstones from the Santo Amaro Group.

The geomorphology of the area is characterized by a coastal depression, represented by lowered hills and plateaus with altitudes below 100m and interfluves with slopes with concave aspects, carved in shales of the Santo Amaro Group of rocks (BAHIA, 1996).

3.1.5. soils

"for some, the Recôncavo is, in the strictest sense of the word, the area of massapê soils in the north of the Todos os Santos Bay"

DOMINGUES et al., (1956) apud OLIVEIRA (1997)

This region is constituted predominantly by vertisols, originating from greenish shales interspersed with limestone from the Santo Amaro Group (Figure 3-3). The vertisols are characterized as clayish to very clayish soils, with clay content of the montmorillonite group, which presents contraction and expansion characteristics depending on its moisture content, moderately drained to poorly drained and with low permeability (BAHIA, 1996). .

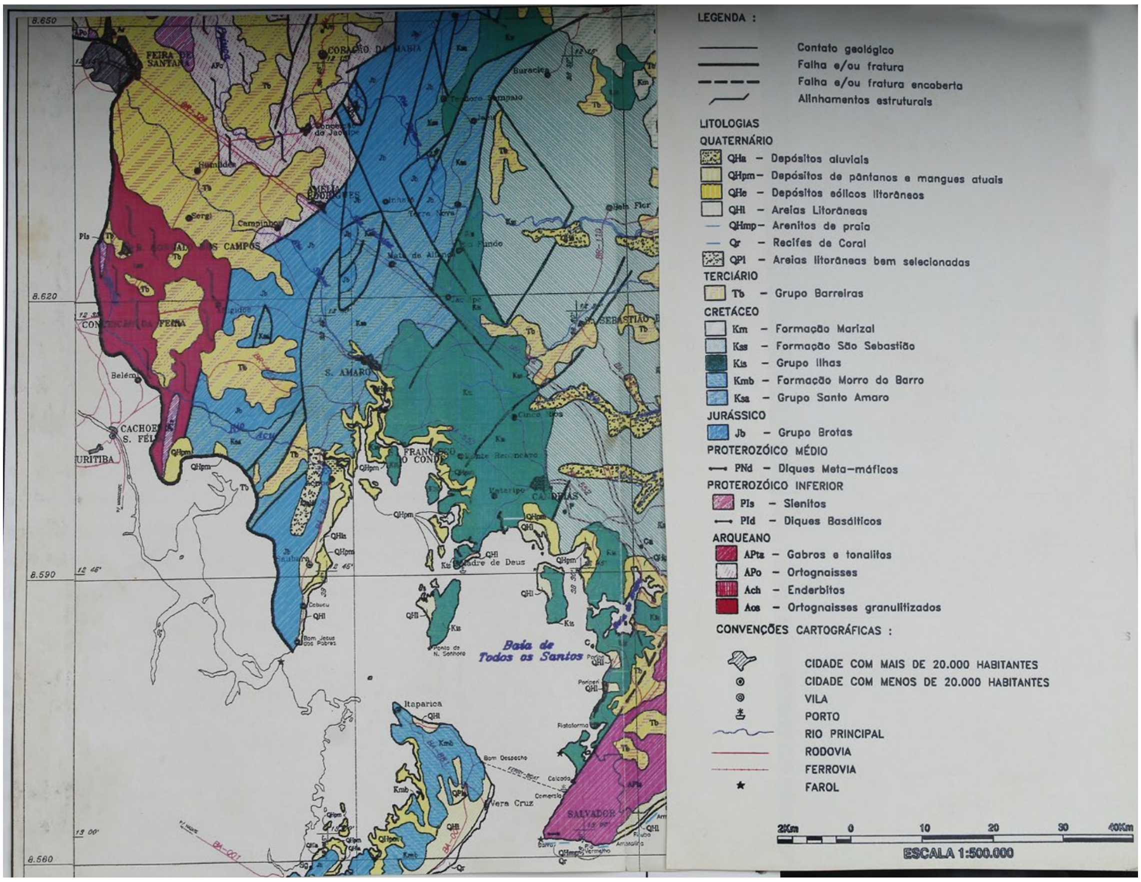

Figure 3-3. Geological map of the Santo Amaro region showing the main variations of the lithology. Plumbum Co. is located on shales of the Santo Amaro Group of rocks, which occurs in an elongated form predominantly in the north/south direction, with approximately 70 km in length and around 10 km in width. Adapted from BAHIA (1996)

3.2 Anthropic action

"And if the damage he does to the trees is worth four thousand reis, he will be flogged and deported for 4 years to Africa. And if it is worth 30 cruzados, and from there onwards, he will be deported forever from Brazil!".

Hombeeck Jr., (1977) apud TAVARES et al., (1997)

According to PINTO (1958) apud OLIVEIRA (1997), the Recôncavo is characterized as the area where for more than four hundred years "one of the oldest chapters of the colonization of Brazil has been unfolding". This is related to the main aspects of territorial occupation (military, religious and civil) and their respective economic cycles, such as pau-brasil, sugarcane, whale fishing, tobacco; cassava flour; textile industry; petroleum; extractive industry; transformation industry; petrochemicals and tourism (SENNA, 1997).

This socioeconomic-cultural evolution transformed the physical landscape, compromising the quality of the environment, and leaving for the current and future generations a desolate and pessimistic legacy of an extractive society uncommitted to the environment.

The first and major environmental damage came with the sugarcane cycle, which, started in 1655, lasted as the main economic driver in the Recôncavo region until the 19th century, with the construction of 80 sugar mills in the 16th century, 300 in the 17th century and 1500 in the 18th century (SENNA, 1997).

According to TAVARES et al., (1997), the intensity of the devastation of the forests was so great, to the point of creating a Portuguese legislation to contain wildfire in Brazil[11].

After the sugarcane cycle came the oil cycle, largely responsible for the contamination of the Bay with crude oil and lead, especially in the vicinity of the Landulfo Alves Refinery (TAVARES et al., 1997), in addition to drilling wells in terrestrial and maritime platforms without any zeal for the environment, causing the pollution of countless beaches, mangroves and inducing the expansion of slums in their surroundings (SENNA, 1997), not to mention the reduction of fishing and the decrease in the number of fishermen and shellfish gatherers in the surrounding areas.

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[11] "And if he is found guilty of setting of the fire, whereupon damage ensues, he is to be flogged publicly, and be at the will of his master to pay the damage, which the fire has done, or to give the slave to be sold to pay the said damage. And if the culprit is a free man, being a pawn, he should be arrested to pay the damage in jail, and lashed out publicly with a lasso (braided rope) in the Village and exiled for two years to Africa" (HOMBEECK Jr., 1977 apud) TAVARES et al., 1997)

The third impacting cycle came with the implementation of industries with high polluting potential (Figure 3-4), with the installation of the CIA industrial complex - at the same time as the installation of COBRAC - and the largest petrochemical park in the southern hemisphere, COPEC.

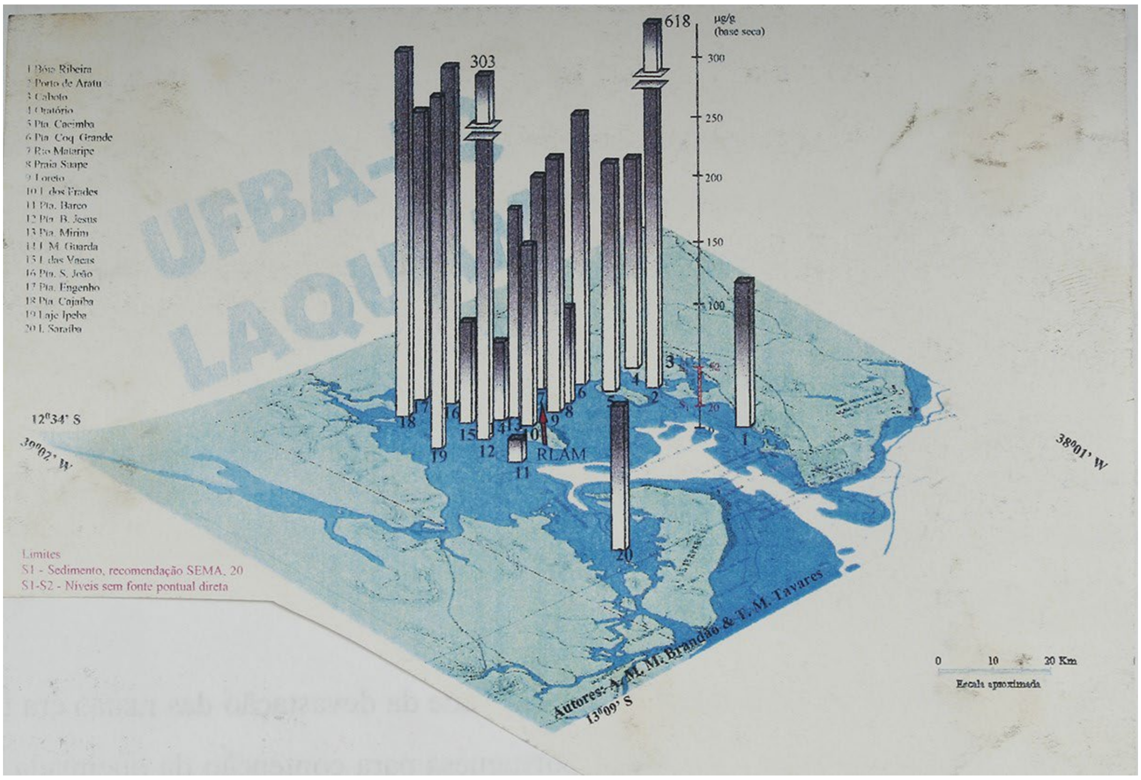

Figure 3-4. Lead concentrations in the sediments of the Todos os Santos Bay, where high concentrations can be observed at the mouth of the Subaé River, caused by the contamination of the Plumbum Co. Source: TAVARES (1996).

These industrial complexes are responsible for the emission of SO2, NOx, basic elements in the formation of acid rain and polycyclic aromatic hydrocarbons, already detected at high levels north of the Bay (TAVARES et al., 1997).

Currently, the main human actions that occur in the Subaé river basin are:

- deforestation of areas close to springs and river courses, favoring the silting process and affecting its water regime;
- the bad use of the soil in agricultural activities, removing the vegetal cover, favoring the erosion of the margins and causing the silting of the riverbeds;
- the use of vinasse for fertilization and irrigation of sugarcane;
- sand mining on the banks and bed of the Subaé River, near the Plumbum Co., facilitating the erosion process and, consequently, silting in the urban area of Santo Amaro da Purificação (Photos 3-1 and 3-2);
- inadequate deposition of slag in urban areas and on the banks of the Subaé River, compromising soil quality and possibly polluting surface and groundwater (Photos 3-3, 3-4, 3-5 and 3-6);
- the disorderly occupation of the river estuary by low-income families and impacting enterprises, causing the destruction of mangroves on the outskirts of the towns of Santo Amaro and São Francisco do Conde; and
- the deposition of garbage close to the drainage network, occurring inappropriately, causing its transport and the percolation of leachate to the drainage in the rainy season.

Photos 3-1 to 3-6. The sand extraction process in the Subaé River has caused contamination of the alluvial soil. This is related to the use of contaminated slag as a landfill, in the mining areas in the riverbed, subsequently causing its incorporation into the soil and the contamination of groundwater, which easily migrates to the Subaé River, given the high porosity and permeability of its soil.

However, some anthropic actions occur notably in the pilot area of this study. Among them:

- the invasion of low-income populations on land belonging to the enterprise contaminated with the slag;
- use of the area where the slag is deposited as a grazing area for cattle and horses (Photos 3-7 and 3-8);
- the use of the slag as a base for the construction of a tailings pond by Boca Loka Paper Co.; and
- the landfill of the slag by Boca Loka Paper Co., not preceded by studies proving that this remediation technique is effective for the area (Photos 3-9 and 10).

Photos 3-7 to 3-10. Upper photos show the slag deposit area used as pasture. In this area, animals have been found dead, which may be putting at risk the health of the population consuming its milk and meat. Lower photos show the slag deposition area backfilled by inert waste.

CHAPTER 4 - HISTORY OF THE ENTERPRISE

"Several questions arise: what to do? How to proceed? Who should do what? When? Does this public office have the legal authority to take action? Whose competence is it? What are the consequences if any action is taken?"

SANCHEZ, (1998)

The legislation requiring environmental licensing for the implementation of potentially harmful activities to the environment has certainly reduced the environmental liabilities of new licensed enterprises. However, this does not occur with the old enterprises, the main perpetrator of the contaminated sites, mostly abandoned today, with improper uses, causing environmental impacts and constituting a danger to health and public safety.

A significant number of approaches to the issue of contaminated sites are illustrated by SÁNCHEZ (1997, and 1998). These procedures range from "negligence", an instrument of omission, highly widespread in developing countries, to "corrective", performed predominantly in Brazil, and "proactive", the most widespread in industrialized countries.

Several countries have already adopted management instruments as corrective policies for contaminated sites. SÁNCHEZ (1998) briefly discusses the effectiveness of these instruments, emphasizing that, in isolation, none of them enabled the most appropriate corrective policy. The main known instruments are:

- inventory of possibly contaminated sites;
- registry of contaminated properties;

- legal liability of agents causing contamination;
- site auditing and evaluation;
- soil quality standards;
- regulation and control of land use;
- charging special fees to finance inventory and cleanup of contaminated sites;
- incentives and subsidies for land remediation and reuse work;
- support for the development of cleaning technologies;
- support for public participation;
- environmental impact assessment; and
- risk assessment.

The environmental management carried out by Plumbum presents procedures in disagreement with what was stipulated at the time of its licensing and inappropriate when deactivating and reusing the contaminated site. This study we do not intended to deal with these instruments, particularly because it is not its objective, but only to present a concise approach for a better understanding of the contamination process and the importance of the application of specific management instruments.

4.1 Licensing

"Nothing prevents the Boca Loka Paper Industry from using Plumbum's industrial facilities, provided that the legal procedures existing in the Environmental Legislation of the State of Bahia are observed".

SANTOS (1995)

Plumbum Co. started its industrial activities in 1960, with an annual production of 5,870 t of refined Pb and 8,450 t of slag (Table 4-1) (OLIVEIRA, 1977). The legal procedures for the location, implementation and initial operation of the enterprise are not reported in the files of the environmental agency. When the enterprise was deactivated, much of its history was lost, including the technical files and dispersion of technicians and employees to other regions.

TABLE 4-1 - PRODUCTION OF REFINED Pb AND SLAG FROM 1960 TO 1976.

YEAR	REFINED Pb (kg)	SLAG (kg)
1960	5.870.728	8.450.000
1961	7.642.249	10.340.000
1962	8.668.979	11.010.000
1963	11.688.352	12.350.000
1964	9.061.718	13.130.000
1965	3.627.179	4.600.000
1966	9.203.628	11.680.000
1967	12.185.880	14.010.000
1968	10.794.270	12.700.000
1969	11.435.523	12.810.000
1970	14.513.445	13.550.000
1971	19.710.742	20.522.000
1972	20.823.210	26.172.700
1973	26.636.648	21.092.000
1974	30.501.778	20.680.000
1975	26.575.395	25.234.000
1976 (1st. semester)	12.857.928	10.330.000
TOTAL	**251.979.652**	**241.979.652**

Source: OLIVEIRA (1977)

The first licensing record found in the CRA files was the one requested in 1976 from the State Environmental Protection Council, at that time linked to CEPED, with the purpose of increasing its production capacity to 30,000 t/year in 1974. for 45,000 t/year of metallic lead and the modernization of the facilities and the existing metallurgical complex.

The licensing request was based on articles 31, 32, 33, and 35 of the State Law No. 3,163 of 04/10/1973, which refers to the preventive control of pollution (OLIVEIRA, 1977).

The technical advice on the expansion license (although the company did not have an operating license due to the lack of specific regulations) was based on studies on the contamination of the Subaé River, and its implications for the implementation of an important fish farming project in the Recôncavo Bay, which would make it self-sufficient in fishing. The team responsible for the analysis presented an unfavorable report to the project presented by COBRAC[12].

The report suggested to the entrepreneur the relocation of the enterprise, taking into account the environmental aspects and the complete state of deterioration in which the metallurgical complex was found.

It is important to emphasize the preventive aspect adopted, perhaps in a pioneering way, by the team that accompanied the licensing process, based on technical studies[13] developed at the time (OLIVEIRA, 1977).

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[12] According to the team responsible for analyzing the license application, even if COBRAC presented the best viable technology, it would not obtain "zero" content of cadmium and other metals in its effluents and, if the expansion or maintenance of the current situation were authorized, there would be a risk of an uncontrollable and irreversible worsening (OLIVEIRA, 1977).

[13] A study called "Polarographic Determination of Pb+2 and Cd+2 in the Subaé River - Santo Amaro-BA", carried out by Prof. José Oscar N. Reis, found contamination of the Subaé River by the effluents of the metallurgical plant, at that time thrown directly into the river, presenting values for the studied metals that exceeded the maximum limits allowed for water and established by the World Health Organization (WHO) (OLIVEIRA, 1977)

In the meantime, UFBa carried out a study and the first assessment of the contamination in the children population residing in a radius of 900m from the Plumbum headquarters, in addition to studies addressing the problem of anemia, lead poisoning and the social factors that determine this intoxication.

The results were presented to the state authorities and served as a basis for the approval of CEPRAM resolution No. 54 in 08/10/1980, which was turned into the Decree No. 27,605 by the State Government, which discarded the previous opinion of the environmental agency, maintained the metallurgy in the condemned area and established several control measures[14]. Among them:

- the removal of the residents living within a radius of 500 m, to other locations;
- the treatment of affected children;
- the construction of a 90 m high chimney;
- the installation of an efficient filtration system for all sources of particulate matter;
- the suspension of the donation of slag and used chimney filters; and
- the supply of clothing for factory employees, for exclusive use at work.

The last license obtained by the enterprise was the operating license[15], granted by CEPRAM in 1993.

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[14] According to TAVARES (1990), the Plumbum Co. complied with the measures, except for the first one, due to its economic unfeasibility alleged by the company, with the evacuated area having a radius of 300m, of which 80% occupied by the company or an area of public domain. In 1981, the total cost for the treatment of children and relocation was US$9,305 and US$154,060, respectively.

[15] This licensing process presented a significant number of problems, due to the short deadline for delivery of the completed script (it consisted of a simplified EIA-Rima), the large number of projects submitting licensing requests at the same time, a restricted number of employees in the environmental agency to analyze the studies, the significant number of studies without technical basis, and the bureaucracy required for licensing.

The resolution that established Plumbum's operating license included an extensive list of control measures[16] and, possibly, was one of the factors that led to the deactivation of the enterprise, since it would be less expensive to implement another enterprise than to carry out what was established in the resolution.

The disqualification of the environmental agency from the technical opinion that proposed the deactivation of the enterprise and its relocation to an environmentally viable area and the proposition of control measures that later proved to be ineffective show the inefficiency of the licensing process for old industries, which favors the occurrence of new areas contaminated with heavy metals.

4.2 Shutdown

"Warned by the newspapers about the shutdown of the Plumbum's operational activities, an inspection was initiated in the plant and it was possible to see that all activities were paralyzed, and all employees of the operational area were fired, leaving only the office staff"

(Santos, 1995)

The process for shutting down an industrial enterprise is not a recent problem. It accompanies the industrialization process and has its causes in the rapid and continuous technological development, which requires successive investments in research, production processes and currently

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[16] Resolution No. 812 of July 20, 1993, which established the operating license, required a significant number of measures, such as carrying out new slag characterization tests, including Pb, Cd, Zn, As, S, and Cu, presenting a groundwater environmental monitoring plan in the slag disposal area of influence, based on the use of piezometric wells, carrying out a monitoring system of the Subaé River, both upstream and downstream of the overflow point of the effluent containment system, for the Pb and Cd measurements, and carrying out epidemiological studies to assess the industrial impact on the health of workers and the population.

follows the process of economic globalization, which promotes the migration of companies or entire industrial sectors (SÁNCHEZ, 1998).

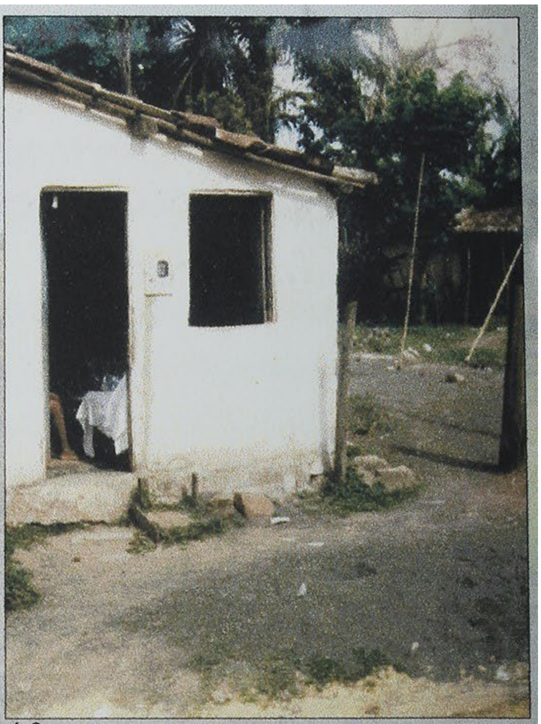
The vast majority of engineering projects have a limited duration. Therefore, closing, dismantling, demolition and deactivation are steps that must be planned either in the development of the project or during the useful life of the enterprise. These procedures are already carried out in industrialized countries in North America and Europe, whereas in Brazil the "abandonment" of industrial projects and human exposure to contaminated soils, polluted aquifers and toxic residues prevail.

Plumbum's case fits these characteristics perfectly. Installed in the urban area of the town, the metallurgy has contributed to widespread contamination, causing the devaluation of the surroundings and its invasion by low-income members of the community, the clandestine disposal of domestic waste, besides increasing complaints about the continued use of slag for landfill (Photo 4-1 and 4-4).

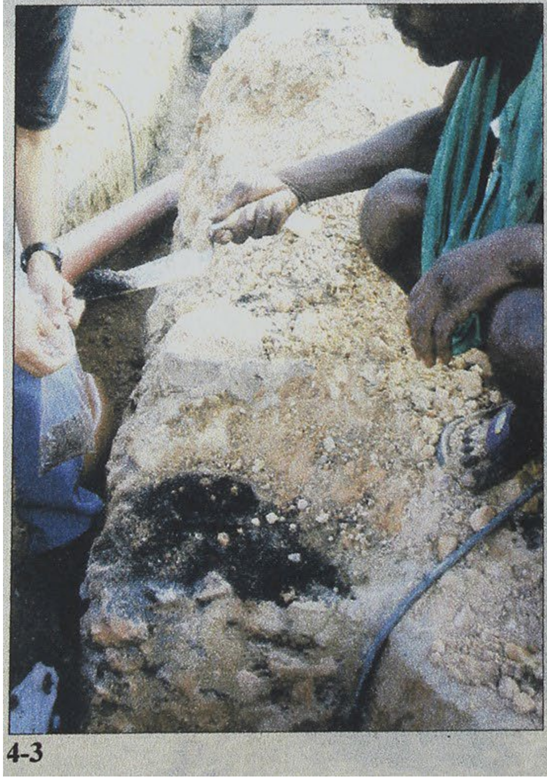
the abandonment of the activities, however, has brought about the investigation on the environmental liabilities, and identified a significant number of damages, including:

a) a lack of medical assistance for dozens of children and employees contaminated with Pb and Cd who were undergoing decontamination treatment;
b) 490,000t of slag deposited throughout the town and a source of contamination for soil and water, in addition to public health;
c) contamination of the soil, the Subaé River and its estuary, the fishermen and certainly a significant portion of the population of Santo Amaro; and

4-1



4-2



4-3

4-4

Photos 4-1 to 4-4. Deposition of slag on the streets of Santo Amaro (June 97), notably during the rainy season. This procedure has been common in the town, as the vertisol at this time of the year expands, and the ground does not adhere, causing falls and difficulties in the locomotion of people, animals and vehicles. Photo 4-3 shows the use of slag as a base for paving the streets.

d) 6,000,000t of tailings contaminated (NASCIMENTO, 1989) with Pb, Cd, Hg and Zn, from the processing of lead ore and deposited without waterproofing, 500m away from the urban area of the town of Boquira/BA.

The abandonment of the Santo Amaro plant took place in January 1994, when CRA Agency became aware of the closure of Plumbum's operational activities through newspaper reports. With the operations closed, the characterization of the slag[17], produced for more than 30 years, was initiated with the purpose of creating a plan for the disposal and monitoring of the groundwater.

In June 1994, Boca Loka Paper Co. requested a technical inspection from the environmental agency, with the purpose of licensing the same facilities (buildings and effluent treatment basins) for the implementation of a napkins producing plant.

4.3. area reuse

"On the request made by Boka Loka Paper Co. to use the Plumbum's facilities, ... we conclude that it is a positive point, as it eliminates once and for all the possibility of Plumbum returning with its activities".

SANTOS (1995)

The reuse of contaminated areas in Brazil is not regulated by the agencies responsible for public policies. The occupation of these sites of great polluting potential occurs without major restrictions.

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[17] A significant amount of analysis to determine the toxicity of the slag was carried out by CEPED, at the request of CRA, and by SGS at the request of Plumbum. The CEPED results, in the vast majority of samples, characterized the slag as solid hazardous waste, while the SGS results, as non-inert waste. This impasse led CRA and Plumbum to request that analysis be carried out by an independent laboratory, and CETESB was contracted. All samples analyzed confirmed toxicity, that is, hazardous waste.

Basically, the use of industrial areas depends on the characteristics of the soils and on the criteria adopted for reuse (SÁNCHEZ, 1998). Once contamination is confirmed, there is a significant loss of land value, and they become improper for the installation of community facilities such as daycare centers, schools and parks, residential buildings for low-income citizens, or occupation by "homeless people".

The reuse of contaminated soils in some countries, such as Holland, Germany, Canada, and in the State of São Paulo (under implementation by CETESB) is based on reference standards for soils and groundwater. Usually, public policy instruments cover the multi-functionality of the soil[18].

The Plumbum metallurgical plant, on the other hand, was occupied by the napkin manufacturer without any communication to the environmental agency[19], in 1995.

The legal procedure adopted by CRA for the reuse of the Plumbum facilities was based on the provisions of the environmental legislation of the State of Bahia[20], dealing with the licensing system for activities with potential impact on the environment.

The reuse of the area has been questioned by several entities, including the City Council of Santo Amaro and the Federal University of Bahia, based

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[18] In São Paulo, the definition of procedures and criteria for establishing the multi-functionality of the soil is determined through Reference Standards (natural level) for different types of soil in the state. To determine the Intervention value of the area (i.e., the level of environmental quality, above which there is a risk to public health and the environment and are determined by toxicological and ecotoxicological studies) a C-Soil computational model is used. Four exposure scenarios are adopted to derive intervention values: Areas of maximum protection, Agricultural, Residential and Industrial/Commercial (CETESB, 1996).

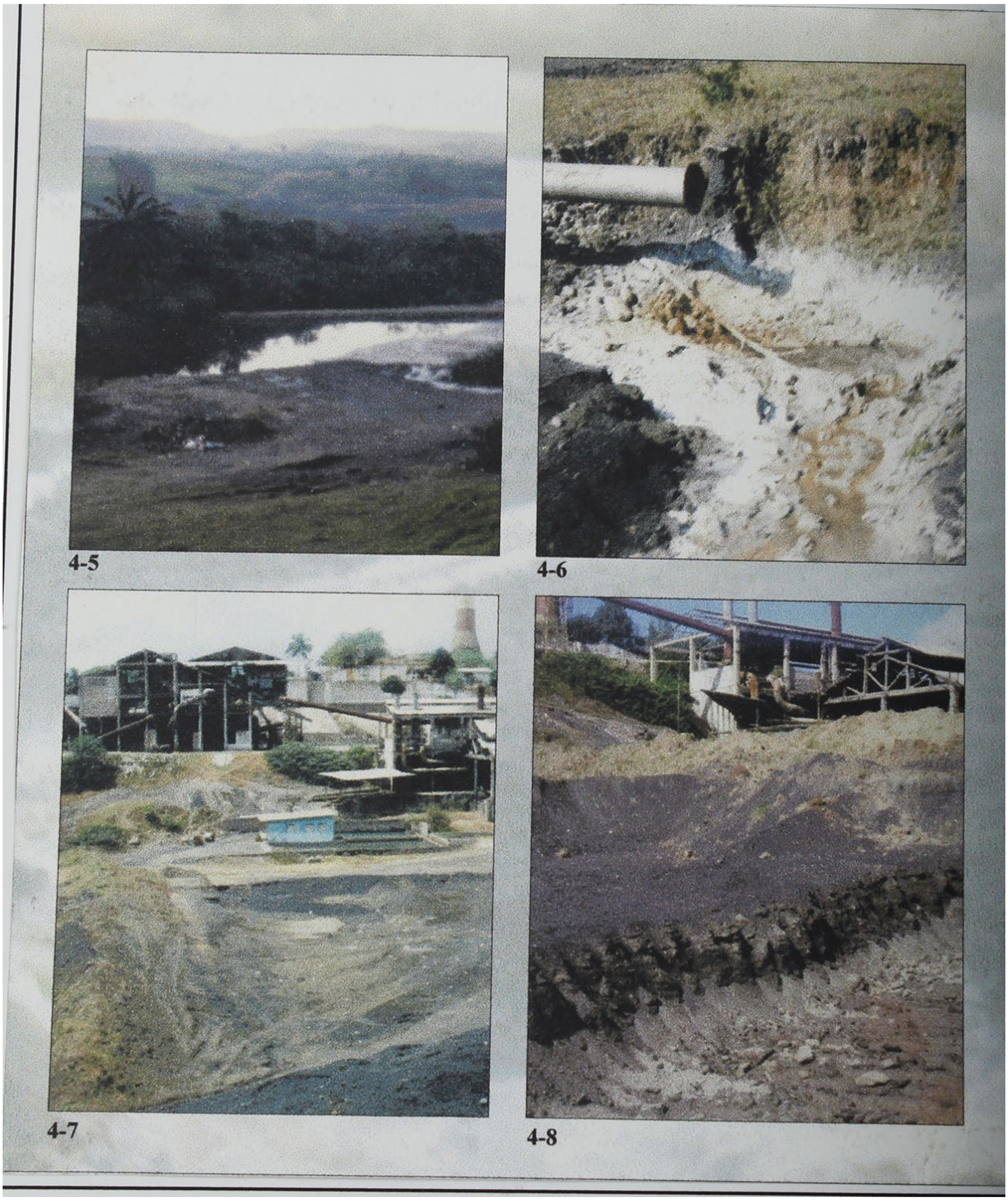
[19] Accompanying investigators from Germany and UFBa to Plumbum in September 1995, technicians from the CRA met employees from the napkin company who declared that there was a lease on the property. In view of that, CRA notified the aforementioned company to request a license (SANTOS, 1995). In 1996, the company applied for a license with the napkin production already well advanced.

[20] CEPRAM complies with the Environmental Legislation of the State of Bahia, based on Law No. 3,838 of November 3, 1980, regulated by Decree No. 28,687 of February 11, 1982, and modified by the Laws No. 6,074 of May 22 of 1991, Law 6,424 of October 26, 1992, and Law 6,529 of December 29, 1993. This legislation delineates in Chapter II, article 100, the procedures for granting Location, Implementation, Expansion and Operation licenses (BAHIA, 1985).

on the large potential for contamination in the area and the contradictions observed in the licensing process, such as:

a) CRA's Technical Report No. 055/95 requires that the paper manufacturer, among other measures, start operations after Plumbum Co. implement the Monitoring Plan for the slag valley. This procedure was not done by Plumbum, which claimed lack of resources;
b) the area has been used by animals for grazing and the consumption of water, causing a risk to public health, without any action by the licensing company, Plumbum or CRA;
c) the slag and soils close to the metallurgy continue to be used as landfill by the city hall and by the State Construction Department for paving roads;
d) the company built two tailings basins, without submitting the technical projects to CRA, and used slag contaminated with heavy metals as material for the construction of dams (Photo 4-5- to 4-8); and
e) Plumbum Co. is under a civil action at the Public Prosecutor's Office of Santo Amaro da Purificação, under the charges of contamination of the area, employees and the community in the surroundings of the metallurgy.

In September 1998, the paper manufacturer was fined for not submitted to CRA the documents required for the environmental licensing process, and for the construction of tailings basins using contaminated slag. The officers also requested the immediate termination of its activities at Plumbum's premises.



Photos 4-5 to 4-8. The tailings dams built by the paper manufacturer presented several irregularities (Photos 4-5 and 4-7), including the use of slag as a construction material (Photos 4-6 and 4-8).

CHAPTER 5 - POLLUTANTS STUDIED

The term “heavy metal” is usually used to refer to metals with a density of 5 or 6g/cm^3 or with an atomic number greater than twenty (WILD, 1993; MALAVOLTA, 1994; AMARANTE, 1997 and ELEUTÉRIO, 1997). It usually encompasses metals, semi-metals and even metalloids such as selenium (MALAVOLTA, 1994), and are often applied to the elements Pb, Cd, Mo, Co, V, Al, Cr, Cu Hg, As, Ni, Zn and As. .

According to Hillert (1997), the term “heavy metal” has been used among policy makers to refer to metals with high toxicological potential, as human activities have significantly increased their concentrations in soils in urban and agricultural areas.

Lead and cadmium are among the most studied heavy metals in the world. This is related to the great dispersion of these elements as anthropogenic metals, their high toxicity and because they usually occur associated with ores.

A survey of its main properties, uses, source of exposure and effects on humans are summarized below:

5.1 Physical, chemical properties, main uses and analytical methods

5.1.1. Lead (Pb)

Lead is a soft, silvery gray metal, melts at 327.5 °C, its atomic number is 82, atomic weight 207.19 and density 11.35 g/cm^3 (MALAVOLTA, 1994). It is a lustrous metal when exposed to air, flexible, and can be molded, rolled and pressed. It presents low mobility and persistence in marine sediments.

It forms salts with organic acids, such as lactic and acetic acids, in addition to forming stable organic compounds, such as tetraethyl lead and tetramethyl lead.

The EPA - Environmental Protection Agency (1984, apud SMITH et al., 1995) pH/Eh stability diagram shows the following forms for lead (Figure 5-1): PbO_2 for high Eh; Pb+2, $PbSO_4$, $PbCO_3$ and $Pb(OH)_2$ for intermediate Eh; PbS to Eh low and Pb to Eh very low.

It usually accumulates in the first centimeters of the topsoil, decreasing with increasing depth of the profile (MALAVOLTA, 1994).

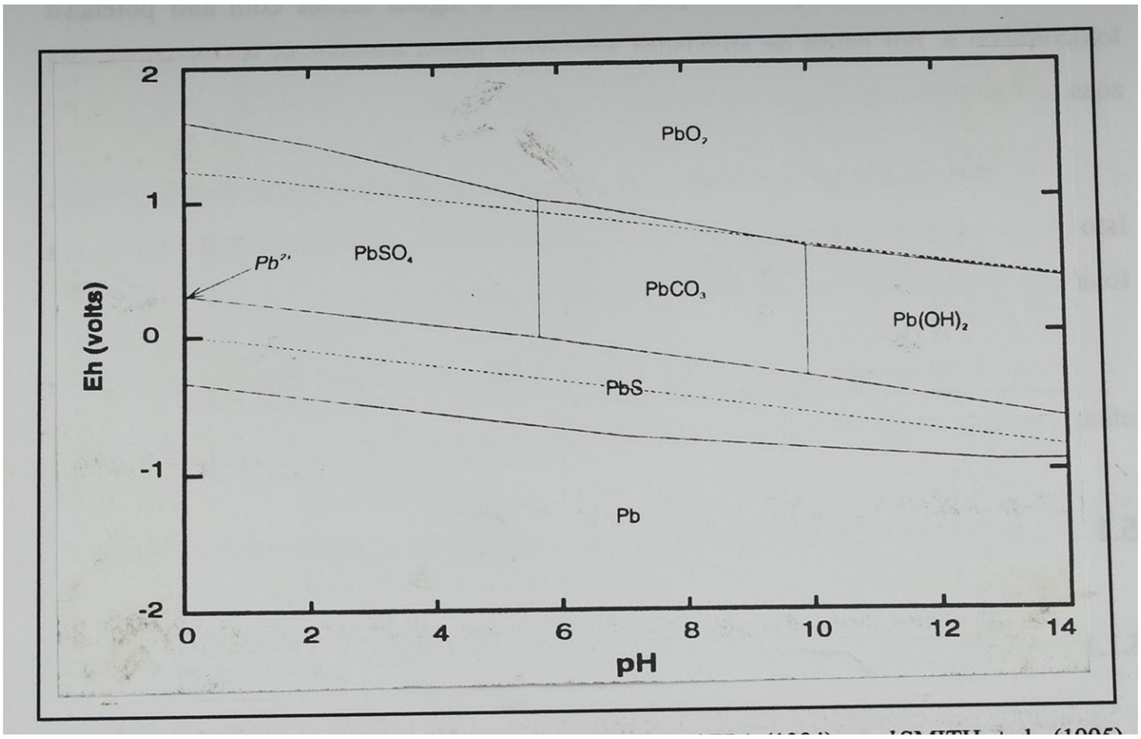


Figure 5-1. Lead species stability region. Source: USEPA (1984) apud SMITH et al., (1995)

Tetraethyl lead has been considered the major anthropogenic source of lead in the environment, as it has been added to gasoline since the 1920s (TAVARES, 1990). In Brazil, since the 1980s it has been replaced by alcohol.

The United States Resource Conservation and Recovery Act (RCRA) characterized tetraethyl lead as one of the compounds with the greatest restrictions for use, setting standards for soil at 0.008 ppm dry weight and for groundwater 0.000004 mg/l (CETESB, 1997).

Currently, 69.5% of the world production of lead is used to manufacture batteries (WILSON, 1997), in addition to pigments and additives in gasoline (Figure 5-2).

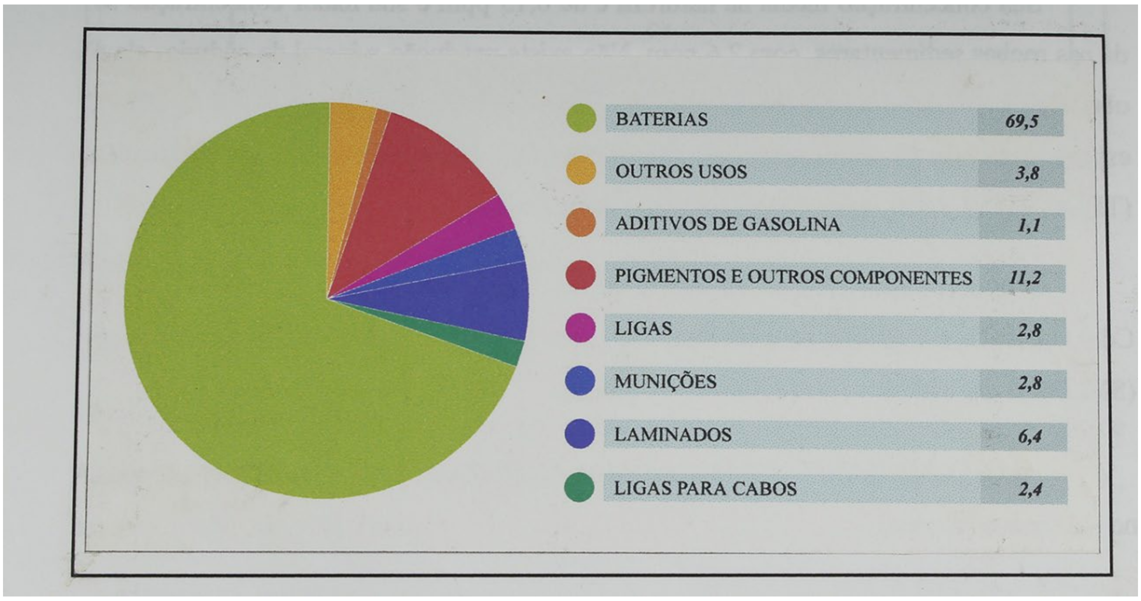


Figure 5-2. Analysis of the uses of lead in the year 1995. SOURCE: WILSON (1997)

The methods used for the analysis of low concentrations of lead in biological materials in the environment are Flame Atomic Absorption

Spectroscopy and Anodic Separation Voltimetry (WHO, 1995) and X-Ray Fluorescence for soils (RAMSAY, 1995).

5.1.2. Cadmium (Cd)

Cadmium is a non-essential element and relatively rare in nature, it is only found in occurrences of Greenockites (CdS) and Otavite ($CdCO_3$) (SMITH et al., 1995). As a transition metal with Zn and Hg, its atomic number is 48, atomic weight 112.4, density 8.642 g/cm^3 (MALAVOLTA, 1994) and is classified as the 67th element in order of abundance. It presents relatively high mobility in the marine environment, long-term persistence and rapid soil absorption.

Its average concentration in nature is 0.15 ppm and its highest concentration occurs in sedimentary rocks, with 2.6 ppm. There is no mineral production of cadmium, it is obtained as a by-product in ores of Zn, Pb-Zn and Pb-Cu-Zn (MALAVOLTA, 1994), it is always associated and presents a geochemical behavior similar to Zn (THORNTON, 1996 apud AMARANTE, 1997).).

Cadmium presents the following forms of stability (Figure 5-3): Cd+2, $CdSO_4$, $CdSO_3$ and $Cd(OH)_2$ for high Eh; CdS for intermediate Eh; and Cd for low Eh (SMITH et al., 1995).

According to ADRIANO (1986) apud MALAVOLTA (1994), cadmium can be in the soil in the following forms:

- **exchangeable**, when absorbed by electrostatic alteration, in sites with negative charge of clays, organic matter and hydrated oxides;
- **reducible**, when absorbed or coprecipitated with oxides, hydroxides of Fe, Mn and Al, as a clay coating or isolated particles;

- **carbonate**, when precipitated as carbonate, in soils with an expressive amount of free calcium carbonate and bicarbonate;
- **organic**, when complexed or chelated;
- **crystalline lattice**, when fixed in the crystalline lattice of clays; and
- **solution**, when ionic or complexed.

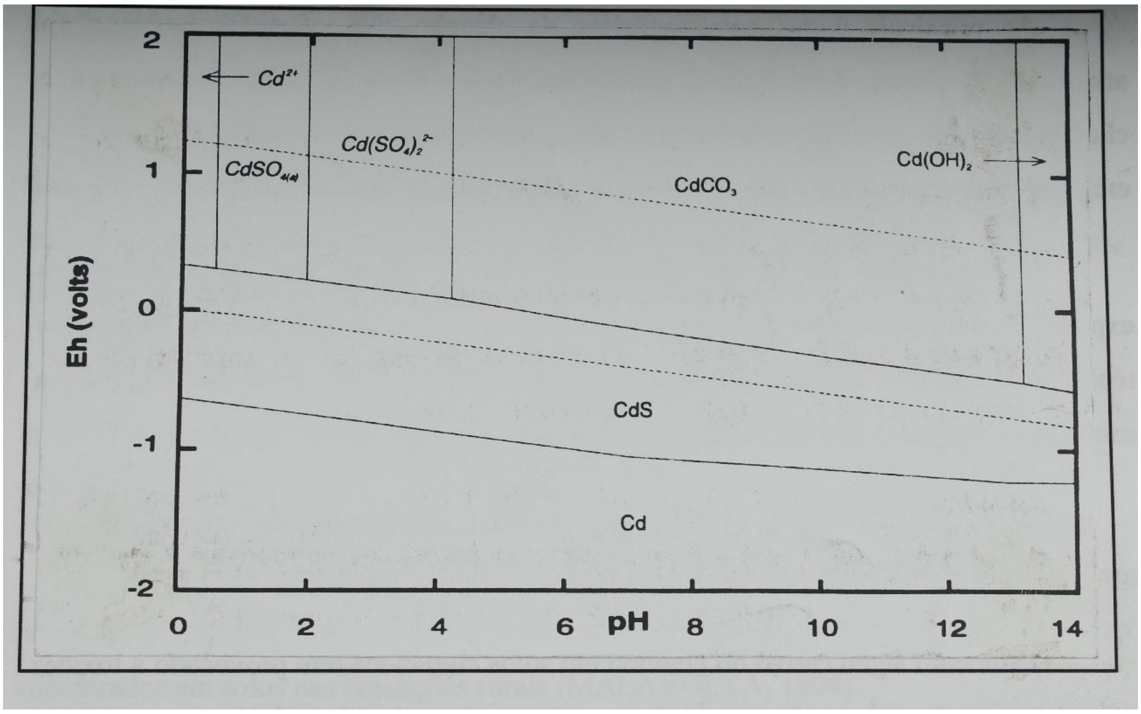


Figure 5-3 Region of stability of cadmium species. Source: USEPA (1984) apud SMITH et al., (1995)

The most common methods used for the identification of the levels of Cd are Atomic Absorption Spectrometry in biological materials (WHO, 1992) and X-Ray Fluorescence, for soils (RAMSAY, 1995).

5.2 Sources of human exposure and transport

5.2.1 Lead (Pb)

All rocks in the Earth's crust contain Pb. The concentration in acidic igneous rocks and in clayey sediments varies from 10 to 40 ppm, while in ultramafic rocks and limestone sediments it varies from 0.1 to 10 ppm.

Natural sources of lead (geological erosion and volcanic emission) produce around 19,000 t/year and anthropogenic sources (mining and smelting) are estimated at 400,000 t/year (MALAVOLTA, 1994).

The main anthropogenic sources of lead refer to atmospheric deposition related to coal burning, production of iron, steel, copper, zinc and lead, mining and transport of ore and chemical industry (tanks, pipes, etc.), sewage sludge, manufacturing of batteries and inks (TAVARES, 1996).

Pb concentrations in the atmosphere, soil and water have reached expressive values over the years, average concentrations of 138 ppm of Pb in the soil have been found in areas close to highways (WHO, 1995), between 2 and 200 ppm in agricultural soils and from 3,000 to 5,000 ppm where Pb deposits occur.

According to TAVARES (1990), the most important way of assimilation of soil contamination by children is through the habit of eating soil (geophagy).

The significant increase in lead in cultivated soils has caused toxicity to plants, animals[21] and humans[22]. Some areas have reached values of up to 20,000 ppm (CETESB, 1997). These concentrations are controlled by processes of adsorption, ion exchange, precipitation and complexation by organic matter.

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[21] Studies on the evaluation of the levels of Pb and Cd in milk in the community of Caçapava, in the Paraíba valley, State of São Paulo, with the objective of "finding the degree of contamination of milk produced in the region, due to the cattle's ingestion of grasses and water contaminated by the lead ingot industry", proved that in 218 samples of in-natura and pasteurized milk, 43 showed Pb levels above the maximum limit established by the Brazilian legislation of 0.05 mg/kg, while for Cd occurrences were below the limit (OKADA, et.al., 1997).

[22] Studies carried out by the UFBA team, in the years 1980, 1985 and 1992, in, respectively, 592, 250 and 101 children from 1 to 9 years old, living within a radius of 900m from the chimney of the Plumbum plant, having as bioindicators lead in the blood (PbB) and cadmium in blood (CdB), found contamination with Pb and Cd in more than 90% of the children surveyed (SILVANY-NETO et al., 1996).

The main parameters that influence the availability (transport) of lead in the environment are (MALAVOLTA, 1994):

- soil texture, when the clay content and cation exchange capacity increase, Pb fixation increases;
- pH, the most important factor as a mechanism influencing solubility, mobility and availability; and
- organic matter is considered the most effective mechanism for Pb fixation.

5.2.2. Cadmium (Cd)

Cadmium is released in the air, soil and water by human activity, and the main sources of contamination are the production and consumption of non-ferrous metals by the automotive industry, in pigments, in stabilizers for plastics, in batteries, besides its use in photo and lithography, rubber curing and fungicides.

In the aquatic environment, Cd is more mobile than Pb (CALLAHAN et al., 1979 apud SMITH et al., 1995), and can be removed from water by precipitation or absorption.

It is relatively immobile in the soil profile. In studies in areas contaminated with smelting, it is observed that, at depths of 30-40 cm, the values are the same as those found in soils in rural conditions (MALAVOLTA, 1994).

However, in soils developed in humid climates, the migration of cadmium in the soil profile is favored by high rainfall, consequently, the enrichment of Cd on the surface can be an indicator of contamination in depth (CETESB, 1997).

Areas close to non-ferrous metal mines and smelters often have severe Cd contamination in the soil, resulting in plant uptake of the metal, usually at low pH.

The application of phosphate fertilizers and the deposition of Cd precipitated from the atmosphere are important sources of Cd in cultivated soils. In addition. semi-solid sewage material, which can be an important source of local contamination (WHO, 1992).

In urban centers, domestic waste incinerators constitute sources of Cd emission, caused by the burning of plastic (TAVARES, 1990).

Organisms such as shellfish, crustaceans and mushrooms are natural Cd accumulators. In horses and some domestic animals, there is an increase in Cd levels in the liver and kidneys when exposed to contaminated areas (TAVARES, 1990).

Tobacco is an important source of cadmium intake for smokers, while for non-smokers, such intake occurs through foods consumed in greater quantities (WHO, 1992).

5.3 Effects on man

5.3.1 Lead (Pb)

The effects of lead in humans depend on the intensity and duration of exposure. For neurological, metabolic and behavioral reasons, children are more vulnerable to the effects of lead than adults.

Lead affects many organs and systems. Among its effects, the following stand out (WHO, 1995):

- decrease in the Intelligence Quotient (IQ);
- effects on the nervous system, with deficit in cognitive functions;

- decrease in involuntary motor, nervous and renal sensory functions; and
- some epidemiological studies have demonstrated the occurrence of preterm births.

According to TAVARES (1990), lead inhibits the formation of hemoglobin, causing a metabolic block and increasing PbS concentrations in the blood. Symptoms of the affected nervous system are ataxia, coma and convulsions, while long-term exposure can cause kidney damage, affecting heart and blood pressure.

5.3.2. Cadmium (Cd)

Prolonged occupational exposure to Cd has caused severe chronic effects, predominantly on the lungs and kidneys. Chronic renal effects have been observed among the general population, and long-term inhalation exposure causes emphysema and other chronic pulmonary effects (TAVARES, 1990).

Cadmium is absorbed by the lungs or gastrointestinal tract and stored mainly in the liver and kidneys, where more than half of the Cd load will accumulate (WHO, 1992).

In people exposed to Cd and who have kidney damage, Cd elimination increases, decreasing its concentration with time, whereas in people without kidney damage, Cd concentration increases (WHO, 1992).

Metallothionein is an important protein for the transport of Cd and other metals. There is evidence that prolonged exposure to cadmium may contribute to the development of lung cancer. On the other hand, the absorption of cadmium from the air depends on the size of the particle, its introduction, retention in the respiratory tract and its solubility, which determines its chemical availability (TAVARES, 1990).

One of the most disturbing aspects of Cd metabolism is its long biological half-life, with its bioaccumulation in blood and kidneys on the order of decades.

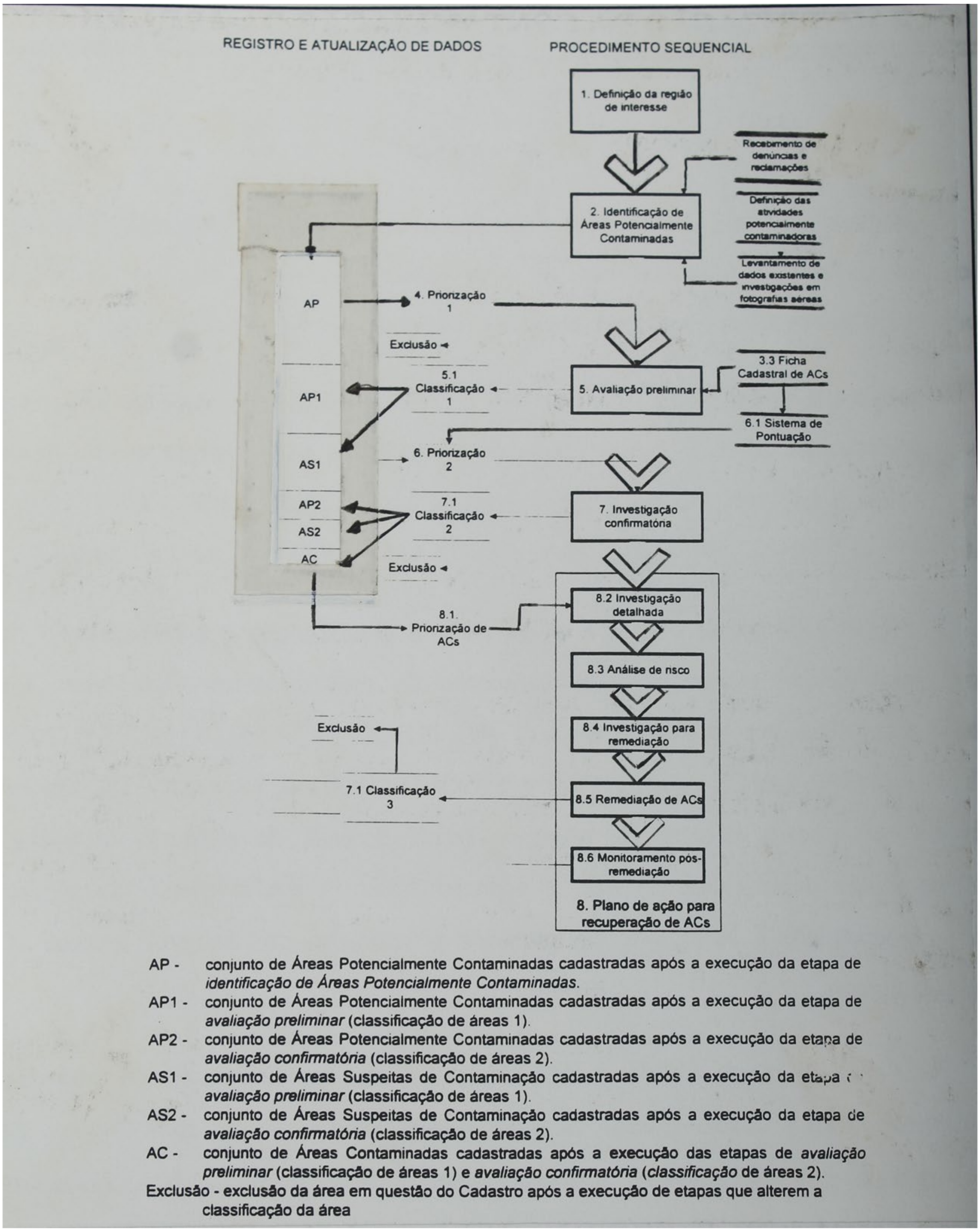
CHAPTER 6 – CHARACTERIZATION OF THE PILOT AREA CONTAMINATION

The investigation and characterization of sites contaminated with toxic residues have been the subject of intense research. This is especially so because of the high costs of prospecting, sampling and analytical methods for detecting contaminants.

The quality of the data collected and the level of analysis to be focused depend on the procedures established in the investigation and characterization phases. In Brazil, these studies are generally determined by technical standards (NBRs 10004, 10005, 10006 and 10007/78) and quality standards (CONAMA 20/86 and Ordinance No. 36/90).

Research planning involving the identification and characterization of contaminated sites requires the development of specific procedures. This method is addressed by MARKER et al. (1994), POMPEI (1994), SÁNCHEZ (1995), CETESB (1996), LEITE et al. (1997) and SÍGOLO (1997) and, due to the numerous variables that can occur in the process (multiple chemical products and raw materials deposited at the site and especially the knowledge of physical, geochemical and biological aspects of the environment under investigation) are defined only its main steps.

GLOEDEN et. al., (1997) and HASSUDA (1997), present more detailed steps for the management of sites contaminated with toxic residues. This method addresses sequenced procedures as a management basis, taking as a strategy the chaining of information obtained in each step (Figure 6-1).



AP - conjunto de Áreas Potencialmente Contaminadas cadastradas após a execução da etapa de *identificação de Áreas Potencialmente Contaminadas*.

AP1 - conjunto de Áreas Potencialmente Contaminadas cadastradas após a execução da etapa de *avaliação preliminar* (classificação de áreas 1).

AP2 - conjunto de Áreas Potencialmente Contaminadas cadastradas após a execução da etapa de *avaliação confirmatória* (classificação de áreas 2).

AS1 - conjunto de Áreas Suspeitas de Contaminação cadastradas após a execução da etapa de *avaliação preliminar* (classificação de áreas 1).

AS2 - conjunto de Áreas Suspeitas de Contaminação cadastradas após a execução da etapa de *avaliação confirmatória* (classificação de áreas 2).

AC - conjunto de Áreas Contaminadas cadastradas após a execução das etapas de *avaliação preliminar* (classificação de áreas 1) e *avaliação confirmatória* (*classificação* de áreas 2).

Exclusão - exclusão da área em questão do Cadastro após a execução de etapas que alterem a classificação da área

Figure 6-1. Sequential steps to base contaminated areas management. Source: GLOEDEN et al., (1997) According to these authors, the investigation is part of the sequential procedure of the action plan for the recovery of contaminated areas, consisting of a confirmatory investigation in the classification phase of Potentially Contaminated Areas (PCA), Suspected Contamination Areas (SCA), Contaminated Areas (CA) , detailed investigation into the CA prioritization phase and investigation into CA remediation.

The characterization of contamination in the Plumbum pilot area allowed preliminary knowledge of the processes of transfer and transformation of pollutants in the environment, through predominantly geochemical assessments, with the aim of predicting the concentrations and fate of contaminants. To characterize the processes of transfer and transformation of pollutants, established parameters were used (pH, CEC, OM, soil texture and type of clay), which provided quantities in quantitative terms of the environmental change.

The environmental indicators[23] represented in this research by the concentrations of Pb and Cd in the water and soil samples were initially researched by the CRA, during the preliminary assessment of the contamination of surface and underground waters (SANTOS, 1995).

In the development of the research at the Plumbum Co. site, the first step to be identified in the process of transferring and transforming the pollutants was the characterization of the source of pollution, by evaluating the degree of contamination of the slag, through chemical analysis for leaching and solubilization of the residue.

Once the existence of pollution caused by the slag was defined, the characterization of the concentrations of contaminants in the vicinity of the

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[23] According to MUNN (1975) apud BITAR (1997), the environmental indicators must translate quantitatively and qualitatively the degree of degradation existing in the evaluation of degraded areas. While for SÁNCHES (1995), they are parameters that provide a measure of the magnitude of the environmental change.

source (soil and surface and underground water) was carried out in a pilot area on the premises of the plant, by means of a technique (installation of wells for water collection) and standardized procedures (soil sampling, water sampling and chemical and physical analysis of pre-established parameters).

Based on these data, the main physical and chemical processes responsible for the retention or availability of metals in the researched area were defined in a preliminary way.

Based on the survey, a summarized conceptual model was formulated for the pilot area, having as basic premises the input, output, transfer, and transformation of Pb and Cd metals in the system (Figure 6-2).

6.1 Investigation of the area

The investigation of a contaminated area represents the starting point for knowledge of the source of pollution, the possible means of contamination and the physical and chemical processes at work.

At this stage, it is essential to know the following factors: the time in which the release of pollutants has occurred; the effective amount released to the environment; and the toxicity of the contaminant involved. According to POMPÉIA (1994), knowledge of these parameters will define the urgency for intervention in the area. The initial investigation in the Plumbum pilot area (Figure 6-3) was based on a survey of the contamination history, which had the following sources of information: maps, photographs, and newspaper articles; technical opinions on environmental licensing; inspection reports and technical visits; testimonies, dissertations and theses developed in the area.

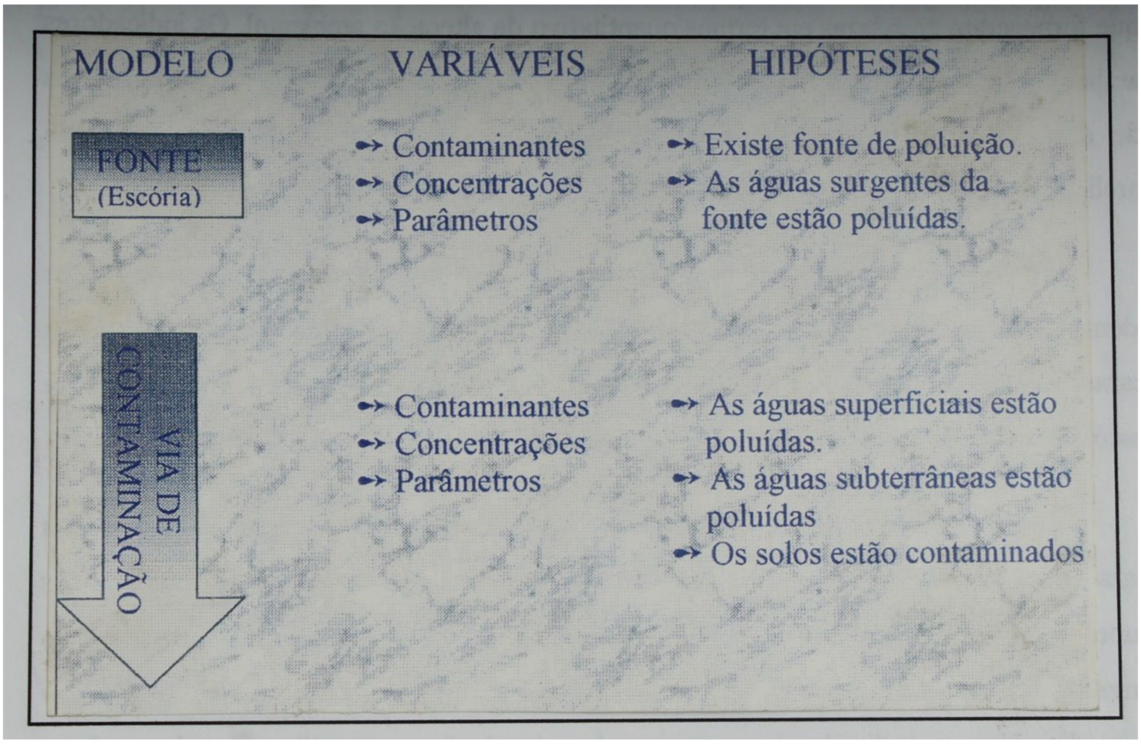


Figure 6-2 Conceptual model of contamination. Modified from USEPA (1989)

This research identified that the contamination resulting from Plumbum came from several sources, namely:

e) From the particulates expelled by the chimney, characterized as a dispersed source of pollution and responsible for the contamination in the surroundings of the metallurgical plant;

f) Liquid effluents from the tailings basin, characterized as a point source of contamination and responsible for the discharge of effluents into the Subaé River; and

g) Slag, considered innocuous by the entrepreneur until 1994, and used as coating and floors for homes, landfills and paving of streets and roads and, therefore, characterized as a dispersed source of pollution, besides representing, according to TAVARES (1990) and SANTOS (1995), the main source of pollution in the surroundings of the project.

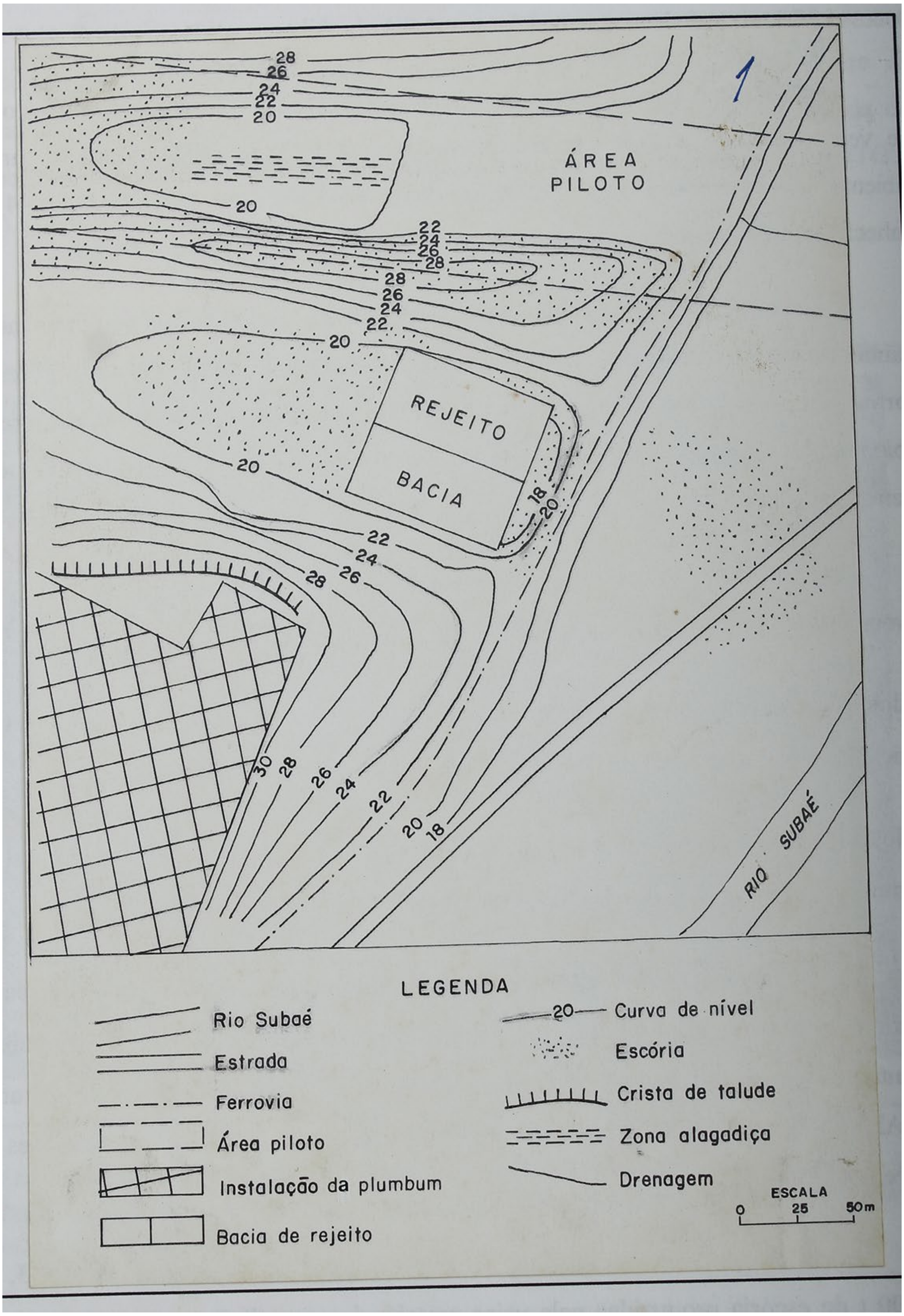


Figure 6-3. Topographic map with Plumbum facilities and pilot area

However, after the "abandonment" of the Plumbum facility in 1993, the 490,000 t of slag produced by the metallurgical plant constituted the only dispersed source of remaining pollution. Based on this finding, strategies were established for classification as solid waste, through procedures established in NBRs 10,004, 10,005, 10,006 and 10,007/87.

6.2 Characterization of the source of pollution.

During its entire production phase, the slag contaminated with heavy metals was deposited in the open and in places without waterproofing on the industrial site (Photo 6-1).

Photo 6-1. Aspect of the slag deposited on the external premises of the metallurgy, where its distribution in the yards and lanes of the enterprise can be observed. In the background, there is the surface of the slag dam deposited in the valley of the pilot study area.

Subsequently, at the request of CRA, the slag that was scattered on the premises of the project was collected and deposited in a valley, between the buildings of the metallurgical plant and the Subaé River, again without any measure to prevent contamination of the soil and surface and groundwater (SANTOS, 1995).

During its thirty-three years of operation, Plumbum Co. produced slag from concentrated Pb ore, benefited from a mine in Boquira, BA. The basic metallurgical processes were sintering and sinter reduction.

According to SANTOS (1993), sintering basically consists of roasting galena, transforming it into oxide:

$$2PbS + 302 \rightarrow 2PbO + 2S02$$

The purpose of this process is both to remove the sulfur in the form of SO_2 and SO_3 and to eliminate, by volatilization, the undesirable impurities.

Sinter reduction basically consists of the reduction of lead oxide by carbon monoxide. Schematically, we have:

$C + 0_2 \rightarrow CO2 + \text{Heat}$

$C + CO_2 \rightarrow 2CO$

$Pb + C + CO + \text{Heat} \rightarrow Pb + CO_2$

$PbO + C \rightarrow Pb + CO$

The slag produced in the sintering and sinter reduction process has the following chemical composition: SiO_2 (20 to 25%); FeO (28 to 35%); CaO (15 to 20%); Pb (1 to 3%); Zn (8 to 12%); S (1 to 3%) and Cd (25 g/t) (CRA, 1992).

The residue is in the form of semi-rounded fragments, with diameters around 0.5 to 1.0 cm, dark gray and high density due to the iron, lead and zinc contents in its composition.

Preliminary studies carried out by CRA and Plumbum indicated the characterization of the slag as hazardous toxic waste. These analysis were performed by means of leaching and solubilization tests and had initially, as environmental indicators, the concentrations of Arsenic (As), Barium (Ba), Cyanides (CN), Chromium (Cr), Mercury (Hg), Silver (Ag), Aluminum (Al), Copper (Cu), Zinc (Zn) , Iron (Fe), Manganese (Mn) and Sodium (Na), which presented results below the maximum limits established by NBR 10;004. On the other hand, these analyzes revealed that the concentrations for Cd and Pb contained values above the maximum limits.

To verify the concentrations coming from the Pb and Cd indicators, dozens of chemical analyses were carried out, ordered by CRA and Plumbum. These results revealed, for the most part, values that established in a preliminary way the toxicity of the slag. (Table 6-1).

TABLE 6-1: SLAG ANALYSIS PRELIMINARY RESULTS

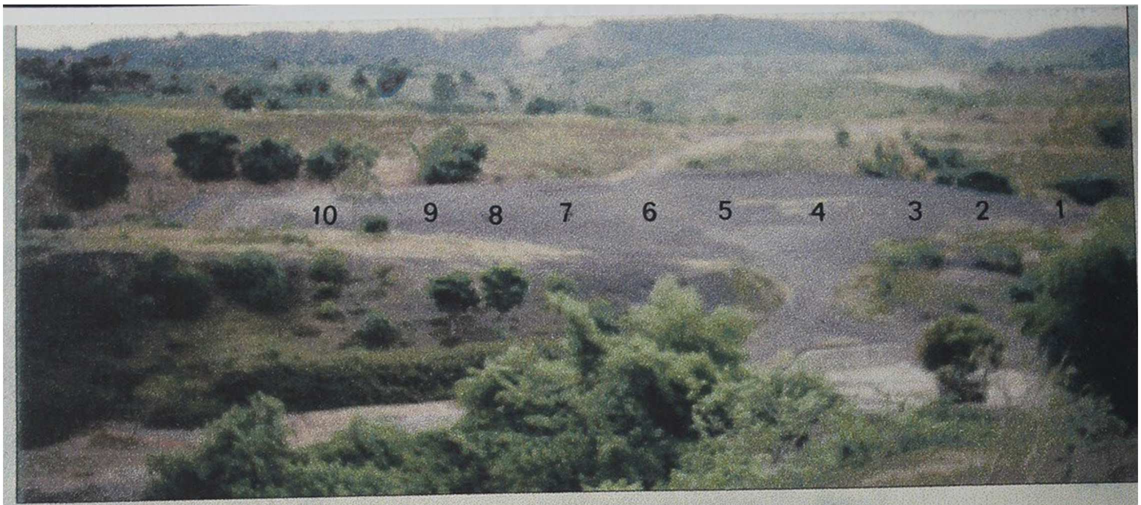
SAMPLE IDENTIFICATION	LEACHING (1)		SOLUBILIZATION (2)	
	Cd (mg/1)	**Pb (mg/1)**	**Cd (mg/1)**	**Pb (mg/1)**
Ceped 7802/93	0.10	**72.0 (3)**		
Ceped 0071-3/94	0.02	0.11	**0.21**	**0.7**
Ceped 1701-2/94	0.5	**68.0**	**0.65**	**0.7**
Ceped 1701-1/94	**0.58**	**76.0**	**0.09**	**0.24**
Cetesb 134/94	0.005	0.10	**0.28**	**1.15**
Cetesb 135/94	0.005	0.10	**0.16**	**0.70**
Cetesb-1/TA VL/95		**10.6**		
Cetesb-2/TA VL/95		**14.1**		
Cetesb-3/TAVL/95		**13.1**		
Cetesb-4/TAVL/95		**10.9**		
Cetesb-5/TAVL/95		**15.8**		
Cetesb-6/TA VL/95		**11.4**		
Cetesb-7/TAVL/95		**13.8**		

Source: SANTOS (1995)

(1) threshold for leaching: Cd = 0.5 mg/1, Pb = 5.0 mg/1. Source: NBR 10005
(2) threshold for solubilization: Cd = 0.005 mg/l, Pb = 0.05 mg/l. Source: NBR 10006.
(3) Pb and Cd values in bold represent levels above the ABNT limits.

6.2.1 Slag sampling, measured parameters and results

Slag sampling was carried out in the surface area of the dam located in the valley next to the Plumbum facilities (Photo 6-2 and 6-3). The purpose of this procedure was to collect samples for analysis of their toxicity through leaching and solubilization tests (Table 6-2).



6-2

6-3

Photos 6-2 and 6-3. The top photo shows the surface sampling points of the slag. At the bottom the detail of. sampling, carried out by a galvanized gardener's shovel and stored in a plastic bag.

TABLE 6-2: SLAG SAMPLING PROCEDURES

ACTIVITIES	PROCEDURES
Points sampled	10 (ten) points;
Sample distribution	1 point every 10 m;
Sampler type	galvanized garden spade;
Depth	20 (twenty) cm;
Volume	2 (two) liters;
Type of sampler	plastic bag ;
Storage time	360 days;
Delivery to the laboratory	10 (ten) days after collection;
Label and collection form	Name, date and place of collection; number of samples; identification of origin and determinations to be carried out in the laboratory.

Ten samples (ESC/01 to 10) were collected in the superficial portion of the dam (ABNT, 1987d), distributed equidistantly along the longitudinal feature of its body. The samples were prepared and analyzed according to the procedures recommended by NBRs 10,005 (ABNT, 1987b) and 10,006 (ABNT, 1987c).

The parameters established for analysis were Pb, Cd and pH (Table 6-3). The analyzes were carried out at CEPED, using the analytical method of Flame Atomic Emission Spectrometry, Hydride Generation and Cold Vapor, and the analyzed parameters complied with the procedures of the Guidelines for Drinking Water Quality - Vol. I - Recommendations. WHO (1994).

The values for Pb and Cd shown in bold in the Table represent values above the limits established by the technical standards for leaching and solubilization tests of solid waste.

TABLE 6-3: RESULTS OF SLAG ANALYSIS

SAMPLE IDENTIFICATION	LEACHING (1)		SOLUBILIZATION (2)		pH	
	Pb (mg/1)	Cd (mg/1)	Pb (mg/1)	Cd (mg/1)	Initial	Final
ESC/01	115.8	0.22	2.98	0.16	6.3	5.1
ESC/02	159.0 (3)	0.30	0.96	0.26	6.3	5.1
ESC/03	73.2	0.13	0.38	0.07	6.5	5.1
ESC/04	72.5	0.12	4.95	0.10	6.3	5.1
ESC/05	14.6	0.05	0.52	0.28	6.3	5.0
ESC/06	119.1	0.04	0.50	0.28	6.3	5.2
ESC/07	138.2	0.19	0.12	0.01	7.0	5.2
ESC/08	30.6	0.12	0.29	0.03	6.4	5.2
ESC/09	1.8	0.05	0.09	0.005	6.4	5.2
ESC/10	47.2	0.05	0.73	0.03	6.0	5.1

1) threshold for leaching: Cd = 0.5 mg/1, Pb = 5.0 mg/1. Source: NBR 10005
2) limit for solubilization: Cd = 0.005 mg/l, Pb = 0.05 mg/l. Source: NBR 10006.
3) Pb and Cd values in bold represent levels above ABNT limits

6.2.2 Discussion of results

The results of the chemical analysis presented in Table 6-3 demonstrate unequivocally that slag is a hazardous waste (ABNT, 1997a). This conclusion is based on the Pb concentrations in the leaching and solubilization extracts carried out on the surface of the slag dam.

Classification as hazardous waste was verified in the Pb leaching test, which in 90% of the samples shows values above the maximum limit of 5.0 mg/1 (Figure 6-4), established by the technical standard NBR 10.005. In this test, the ESC/02 sample indicates the highest value for Pb (159 mg/1), representing 31.8 times the recommended limit, besides an average value of 77.2 mg/1, corresponding to 15.5 times the maximum limit.

The characterization of slag as hazardous waste is confirmed by the solubilization test (Figure 6-5), when the Pb presents in its entirety values above the maximum limit of 0.05 mg/1, established by the technical standard NBR 10.006. In it, the ESC/04 sample indicated the highest value for Pb, representing 99 times its maximum limit.

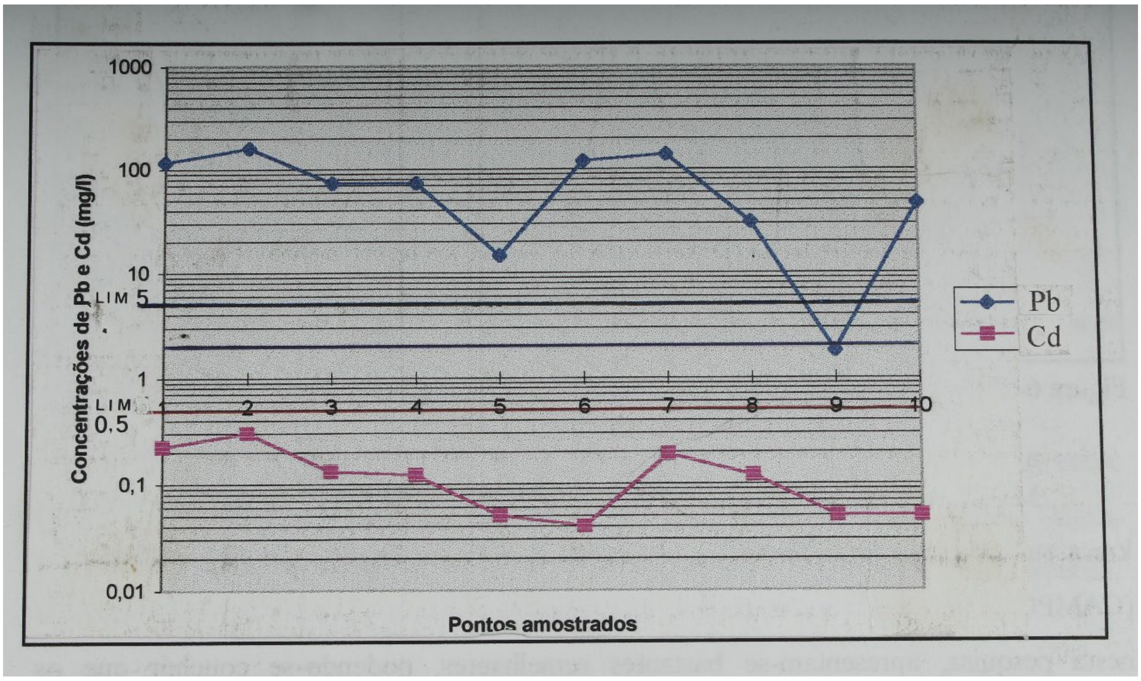


Figure 6-4. Pb and Cd concentrations in leaching test

The analysis for Cd showed that, for the leaching and solubilization tests, there were, respectively, 90% lower and higher results than the limits established by the technical standards. The low values presented in the leaching test may be related to the ease with which Cd is leached by rainwater and its high mobility (TAVARES, 1990 and 1997).

The values referring to the initial pH of the referred tests presented values with a tendency to basic pH, between 6.0 and 7.0. The final pH of the same tests is standardized at 5.0 ± 0.2 and must be adjusted whenever it exceeds this limit and corrected until the end of the measurement, by adding 0.5N acetic acid.

Given the presence of Pb and Zn sulfides in the chemical composition of the slag, an acid pH was expected, however, the presence of CaO (15 to 20%) might be neutralizing the system and raising the pH to the levels found.

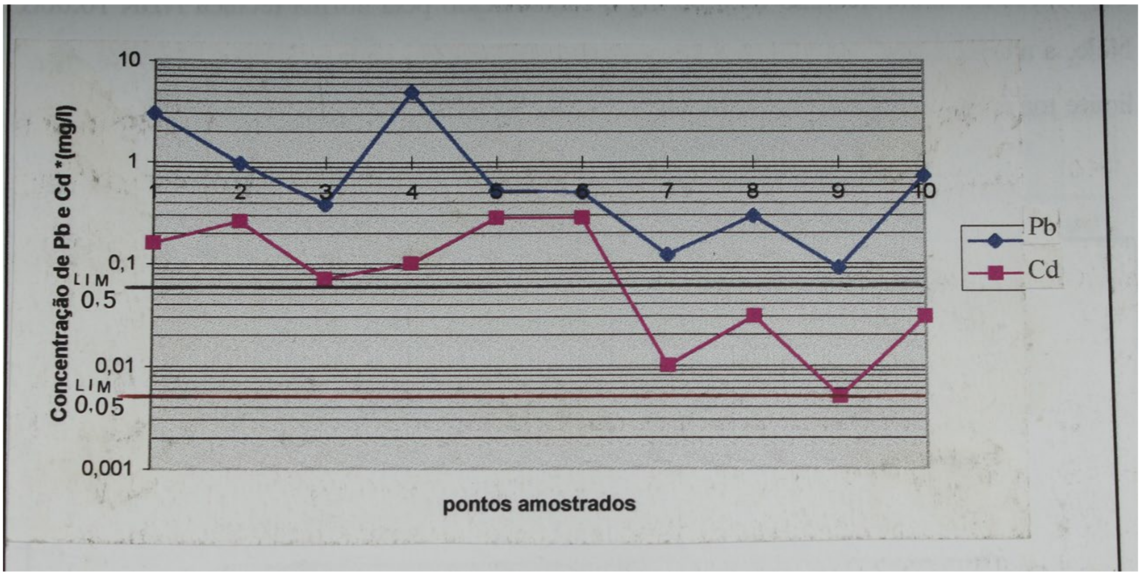


Figure 6-5. Pb and Cd concentrations in solubilization test

Measurements carried out on rainwater in the region (collection station located 10 km south of the pilot area studied) revealed average pH values around 4.9 (CAMPOS, 1995). These results, compared with standardized tests performed in this research, are very similar, and we conclude that the results for Pb and Cd obtained in the laboratory are close to the natural mechanisms of leaching and solubilization induced by rainwater.

This statement presupposes that the great variation in the Pb and Cd contents of the samples show that an expressive amount of the metals is already retained in the soil and groundwater, or bioavailable in plants, animals and humans. These processes may be caused by the time of leaching and/or solubilization to which the samples were submitted, or by other factors, such as peaks of more acid rains favoring the availability of metals (CAMPOS, 1995).

From this survey, strategies were sought to characterize the contamination in the surroundings of the pilot area, especially in the surface and groundwater, and soil.

6.3 Characterization of surface waters

Surface water, soil and groundwater are part of the same context. This statement stems from the coexistence of mechanisms that follow one another from the infiltration of surface water, filling the pores of soil and rocks, to the accumulation in the saturated zone.

However, for methodological reasons, a compartmentalized characterization of each element was delimited for this work to get a better understanding of each context. On the other hand, the conclusive analysis of these characterizations were developed in an integrated way, given the interaction between the components surface water, soil and groundwater.

Initially, the quality of surface water depends on several factors, including the climate, the chemical composition of the soil and rocks, the living beings present (algae, microorganisms and aquatic plants), their movement and distribution and, in particular, the anthropogenic activities.

In this research, the contamination[24] from the Plumbum site is characterized as the main impact generated by human action. This

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[24] Pollution and water contamination are concepts often confused. This is related to its origin "the introduction of substances foreign to the nature of the aquatic environment" (MESTINHO 1997). The

interference in the quality of surface water comes from the inadequate deposition of the slag, which undergoes leaching and solubilization processes caused by rainfall - about 1600 to 1700 mm per year - and from the drainage system of the facilities of the enterprise, causing the migration of metals for drains.

Photo 6-4. Erosion developed by surface water in the center of the slag dam carrying particulate material towards the Subaé River.

The surface drainage of the Plumbum area is conditioned by the local relief and the form of slag deposition on the plant's land. The deposition in the form of dams or on topographic heights has facilitated the transport of pollutants leached and solubilized by rainwater (Photo 6-4).

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distinction between the two concepts is addressed by REBOUÇAS (1994), who establishes as polluted water, that which presents any change in its quality resulting from direct or indirect anthropic influences, but which do not reach the maximum values defined by the adopted standards. Contaminated waters are those that contain natural substances or substances introduced, directly or indirectly by human activities, whose contents are above the maximum values allowed by quality standards for human, industrial or agricultural consumption.

Preliminary studies carried out by CRA (SANTOS, 1995) in emerging waters immediately downstream of the slag dam, taking as environmental indicators the concentrations of Pb and Cd metals, presented the following results (Table 6-4).

TABLE 6-4: PRELIMINARY ANALYSIS OF SURFACE WATERS

REPORTS	DATES	(Pb)mg/1	(Cd)mg/1
1270-04/94	07/22/94	0.1	0.005
0323/95	02/14/95	2.6	0.03
0709/95	04/18/95	3.3	0.090
3855/95	09/27/95	0.15	0.005
4253/95	10/17/95	0.06	0.005

Source: SANTOS (1995)

This study showed that all values found for Pb and Cd were above the quality standards, respectively, 0.03 mg/1 for Pb and 0.001 mg/1 for Cd, established for class II waters (CONAMA Resolution No. 20 /86) in which the Subaé River Hydrographic Basin falls.

6.3.1 Sampling of surface water

The sampling of surface water in the valley where the slag dam is located included the manual collection of ten samples, specified as Surface Water Point (SWAP) 01 to 10, distributed at selected points throughout the Subaé River drainage (Figure 6-6). The objective of this procedure was to identify trends of contamination with heavy metals in the area.

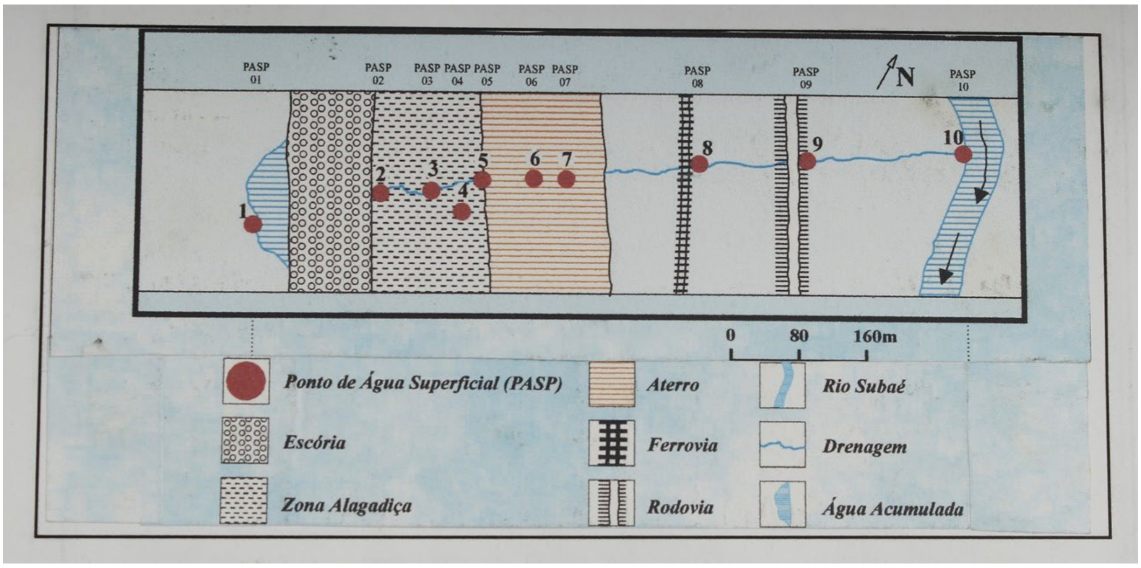

Figure 6-6. Location of sampled points for surface waters.

The drainage is intermittent and its waters usually flows from March to December, due especially to rainfall. During these months, the precipitated water accumulates upstream of the slag dam (Photo 6-5), migrates through it to form the wetland (Photos 6-6 to 6-8), percolates through the embankment zone piping (Photo 6-9), where they receive the wastewater from the plant, reaching the upstream portion of the railroad and continuing until it reaches the Subaé River (Photo 6-10). However, during the months of January and February, the drainage is usually dry.


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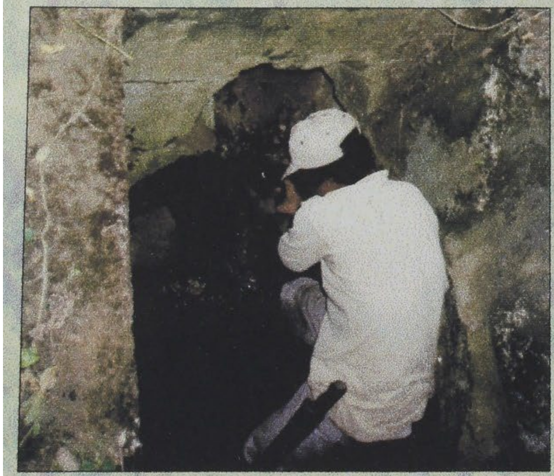
6-9


6-10

Photos 6-5 to 6-10. The photos show the sequence of surface water sampling, starting with the water accumulated upstream of the slag dam (Photo 6-5), emergence of the slag downstream (Photo 6-6), wetland area (Photos 6-7 and 6- 8), piping in the landfill area (Photo 6-9) and Subaé River (Photo 6-10).

The sampling of surface water was used to determine the levels of Pb and Cd by quantitative chemical analysis and pH analysis. It was carried out in compliance with the procedures (Table 6-5) of the Water Sample Collection and Preservation Guide (CETESB, 1988).

TABLE 6-5: SURFACE WATER SAMPLING PROCEDURES

ACTIVITIES	PROCEDURES
Parameters	Chemical analysis for Pb and Cd; and pH
Sample volume	01 liter
Sampler type	Glass bottle
Points sampled	10 points
Sampling locations	SWAP-01 upstream damming SWAP-02,03,04 and 05 wetlands SWAP-06 and 07 piping systems SWAP-08 downstream of railroad SWAP-09 downstream of the highway, and SWAP-1 The Subaé River
Sampling	surface sampling
Preservation	05 ml of concentrated HN0 3 per liter
Storage time	180 days
Delivery to the laboratory	05 days after collection
Identification tag,	point identification; localization; parameters to be measured; individual responsible for the collection; project name; contact phone number, and equipment used in the collection.

6.3.2- Measured parameters measured and results

The quality indicators for surface water used in this research had the following parameters: pH and the metals Pb and Cd.

pH is considered one of the main parameters in controlling the retention or availability of metals. Depending on its acidic or basic state, it is responsible for triggering chemical processes (adsorption and desorption, precipitation and solubilization, and complexation) (LINHARES, 1997), besides indirectly interfering with other environmental factors (salinity, temperature and dissolved oxygen) (BOULDING, 1995).

The pH for surface waters was determined by "in situ" analysis, and its measurement was carried out using a manual electrode potentiometer, brand SCHOTT GERATE (Photo 6-11).

Photo 6-11. Electrode potentiometer used to measure the pH of surface water.

Table 6-6 below shows the pH values for the surface water samples. In this sampling, the pH trend was from slightly acidic to basic.

TABLE 6-6: pH VALUES IN THE SURFACE WATER OF THE PILOT AREA

SAMPLE IDENTIFICATION	pH
SWAP-01	9.6
SWAP-02	8.3
SWAP-03	8.0
SWAP-04	6.8
SWAP-05	6.8
SWAP-06	6.7
SWAP-07	6.5
SWAP-08	6.5
SWAP-09	7.5
SWAP-10	7.6

As for the metals, the survey had the purpose of evaluating their concentrations at previously selected points, from upstream of the dam to the mouth of the Subaé River.

Pb and Cd concentrations were determined through chemical analysis for the characterization of the surface water pollution. The analysis were carried out by CEPED, using the analytical method of Atomic Absorption and Atomic Emission Spectrophotometry, following the procedures of the Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

The results of chemical analysis for Pb and Cd presented in Table 6-7 were compared with the limits established for class II waters and applied to the Subaé River. Values in bold are above the limits defined in that framework:

TABLE 6-7: CONCENTRATIONS OF Pb and Cd, AND pH IN SURFACE WATER SAMPLES OF THE PILOT AREA

SAMPLE IDENTIFICATION	Pb (mg/l)$^{(1)}$	Cd (mg/l)$^{(2)}$	pH
SWAP-01	<0.05	<0.005	9.6
SWAP-02	**3.13 (104.3)**	**0.013 (13)**	8.3
SWAP-03	**4.67 (155.6)**	**0.069 (69)**	8.0
SWAP-04	**7.81 (260.3)**	**0.084 (84)**	6.8
SWAP-05	**0.13 (4.3)$^{(3)}$**	**0.070 (70)**	6.8
SWAP-06	<0.05	<0.005	6.7
SWAP-07	<0.05	<0.005	6.5
SWAP-08	<0.05	<0.005	6.5
SWAP-09	<0.05	<0.005	7.5
SWAP-10	<0.05	<0.005	7.5

(1 and 2) maximum levels for potentially harmful substances: Pb = 0.03 mg/lPb and Cd = 0.001 mg/lCd, according to CONAMA Resolution 20/86 for class 2 water bodies.
(3) number of times the obtained concentration is higher than the maximum allowed concentrations.

The concentrations for Pb and Cd detected at the sampled points (Figure 6-7) showed that: upstream of the dam, the levels of metals are close to the maximum established limits; immediately downstream of the dam, in an area called "swamp", values for Pb and Cd of up to, respectively, 260 and 84 times the maximum values were found in all 4 selected points; whereas all the other 5 (five) points downstream revealed concentrations close to the maximum values.

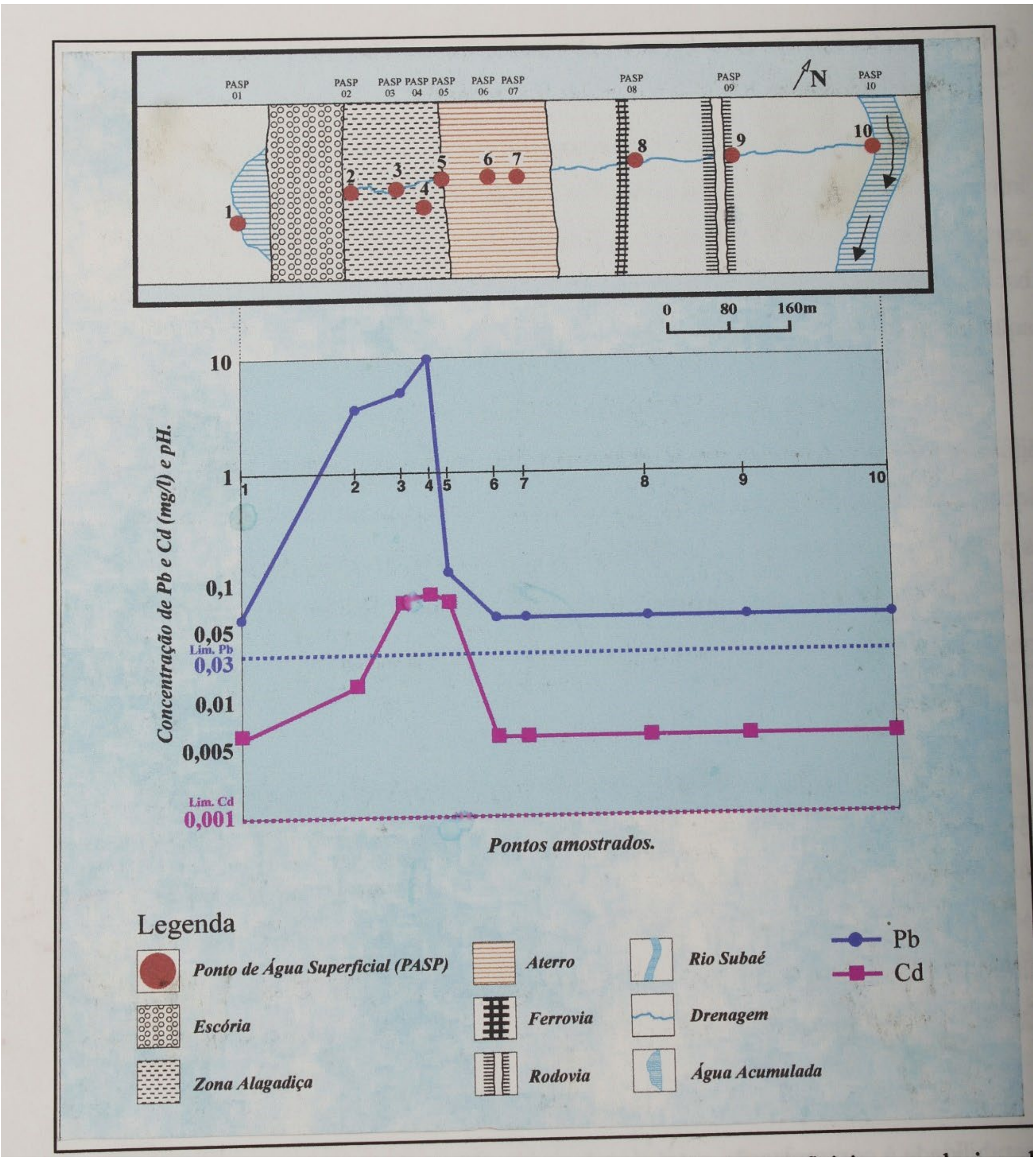

Figure 6-7 - Lead and cadmium concentrations in surface waters, correlated with their sampling points.

The concentrations for Pb and Cd of SWAP points 01 and 06 through 10 present a detection limit above the maximum levels for potentially harmful substances. Given these facts, the results suggest that most of the Pb and Cd leached and/or solubilized from the slag is retained in the wetland, as indicated by the basic pH found in the drainage and the chemical processes acting in the system. The analysis of these processes will be discussed in sections 6-6, 6-7 and 6-8 of this chapter.

6.4 Characterization of groundwater

Currently, the economic importance of groundwater has been intensively addressed, as a factor of sustainable development in the modern integrated management of water resources, as the hydrographic basin is considered a planning unit, including the functions carried out by aquifers[25].

The occurrence of groundwater depends on the movement and distribution of surface water. This system develops in three distinct zones: superficial features, called the root or soil water zone, characterized as a wet zone where plants develop; intermediate feature, called vadose or unsaturated zone and composed of gravitational, skin and capillary waters; and the lower feature, called the saturated zone, where all the interstices of the geological formations are filled with water (REBOUÇAS, potential uses are restricted (REBOUCAS, 1994). However, the existence of a potentially polluting source does not necessarily imply the risk of contamination of an aquifer. This fundamentally depends on local hydrogeological factors like infiltration regulators, contaminant transport and soil attenuation processes (Table 6-8).

A significant number of studies have been carried out to characterize aquifers' vulnerability to human-led contamination. Among them, the most common in Brazil includes as determining parameters the hydraulic inaccessibility to the penetration of contaminants and the attenuation

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[25] In this work, the concept of aquifer refers any geological formation capable of storing and conducting water in appreciable quantities (ABGE, 1981). Aquiludes, in their turn, refer to all "impermeable and non-fractured geological formation, which may contain water, but without the proper conditions to move it from one place to another, under natural conditions and in a significant amount" (MESTINHO, 1997).

capacity of the strata above the saturated zone, allied to processes of physical retention and chemical reactions with the contaminant (FOSTER, et al., 191).

Table 6-8 Hydrogeological classes of rocks.

MATERIAL	HYDROGEOLOGICAL CLASS	HYDRAULIC CONDUCTIVITY (cm/s)	TOTAL POROSITY (%)	SPECIFIC POROSITY (%)
Gravel	Aquifer	1 - 10-2	25 - 50	12 - 35
Sand	Aquifer	10-1 - 10-3	20- 35	15 - 35
sandy silt, fine sand	Aquitards	10-3 - 10-5	10 -20	10 - 28
Silt, silty sand and sandy clay	Aquicludes	10'-4 - 10-6	35 - 50	3 -19
Clay	Aquieludes	10-6 - 10-9	33 - 60	0-5

Source: MESTINHO (1997)

The evaluation of the functions that characterize the vulnerability of the aquifer, allied to the mobility and persistence of the contaminants, allows for the assessment of the risk of contamination of the groundwater (POSTER et al, 1993).

This risk comes from two fundamental factors: the characterization of contaminant loads, represented by the form of application, volume, extension, intensity, duration and composition; and the vulnerability of the aquifer, supported by its natural characteristics, such as porosity and permeability, transit time and physical-biogeochemical attenuation capacity (REBOUCAS, 1996).

A preliminary characterization of the contamination of groundwater at the Plumbum site was carried out by CRA, through the collection of water in piezometers installed in the area. The analysis based on samples taken from these wells do not present references on the installation method and its location. They were carried out by CEPED and have as environmental indicators the concentrations of Pb and Cd (Table 6-9).

TABLE 6-9: CONCENTRATIONS OF Pb AND Cd (mg/1) IN GROUNDWATER.

REPORT	DATE	WELL	Pb(mg/L)	Cd (mg/L)
1270-02/94	07/22/94	PS-2	0.1	<0.005
4253 to 4255/95	10/17/95	PS-1	<0.05 (1)	<0.005
4133 to 4135/95	10/10/95	PS-1	<0.05	<0.005
2439/95	07/20/95	PS-3	<0.05	<0.005
2438/95	7/20/95	PS-2	<0.05	<0.005

Source: SANTOS (1995)

(1) detection limit of the analytical method is for Pb = 0.05 and Cd = 0.005

CRA compared these results with Class 2 water, which sets Pb = 0.03 mg/1 and Cd = 0.001 mg/1 (CONAMA nº 20).

The results showed that, except for the analysis for Pb, referring to the report 1270-02/94, carried out in the PS-2 well, all the results were close to or below the maximum limits established in the mentioned legislation.

Based on the mentioned standards, this survey allows us to preliminarily affirm the inexistence of contamination in groundwater at the Plumbum site. This is related to the lack of information on the location of the sample collection points, whether upstream or downstream of the contaminated slag and by the analytical method used to quantify its results above the standards employed as a reference.

In view of this fact, a new assessment was carried out in a representative area to determine the explicit relationship between the source of pollution and the existence of a possible contamination plume.

Based on the pilot area, a distribution of wells was defined in representative locations susceptible to measuring significant data on groundwater contamination.

6.4.1 Sampling of groundwater

The sampling of groundwater in the pilot area of the study used the water from the saturated zone to define trends in contamination with Pb and Cd metals. The procedure was done in the valley where the slag dam is located, with the installation of three monitoring wells distributed as follows: a well upstream of the slag dam (GWSP 01); and two downstream wells, GWSP 02 in the wetland area, GWSP 03 in the landfill area. A fourth point was GWSP 04, represented by a cistern downstream of the landfill (Figure 6-8).

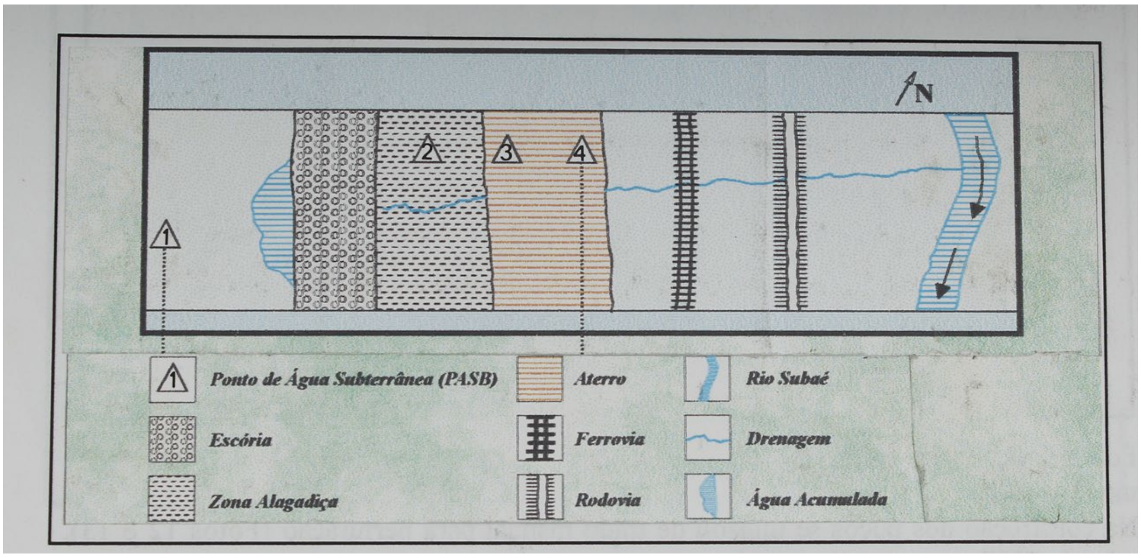
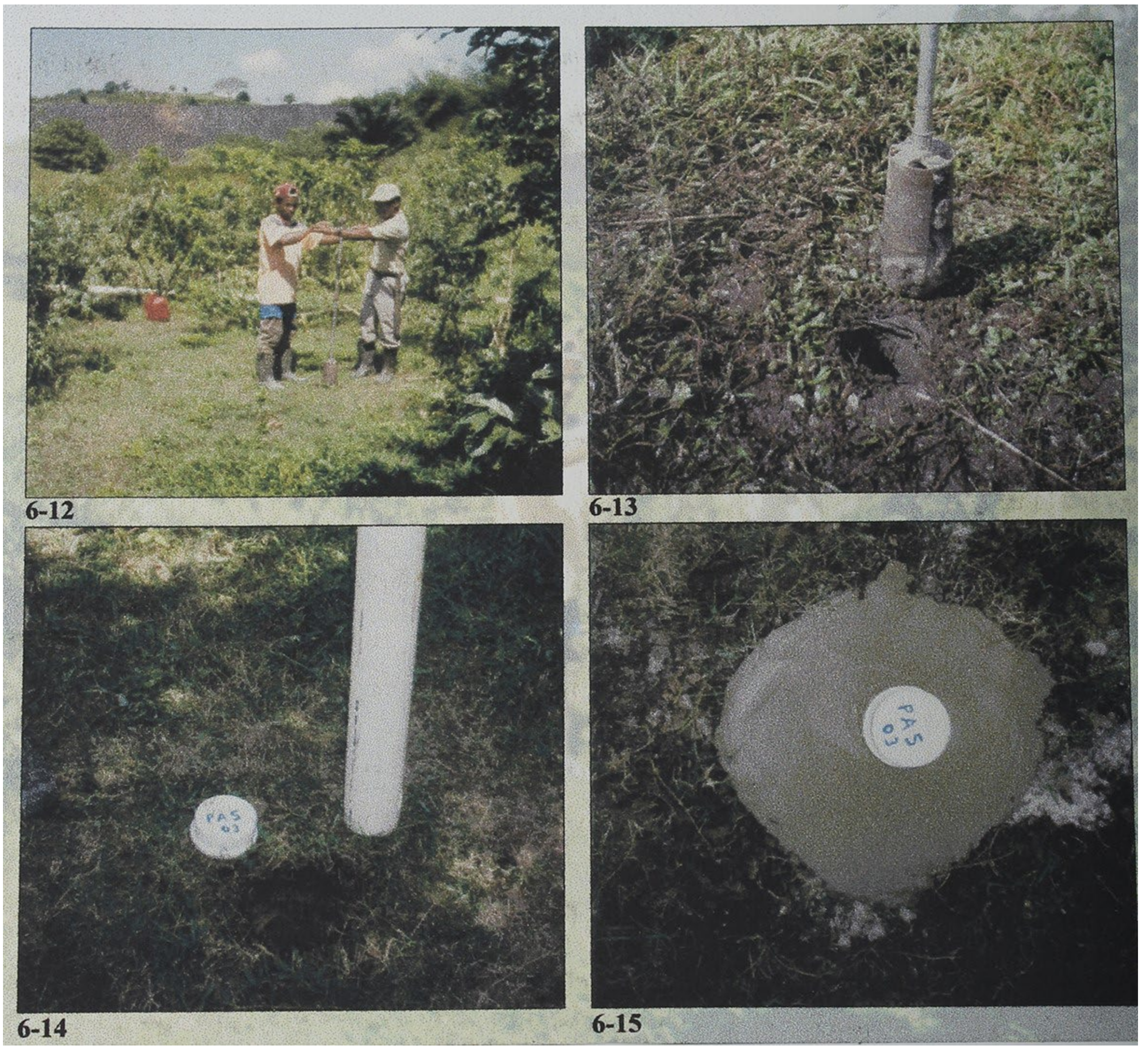


Figure 6-8. Groundwater sampling points

The construction of the wells (Photos 6-12 to 15) was intended to collect water from the saturated medium for quantitative chemical analysis of metals (Pb and Cd) and pH. Instructions for installing the wells were obtained from CETESB 06.010 - Construction of groundwater monitoring wells - Procedures[26] (CETESB, 1987).



Photos 6-12 to 15. The sequence of photos shows the construction of monitoring wells located in the wetland (Photo 13) and landfill (Photos 12, 14 and 15). In the construction of the wells, a manual auger was used for drilling (Photos 12 and 13), a PVC tube for internal coating, with a slotted filter and a plug for the upper end of the tube (Photo 14).

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[26] The purpose of this instruction was to establish the conditions required for the construction of wells (monitoring of groundwater aquifers, in addition to developing a number of data considered minimum for the presentation of a monitoring network project (CETESB, 1987).

The pilot area wells (GWSP 01, 02 and 03) were built with the following parameters: depth 1.90 cm; inner lining of PVC pipe (diameter 10cm); slot type filter, with 1cm spacing; quartz washed sand pre-filter; fill seal used cement; sanitary protection composed of a cement seal around the well; and PVC top cap.

Sampling for groundwater complied with the "Guidelines for the collection of samples", included as an annex to the CETESB standard (1987) and presented the following procedures (Table 6-10).

TABLE 6-10: PROCEDURES FOR GROUNDWATER SAMPLING.

ACTIVITIES	PROCEDURES
Parameters	chemical analysis for Pb and Cd; and pH
Sample volume	1 liter
Sampler type	Glass bottle
# of sampled points	3
Sampled locations	Upstream (GWSP-01), downstream, wetland (GWSP-02), embankment (GWSP 03) and cistern (GWSP-04)
Sample collection	heavy sampler bottle;
Preservation	05 ml of HN0 3 concentrates per liter
Storage time	180 days
Delivery to the laboratory	05 days after collection
Identification tag	Project name; identification and location; measured parameters and person responsible for the collection

6.4.2 Measured parameters and results

The quality indicators for groundwater used in this work presented the following parameters: concentrations of Pb and Cd metals and pH.

For the characterization of the metals, chemical analysis were done for Pb and Cd total metal (Table 6-11). These analyses were performed by CEPED using Atomic Absorption and Atomic Emission Spectrophotometry, following the procedures of the Standard Methods for the Examination of Water and Wastewater, J7Th Edition, (SWEWN, 1989).

TABLE 6-11: CONCENTRATIONS OF Pb, Cd, AND pH IN GROUNDWATER.

SAMPLE NO.	Pb (mg/L)	Cd(mg/L)	pH
GWSP-01	<0.05	<0.005	**8.1**
GWSP-02	**0.18**	0.007	7.9
GWSP-03	0.72	0.008	**8.0**
GWSP-04	<0.05	<0.005	**8.0**

The concentrations found for metals in the water of the wells described above were compared with the values for Pb = 0.05 mg/1 and Cd = 0.005 mg/1, established by Ordinance No. 36, of 10.01.90, of the Ministry of Health (CETESB, 1997).

As for the pH, it is characterized as one of the main parameters responsible for chemical processes in groundwater (BOULDING 1994), acting in the precipitation processes, with the reduction of the mobility of the metals or dissolution, increasing the mobility of the contaminants, in addition to combining with Eh, strongly bearing on the types of bacteria involved in the biotransformation process.

The groundwater pH was determined by a manual electrode pot, brand SCHOTT GERATE, and the evaluation of the four groundwater points sampled in the pilot area and observed in Figure 6-9, showed that upstream of the dam, point PASB-01, the limits for Pb and Cd were below the already mentioned limits. On the other hand, points GWSP-02 and 03, downstream the dam, and inserted respectively in the wetland and landfill zone, present levels above the standard limits, while point GWSP-04, downstream, presents values below the limits established for Pb and Cd.

Analysis of these data makes it evident that there is Pb and Cd contamination in the groundwater in the wetland and at the beginning of the embankment zone.

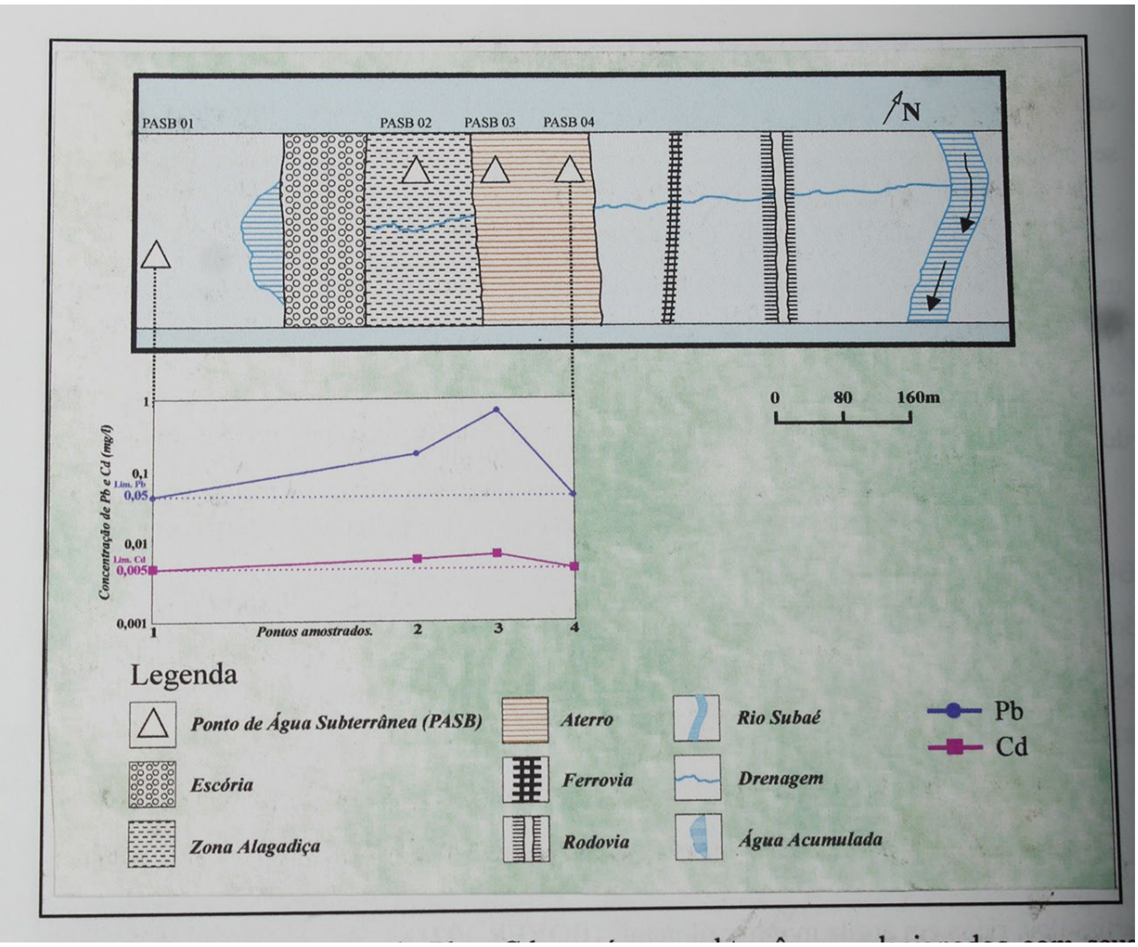

Figure 6-9. Pb and Cd concentrations in groundwater related to their sampling points.

6.5 Soil characterization

Soil is naturally characterized as an obstacle for persistent or mobile contaminants, delaying the arrival of compounds to the aquifer. This is related, particularly, to the processes of physical attenuation and retention by chemical and biological reactions that occur with the contaminants.

According to BATAS (1980) apud HIRATA (1992), soil texture is a critical component in the attenuation or transport of metals, with fine sediments presenting a better immobilization capacity than thick sediments.

This can be confirmed by a study on the mobility of heavy metals in clayey soils carried out by BORMA et al. (1996). The author demonstrates that the mechanisms of interaction between the soil and the contaminant are altered by the variation of pH and Eh, by the reactions of sorption and desorption, solubilization and precipitation, besides the formation of complexes.

Some researchers (SOLOMONS, 1995; KABAT-PENDIAS, 1995; BOULDING, 1995 and MESTINHO, 1997) claim that the concentration and mobility of heavy metals in the soils of the vadose and saturated zones are mostly controlled by the following parameters: pH; Eh; soil texture; percentage and type of clay minerals; percentage of MO; CTC; Fe, Ale Mn oxyhydroxides; and free CaCO3.

Soils found to a large extent in the Recôncavo Bay (Photos 6-16 and 6-17) and, particularly in the place where Plumbum is located, are classified as vertisols rich in montmorillonite clay[27] (BOYER 1971).

In the pilot area of the study, the vertisols originate from greenish shales, arranged in a gently undulating relief, presenting a clayey to very

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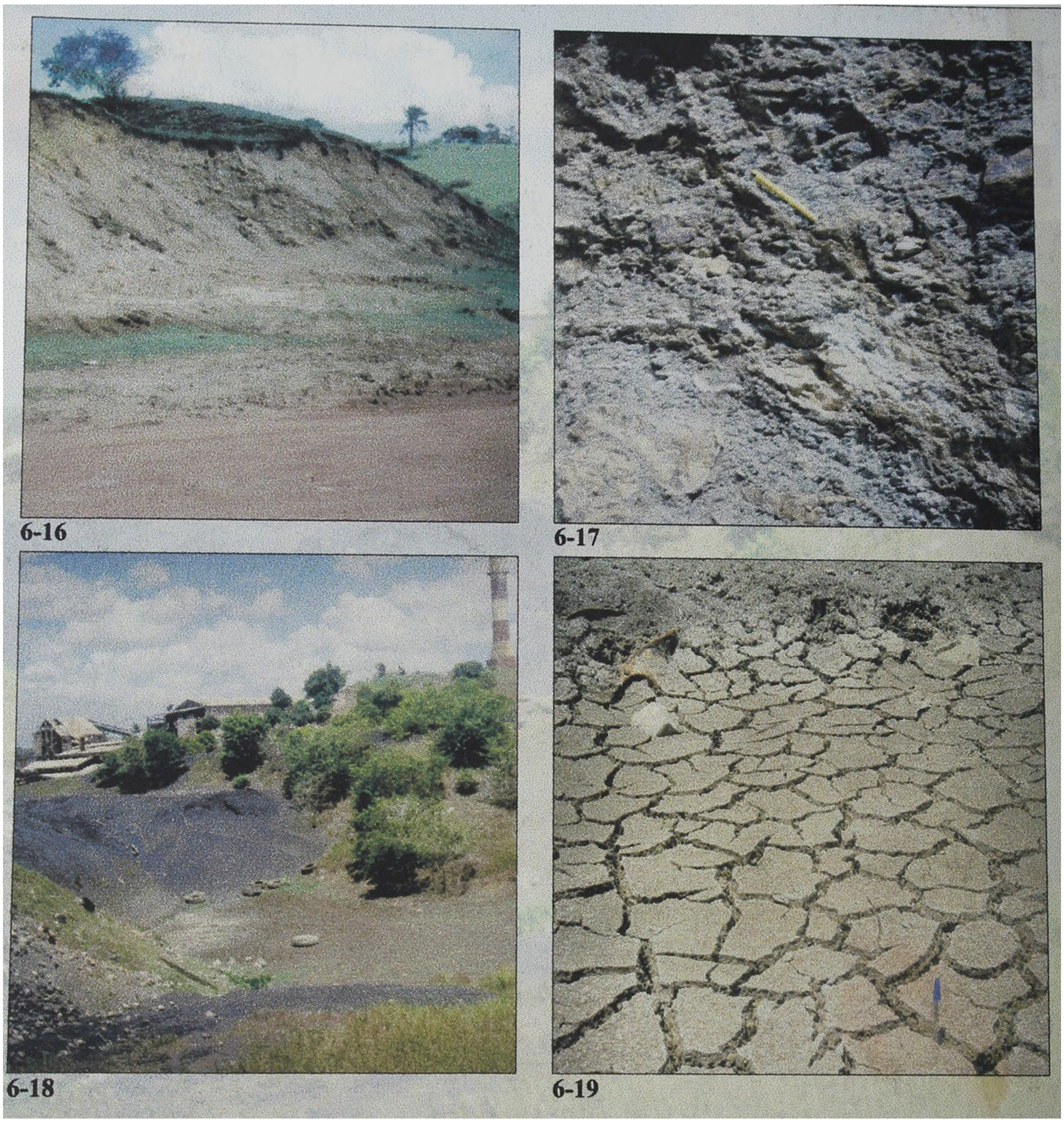
[27] Montmorillonite presents a chemical composition $(OH)_4Al_4Si_8O_{20}.xH_2O$, and consists of a structural unit formed by a layer of gibbsite between two silica groups. Between these units there are x molecules of water aggregated to the crystal. However, it is the interstitial water of the soil that is responsible for the expansion of the structure (VARGAS, 1977).

clayey composition, with clay content of the montmorillonite group. This type of soil is characterized by the mass movements of contraction and cracking (Photo 6-18 and 6-19) when dry, and by expansion when wet (BAHIA, 1996).



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Photos 6-16 to 6-19. Upper photos show a slope close to the pilot area and in detail a dark gray vertisol outcrop with yellowish silica nodules (Photos 6-16 and 6-17). Lower ones (Photos 6-18 and 6-19) show, respectively, the water accumulation zone upstream of the dry slag dam and, in detail, the soil with a cracking structure.

6.5.1 Soil sampling

Soil sampling in the pilot area included collecting surface points and soil profiles. The points of the soil profile located in the embankment and swamp areas, for an evaluation of the spatial distribution and behavior of the parameters - heavy metals, pH, CTC, MO and texture -, complemented by the superficial points.

The collection of samples was carried out with the material removed from the perforations for the construction of the groundwater sampling wells (GWSP-01, 02 and 03) and from a point in the wetland. For this study, the entire topsoil plus the underlying rock composed of the altered shale were established as a soil profile.

Soil collection included the following samples:

a) upstream of the slag dam, the surface portion of the soil (PPS-01.01) and a subsequent sample (PPS-01.02) were collected. These samples come from the drilling of the GWSP-01 well;
b) two samplings were collected from the wetland area, the first with material from the soil profile for the installation of the GWSP-02 well, with the collection of ten samples (PPS-02.01 to 10), and the second, within the waterlogged area , with the sampling of surface points PPS-04.01 and 02;
c) in the landfill zone, seven samples were collected in the soil profile PPS-03 (01 to 07), from the drilling of the GWSP-03 well (Photo 6-20) (Figure 6-11); and
d) the reference point was collected in soil of the same lithology as that found in the pilot area (PPS-05.01), located 7 km southwest of the area.

Photo 6-20. The sampling of the soil profile shows the variation in the color of the vertisol, presented in its upper feature (top) the orange-yellow color (material from the landfill), to dark gray at the base (shale).

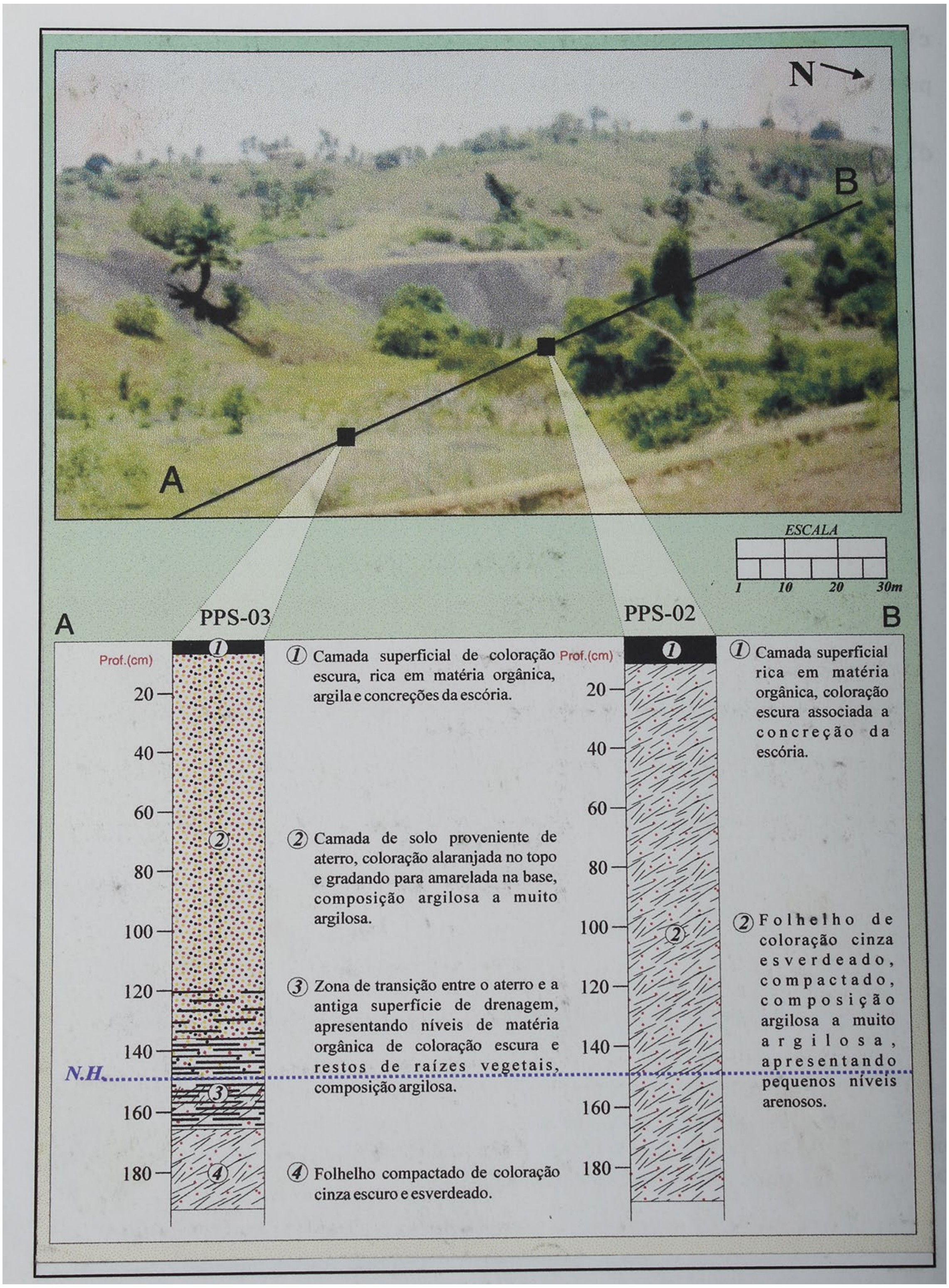

Figure 6-11. Locations of the two profiles surveyed (PPS-02 and 03); in addition to the schematic drawing with the texture of the soil.

Instructions for soil sampling complied with NBR 10.007 - Residue sampling: procedures, ABNT (1987d). The method was considered more adequate because this study recognizes contaminated soils in a similar way to residues. Sampling procedures are summarized in Table 6-12.

TABLE 6-12 PROCEDURES FOR SOIL SAMPLING

SAMPLE NO.	Pb (mg/L)	Cd(mg/L)	pH
GWSP-01	<0.05	<0.005	8.1
GWSP-02	0.18	0.007	7.9
GWSP-03	0.72	0.008	8.0
GWSP-04	<0.05	<0.005	8.0

6.5.2 Measured parameters and obtained results

The parameters analyzed for the soils were the following: Pb and Cd metals, pH, CEC, OM, soil texture and clay type.

Pb and Cd metals

Chemical analysis for Pb and Cd for samples from the profiles and surface soil sampling had the concentrations shown in Table 6-13.

In Brazil, there are no standards or norms for contaminated soils[28] and no classification for their multiple uses nor any procedure making possible their remediation. However, several countries already have established the average concentrations of heavy metals for their soils (Table 6-14), which serves as a reference for decision making when remediating these sites.

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[28] For this study, soils are understood as "those that contain chemical substances in concentrations considered harmful, directly or indirectly, to humans or other living beings" (SÁNCHEZ, 1998).

TABLE 6-13: CONCENTRATIONS OF Pb AND Cd (pg/g) IN THE SOIL OF THE PILOT AREA

SURFACE SAMPLING (PPS-01, 04 and 05) AND SOIL PROFILE (PPS-02 and 03)	Depth (cm)	Pb (pg/g)	Cd(µg/g)
PPS-01.01	10cm	50	1,0
PPS-01.02	10-30cm	<5,0	<0,5
PPS-02.01	10cm	1.800	38,0
PPS-02.02	10-30 cm	1.300	18, l
PPS-02.03	30-50 cm	821	12,4
PPS-02.04	50-70 cm	307	3,7
PPS-02.05	70-90 cm	175	1,7
PPS-02.06	90-ll0cm	<5,0	<0,5
PPS-02.07	110-130 cm	<5,0	<0,5
PPS-02.08	130-150 cm	<5,0	<0,5
PPS-02.09	150-170cm	182	2,2
PPS-02.10	170-190 cm	157	2,1
PPS-03.01	10cm	2.000	27,9
PPS-03.02	10-40 cm	390	5,0
PPS-03.03	40-70 cm	89	1,3
PPS-03.04	70-100 cm	256	2,5
PPS-03.05	100-130 cm	3.000	39,9
PPS-03.06	130-160 cm	1.400	20,4
PPS-03.07	160-190 cm	78	1,1
-PPS-05.01	10cm	<5,0	<0,5
PPS-01.01	10cm	50	1,0
PPS-01.02	10-30cm	<5,0	<0,5
PPS-02.01	10cm	1.800	38,0
PPS-02.02	10-30 cm	1.300	18, l

TABLE 6-14: CONCENTRATION OF Pb AND Cd (ppm) ON THE SURFACE OF SOILS FROM METAL PROCESSING INDUSTRY

Source	Country	Pb(ppm) variation	Cd(ppm) variation
Metal Processing Industry	Canada	291 - 12,123	2 - 36
	Greece	1,250 - 18,500	-
	Netherlands	628 - 1,334	9 - 33
	Norway	104	-
	Japan	310 - 2,100	2.2 - 88
	Poland	72 - 1,350	6 - 40
	United States	500 - 6,500	26 - 160
	Zambia	92 - 2,580	0.6 - 16
	Bulgaria	-	2 - 5
	Russia	3,000	-

Source: KABATA-PENDIAS & PENDIAS (1984) apud CETESB (1997)

As shown in Table 6-13, the concentrations[29] found in the soil of metal processing industries, compared with the levels found in the surface samples from the Plumbum pilot area, reveal that only countries like Greece (18,500 ppm) and Canada (12,123 ppm) have higher values than those found so far at the Plumbum site (8,200 ppm).

As for Cd, only the United States (160 ppm) has a value higher than that found at the Plumbum site (117 ppm). These results lead to the conclusion that the Plumbum site has one of the highest concentrations of Pb and Cd retained in the soil.

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[29] The usual units that measure concentrations of metals in soil are ppm (part per million) and pg/g (microgram/gram), where lppm=lpg/g.

Hydrogenionic potential (pH).

The pH was the main factor controlling the precipitation of metals through its capacity (concentration of H+ in the water) to attack rock minerals, inducing leaching and/or solubilizing its constituents.

Studies by BORMA et al. (1996) suggest that the mobility of heavy metals in clayey soils fundamentally depends on the behavior of pH. In this study, the author quantifies the main interferences caused by pH in contaminated clay soils, highlighting, among them:

a) the sorption and desorption, solubilization and precipitation and complex formation reactions are dependent on the pH of the soil solution;
b) for high pH values, precipitation mechanisms prevail, while as the pH decreases, the precipitates redissolve releasing metal ions, and cation exchange prevails;
c) for pH values in which cation exchange prevails, the metal ion retention capacity is directly influenced by the clay minerals present.

In the Plumbum pilot area, the pH of the soil was classified according to the Soil Survey Staff (1993) apud BOULDING (1994). This classification is used by the EPA, and presents the following specifications: ultra-acidic (UA): $pH < 3.5$; extremely acidic (EA): $3.5 \leq pH \leq 4.4$; very strongly acidic (VS): $4.5 \leq pH \leq 5.0$; strongly acidic (SA): $5.1 \leq pH \leq 5.5$; moderately acidic (MA): $5.6 \leq pH \leq 6.0$; slightly acidic (SA): $6.1 \leq pH \leq 6.5$; neutral (NA): $6.6 \leq pH \leq 7.3$; slightly alkaline (MA): $7.4 \leq pH \leq 7.8$; moderately alkaline (MO): $7.9 \leq pH \leq 8.4$; strongly alkaline (SA): $8.5 \leq pH \leq 9.0$; and very strongly alkaline $pH > 9.0$.

To evaluate the pH, 22 analyses were carried out by CEPED, following the procedures of the EMBRAPA Soil Analysis Methods Manual.

The values found ranged from 7.9 to 8.7 or moderately alkaline to strongly alkaline. These values are within the research range and confirm the influence of pH on the retention of heavy metals in clayey soils and suggest that for soils rich in clays, from pH around 6.0, Pb can be retained by 100%. Whereas for Cd, from pH 7.0 onwards, retention occurs in practically 100%. The evaluation of the concentrations of metals in the superficial points of the pilot area (PPS-01, 02, 03 and 04) and the pH points to the close relationship between the high concentrations of Pb and Cd with alkaline pH values (Table 6- 15).

In view of these data, the basic pH is probably one of the effective factors influencing the retention of metals (SOLOMONS, 1995; KABAT-PENDIAS, 1995 and BORMA et al., 1996) in surface samples from the pilot area. However, the PPS-02 (Figure 6-13) and PPS-03 soil profiles demonstrate that, for clayey soils, alkaline pH values do not influence the retention of metals with increasing depth.

TABLE 6-15: SUMMARY OF CONCENTRATIONS

Sample	Pb (µg/g)	Cd (µg/g)	pH
PPS-01.01	50	1.0	8.0
PPS-02.01	1,800	38.0	8.1
PPS-03.01	2,000	27.9	8.0
PPS-04.01	8,200	117.0	8.0

Cation Exchange Capacity (CEC)

Cationic exchange or physical adsorption (BORMA, 1996) is characterized as a reversible process in which cations (Ca+ 2, Mg+ 2, Na+ and K+) and anions are exchanged between the liquid and solid phases, or between two solid phases in touch with each other. CEC is measured in milliequivalents per 100 grams of soil (meq/lO0g).

The organic matter and the type of clay are the parameters that directly influencing the CEC in the retention of heavy metals (SOLOMONS, 1995). According to the same author, in some organic soils, their values can reach 200 meq/100, given to the exchange of cations between the carboxyl group present in organic matter molecules, with metallic ions (ALEXANDRE, 1995).

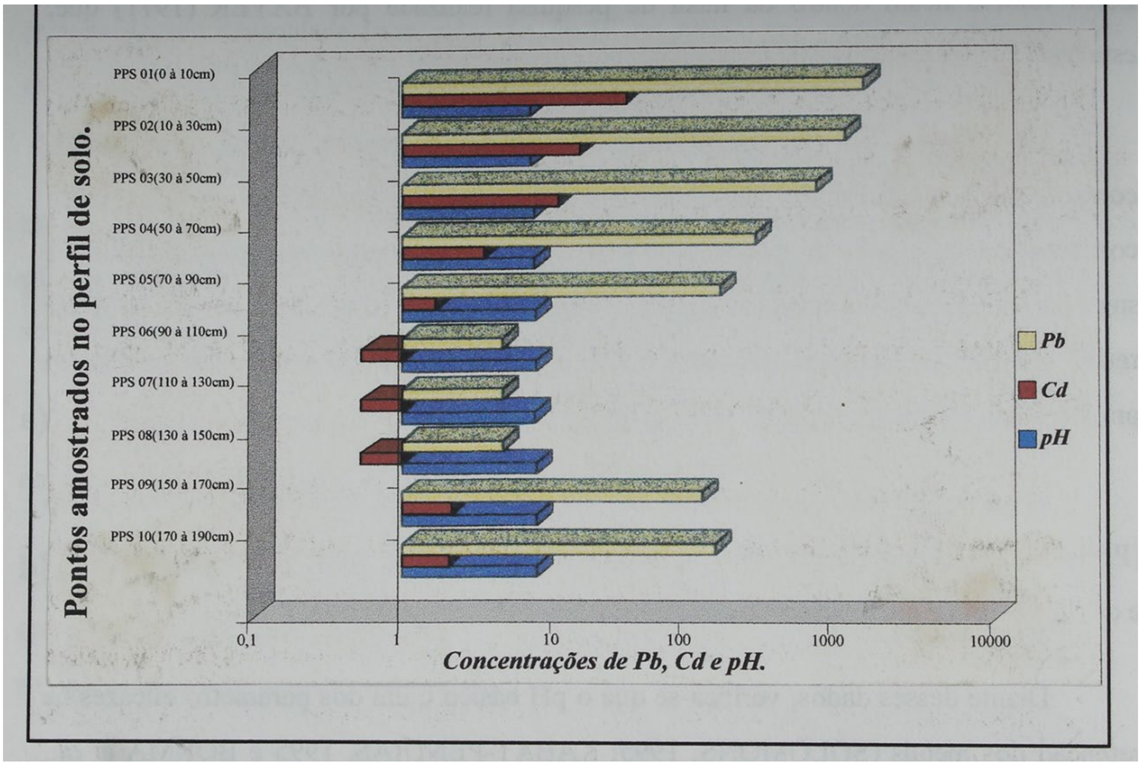

Figure 6-12. Variation of Pb and Cd concentrations and pH values with the depth of the PPS-02 soil profile.

According to Hirata (1992), cation exchange represents a temporary mechanism of retention of heavy metals and is limited by competition with common metal ions (Ca+ 2Na+, Ir and K+), as most heavy metals exist in the form of cations in solution (BORMA et al., 1996).

The CTC analysis for the pilot area were carried out by CEPED using the EMBRAPA Soil Analysis Methods Manual. The results are summarized in Table 6-16.

The rating for cation exchange capacity will be the same as that followed by the EPA and establishes the following: high > 20 meq/l00g; neutral of 12 - 20 meq/l00g; and low < 12 meq/100 g (BOULDING, 1994). Based on this classification and comparing with the data obtained in the pilot area, it appears that all samples presented values much higher than those established in the classification proposed by the EPA. In other words, the studied soils present very high CEC.

As verified, the points on the surface (PPS 01-02, 01-03 and 01-04) present, respectively, high concentrations of metals (1,800; 2,000 and 8,200 μg/g for Pb and 38; 27.9 and 117 μg/g for Cd). These concentrations are, respectively, related to high CTC (44.3; 32.2 and 47.1 meq/100 g) and high percentages of MO (2.9; 4.5 and 10.9%).

The influence of organic matter can be observed even in the subsurface, notably in profile 03, where points 03/05 and 03/06 present, respectively, values for Pb equal to 3,300 and 1,400 μg/g and for Cd equal to 39.9 and 20.4 μg/g; while, for the cation exchange capacity and organic matter, it presents, respectively, 45.4 and 45.1 meq/100 g and 3.6 and 4.9%.

TABLE 6-16: COMPILATION OF CONCENTRATIONS OF Pb, Cd, CTC AND MO.

Sample/Profile	Pb (µg/g)	Cd (µg/g)	CTC (meq/l00g)	MO%
02/01	1,800	38.0	44.3	2.9
02/02	1,300	18.1	41.0	0.7
02/03	821	12.4	35.6	0.9
02/04	307	3.7	38.6	1.1
02/05	175	1.7	39.0	0.9
06/02	<5.0	<0.5	23.7	0.4
02/07	<5.0	<0.5	53.0	0.9
02/08	<5.0	<0.5	20.0	0.3
02/09	182	2.2	41.7	0.9
02/10	157	2.1	40.4	0.6
03/01	2,000	27.9	32.2	4.5
03/02	390	5	37.4	1.3
03/03	89	1.3	35.6	0.8
03/04	256	2.5	39.0	0.7
03/05	3,300	39.9	45.4	3.6
06/03	1,400	20.4	45.1	4.9
03/07	78	1.1	46.4	4.3
01/04	8,200	117	47.1	10.9
04/02	1,800	38.9	42.5	4.5

These results confirm the observations of SOLOMONS (1995), which establishes an intrinsic relationship between the retention of metals, with high values for the cation exchange capacity and organic matter.

Soil texture

As argued by many authors, because of the specific conditions of soil porosity and permeability, soil texture is the most important physical parameter in the attenuation of heavy metals for the unsaturated zone.

As confirmed by lab analysis carried out by SCOKART et al., (1985) apud TAVARES (1990) and SOARES et al., (1994), using strata with different granulometries, the immobilization of heavy metals in fine texture (clays) are associated with basic pH values.

The soil in the Plumbum pilot area is very thin, ranging from 5 to 10 cm in the wetland area and between 40 to 100 cm in the embankment zone. The surface layer of the wetland area shows a predominance of organic matter, from dark gray to black, while the landfill area has a thin layer of surface organic matter and, in its remainder, predominantly yellow-orange clayey soil. In contact with the ground, the greenish shale of the Santo Amaro group occurs.

The studies carried out on soil texture tried to quantify and classify soil texture, allowing the prediction of possible physical and chemical processes associated with it.

The procedure was carried out according to the ABNT Standard - 7181- Soil - Granulometric Analysis (ABNT, 1984), and physical analysis by CEPED. The granulometric characterization of the soils was given by the percentages of clay, silt, sand and gravel, following the Soil Texture Classification Diagram, used by the Soil Conservation Service of the United States Department of Agriculture and adapted in ABNT 7181.

The soil texture classification diagram (Figure 6-13) shows the distribution of the percentages of sand, clay and silt, from the 19 points sampled in the soil profiles and from the surface sampling.

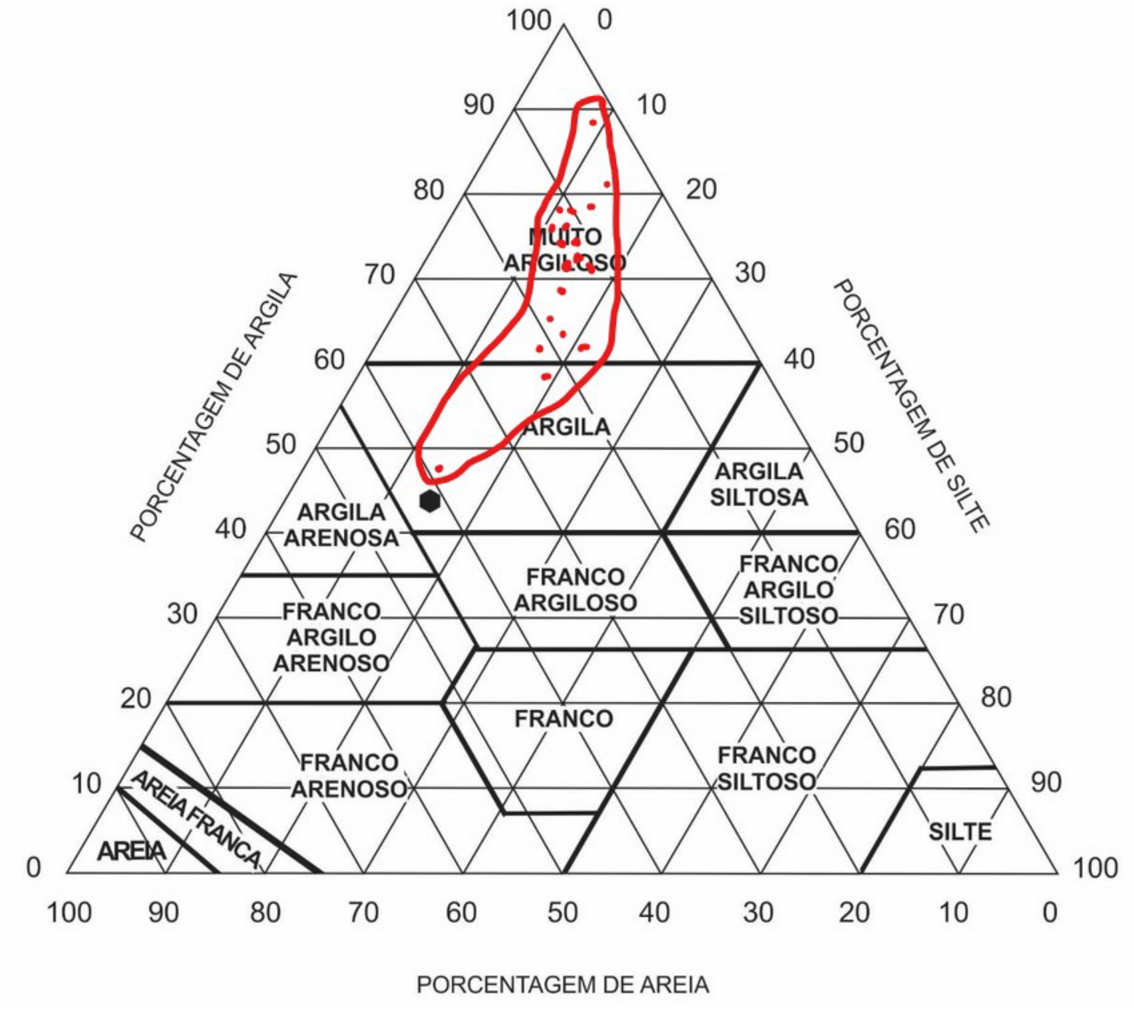

Figure 6-13. Classification of soil texture in the pilot area

The soil textural classification diagram considers four textural classes:

a) Sand group: represented by soils whose granulometric fractions of sand total 70% and the granulometric fractions of clay less than 15%;
b) Clay group: represented by soils whose granulometric fractions contain at least 35% of the clay fraction;
c) Loam group: represented by soils mixed with sand, silt and clay particles; and
d) Group of silts: represented by soils whose granulometric fractions of silt are above 80% with less than 25% of clay.

Soils in the pilot area have a predominantly clayey to very clayey texture, as the underlying rock (shale) has a predominantly clay mineralogical composition.

Due to the distribution of pore sizes in unsaturated soils (HIRATA, 1992, hydraulic conductivity becomes a soil texture parameter acting as a regulator of physical attenuation processes.

This fact is confirmed when researched in shales, which, according to MESTINHO (1997), present high total porosity (33 - 60%), but small hydraulic conductivity (10-6 - 10·9 cm/s), as their pores are very reduced and, consequently, allow for a very slow circulation of water.

The dispersion coefficients present their lowest values in clayey soils, considering that the longitudinal and lateral dispersion in these soils are, respectively, < l x l04 and < l x l0·6 m/day (BEST et. al., 1993) . Applying these values to the pilot area and considering the migration of metals from the deposition of the slag in its first year of production, in thirty years, lateral and longitudinal dispersion of 0.11 and 1.10 cm are obtained, respectively, through a simple rule of three between the values of lateral and longitudinal dispersion in m/day, times the total number of days analyzed.

The reference values used in the research were those obtained in a chemical analysis for total metal, in a sample collected in soil correlated to the one studied, sampled in an area with little anthropic action. The values found were Pb less than 5 pg/g and Cd less than 0.5 pg/g.

Organic Matter (OM)

Due to its high cation exchange capacity, the literature indicates OM as the parameter with the greatest influence on the mobility of contaminants[30]. It is generally found, in greater proportions, in the surface layers of soils and is a result of processes of natural origin or human activities that occur on the surface.

When of natural origin, it is composed of humic substances, which are organic macro cells existing in the environment (water, soil and sediments) (Figure 6-14) and are characterized as a product of chemical and biochemical reactions on 1 1 substances of origin biological, mainly vegetables (PORTO ALEGRE et. al., 1994).

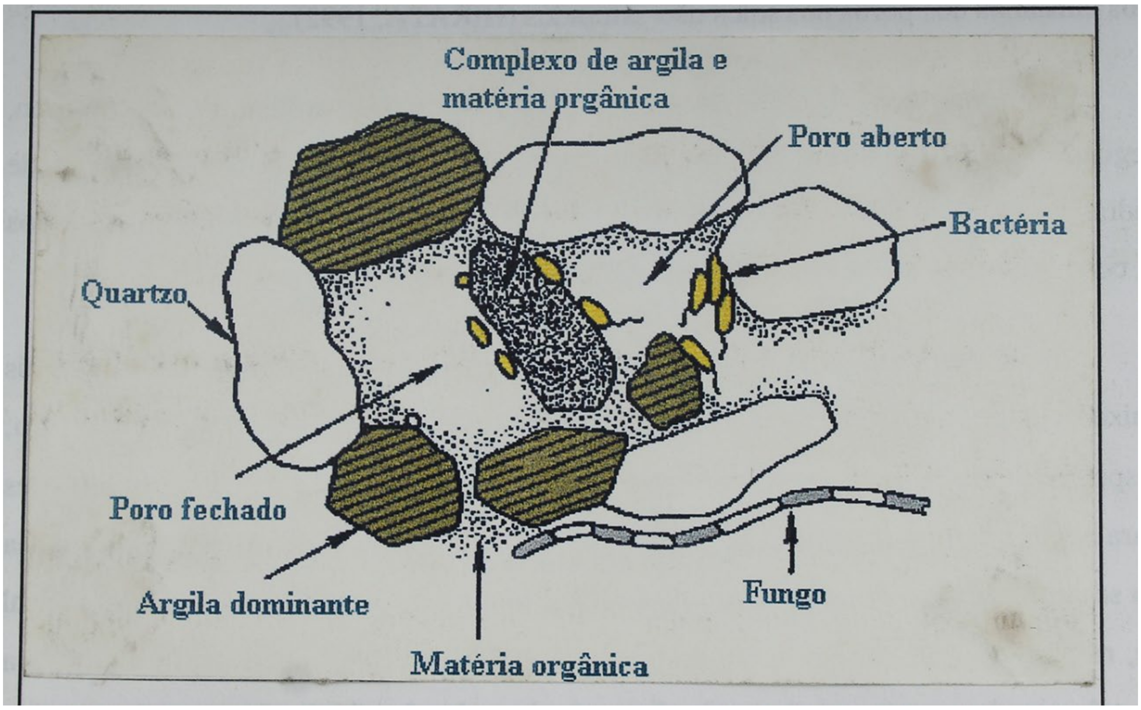

Figure 6-14. Association between organic matter, organisms and mineral particles. Source: PAUL & CLARK (1989) apud SCHULIN et al. (1995)

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[30] Studies carried out by ROBERTS et al., apud TAVAVES (1990) summarizes the rates of Pb accumulation in previously uncontaminated humus. The uncontaminated humus was disposed near the foundry, where particulates from the project were deposited. In the period of thirty days, the humus accumulated about 900 to 1200 11g/g of Pb, while the soil surface gradually increased from 70 11g/g to 300 11g in the period.

According to MESTINHO (1997), the high concentrations of organic matter and clay minerals in subsurface soils promote conjugated reactions of complexation and sorption of organometallic complexes, contributing to a lower amount of Dissolved Organic Carbon (DOC) in groundwater recharge.

Organic matter in the soil can immobilize metals by complexation or cation exchange reactions, behaving more effectively than clays. However, according to IDRATA (1992), it also constitutes a momentary immobilization mechanism, like some biodegradable organic complexes, which release the metal and allow its movement in the subsurface.

The immobilization of metals by organic matter is related to the fact that it has a very high specific surface (700 m2/g). This specific surface influences the physicochemical properties of the soil, increasing the contact area and, consequently, the metal retention capacity (GROHMANN, 1972 apud AMARANTE, 1997).

The analytical method for its determination is the Total Organic Carbon (TOC), which is an instrumental test to measure all the carbon released in the form of CO2 (MESTINHO, 1997).

The determination of organic matter content in the soils of the pilot area was performed by CEPED in 19 samples collected from the soil profile and from surface sampling, as can be seen from Table 6-15.

These samples were classified according to the Soil Classification System (SCS), which defines the following classes for organic matter: very low (VL) < 0.5%; low (LL) 0.5 - 1.0%; moderately low (ML) 1.0 - 2.0%; mean (MM) 2.0 - 4.0%; and high (HH) > 4.0% (BOULDING, 1994). These values are the same as those used for EPA classification.

The percentages of clay and OM in the soil represent the main parameters for the determination of Reference Values[31] (CETESB, 1997).

In the Netherlands, these values are defined to calculate the natural contents of heavy metals, through specific equations for each metal, using as standard values for the soil 10% organic matter and 25% clay. This methodology was developed by the Dutch Ministry of Territorial Planning and Environment (VROM) and is based on empirical relationships.

Comparing the results for organic matter, as discussed in the item on cation exchange capacity, it can be seen that all samples for surface soils present medium to high values, respectively 2.9 at point 02/01, 10.9 at point 03/01 and 4.5 at point 04/01, as well as the percentages found in the intermediate zone of the landfill profile, points 05, 06 and 04/07. These values must be related to the old drainage surface, rich in organic matter, and preserved by the landfill carried out by Plumbum to channel and drain surface water.

From an analysis of the surface samples and the profile, it can be affirmed that: the average to high values of MO are predominantly related to the high concentrations of Pb and Cd and of the CTC, confirming greater retention of these metals, even in the subsurface, when related to higher concentrations of MO and CTC.

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[31] Reference values are used to control the quality of soil and groundwater. Initially they were used in the ABC system, developed in the Netherlands to establish the soil multifunctionality. New guideline values for remediation of contaminated sites were established in 1994 by the Soil Protection law, which reaffirmed the concept of multifunctionality, and established three quality levels for soil and groundwater: reference value (S) indicates the level of quality for clean soils; alert value (T), alteration of soil functional properties; and intervention value (I) indicates the level above which there is a risk to public health and the environment (CETESB, 1997)..

Clay minerals

Soil composition is an important parameter in the mechanism of adsorption of metals, as it favors the retention of metals, especially in the presence of certain clay types, which, interacting with organic matter, provide high cation exchange capacity.

The word clay is generally used in pedology to designate everything in the soil with a size between 0 and 2 microns, while in engineering geology it is defined as an agglomerate of clay-mineral and other elements, such as quartz, feldspars and mica.

The vertisols found in the pilot area are clayey to very clayey soils and, according to BAHIA (1996), represent 2:1 clays of the montmorillonite group, which have planar surfaces with thicknesses of 10 to 16A.

Montmorillonite has the property to swell up in a wet state, reaching 16 A, and returns to a thickness of 10 A in the dry state. These variations give it undesirable engineering properties. However, for metal retention, these variations cause retraction cracks, favoring the entry of mineral ions, as well as fine particles of organic matter (BOYER, 1971).

The high cation exchange capacity of montmorillonite is the main factor responsible for the retention capacity of heavy metals in the soil, especially at low pH values (YONG et al., 1993).

Montmorillonite has the highest specific surface among all soil minerals (BOURG, 1995), around 700 to 800 (m2/g), while vermiculite has 600 to 800 (m2/g) and illite of 65 to 100 (m 2 /g).

Studies on the mobility of heavy metals in clayey soils (YONG et al., 1993) and (BORMA et al., 1996) showed that, for any pH value, montmorillonite has the highest order of selectivity of heavy metals in relation to pure clay minerals: montmorillonite>illite>kaolinite (Table 6-17).

Table 6.17 - Order of selectivity of adsorption of heavy metals by clay minerals and iron oxyhydroxides.

ADSORBENT	ORDER OF SELECTIVITY
montmorillonite	Pb>Cu>Mg>Cd>Zn>Ni
illite	Pb>Cu>Zn>Cd>Mg Zn>Mn>Hg
Smectite, vermiculite and kaolinite Albite and labradorite Fe oxyhydroxides:	Zn>Cd>Mn>Hg Pb>Cu>Zn>Ni>Cd>Co>Sr>Mg
Ferrihydrite Hematite	Pb>Cu>Zn
goethite	Cu>Pb>Zn

Source: ALEXANDRE (1995) apud YONG et al. (1993)

6.6 Geochemical processes acting on the mobility of contaminants

An expressive amount of chemical and biogeochemical processes occur naturally in the vadose and saturated soils of a system. This stems from the interaction mechanisms involving water, mineral and gaseous phases, as well as organisms and plants.

However, the introduction of an anthropogenic source of pollution causes transformations and transfers of some compounds, causing changes in their physical state or chemical form and, consequently, attenuating, delaying or making these compounds available.

The movement of metals in the soil depends on several factors, including the existence of a prolonged period of contamination, the change in pH, and the saturation of the retention capacity of the metals in the system (CETESB, 1997), in addition to some mechanisms of soil/contaminant interaction that are strongly evidenced by reversible reactions, resulting in the retention and accumulation of contaminants in the soil (BORMA et al., 1996).

These interaction mechanisms have been extensively researched, and depending on the parameters and environment studied, the appropriate mechanisms for the retention or availability of heavy metals prevail.

However, it is consensual that, depending on the variations caused by pH and Eh, the mechanisms involved are predominantly adsorption and desorption, precipitation and solubilization, complexation and oxide-reduction (YONG et al., 1993; FARIAS et al., 1994; BOULDING, 1995; BORMA et al., 1996, YARON et al., 1996; and MATTIGOD, 1981 apud CETESB, 1997).

Initially, the studies carried out in the pilot area did not intend to evaluate these chemical processes. However, a preliminary approach was imperative, considering that the understanding of the transfer mechanisms of pollutants in the studied area is a preponderant factor for proposing feasible measures and remediation techniques.

According to the parameters used in the pilot area, the most evident and active chemical processes at the site contaminated by the Plumbum Co. are adsorption, solubilization/precipitation, and complexation.

6.6.1. adsorption process

Adsorption is the mechanism of attraction of solid, liquid or gaseous molecules, ions or atoms of surface particles by physical-chemical forces, which acts usually associated with parameters such as basic or neutral pH, high cation exchange capacity, and high percentage of organic matter.

BORMA et al., (1996) referred to physical adsorption or cation exchange as a mechanism to proceed with the exchange of ions (cations and anions) through reversible processes between liquid and solid phases or between two solid phases.

Clay minerals and organic matter, both characterized in the pilot research area, are materials that behave as adsorbents, as they have a negative surface charge and high specific surface capable of fixing and exchanging cations (MESTRINHO, 1997).

As most heavy metals exist in the form of cations in solution (BORMA et al., 1996), they are adsorbed by clay and organic matter. This is because clays have a higher ion exchange capacity, especially cations, since anions cross the clay layers with relative ease. Therefore, the higher the clay content in the soil, the greater the adsorption capacity of heavy metals (MESTINHO, 1997).

All these mechanisms develop especially due to pH variation. The alkaline pH found in the soil, surface water and groundwater of the researched site induces a higher CEC, and consequent retention of heavy metals.

The selective adsorption of heavy metals in different soils was compiled by YONG et al., (1993), and recorded in the literature by several authors (Table 6-16), demonstrating that the order of selectivity depends on soil type and soil interaction conditions and stability between soil and contaminant. We can see also the prevalence of Pb and Cu, as metals that are preferentially adsorbed, under conditions of different types of soils, solutions and pH. While Cd behaves in the opposite way, being the metal less likely to be adsorbed.

An experiment carried out by YONG (1993), applying a solution of Pb and Cd nitrates separately in clayey soils containing kaolinite, illite, montmorillonite and natural soil (Figure 6-18), demonstrates that montmorillonite has a greater retention field for both Pb and for Cd.

The same experiment was carried out with the pH parameter, maintaining the solution of Pb and Cd nitrates in clayey soils and the results showed that montmorillonite also has a greater metal retention field.

TABLE 6-18: SELECTIVE ADSORPTION OF HEAVY METALS IN DIFFERENT TYPES OF SOILS

MATERIAL	SELECTIVE ORDER	REFERENCES (apud YONG et al., (1993)
Kaolinite (pH 3.5 - 6)	Pb>Ca>Cu>Mg>Zn>Cd	Farrah et al., (1977a, b)
Kaolinite (pH 5.5 - 7.5)	Cd>ZN>Ni	Puls et al., (1988)
Illita (Ph 3.5 - 6)	Pb>Cu>Zn>Ca>Mg	Farrah et a!., (1977a, b)
Montmorillonite	(pH 3.5 - 6) Ca>Pb>Cu>Mg>Cd>Zn	Farrah et al., (1977a, b)
Montmorillonite	(pH 5.5 - 7.5) Cd=Zn>Ni	Puls et al., (1988)
Al oxides	Cu>Pb>Zn>Cd	Kinniburgh et al., (1976)
Mg oxides	Cu>Zn	Murray (1975)
Fe oxides	Pb>Cu>Zn>Cd	Benjamin et al., (1981)
Fulvic acid (pH 5.0)	Cu>Pb>Zn	Schnitzer Ela!., (1967)
Humic acid	Cu>Pb>Cd>Zn	Steverson (1977)
Non-organic soils (pH 5.0)	Pb>Cu>Zn>Cd	Elliot et al., (1986)
Soils (20 - 40 g/kg organic)	Pb>Cu>Cd>Zn	Elliot et al., (1986)

Source: YONG et al., (1993)

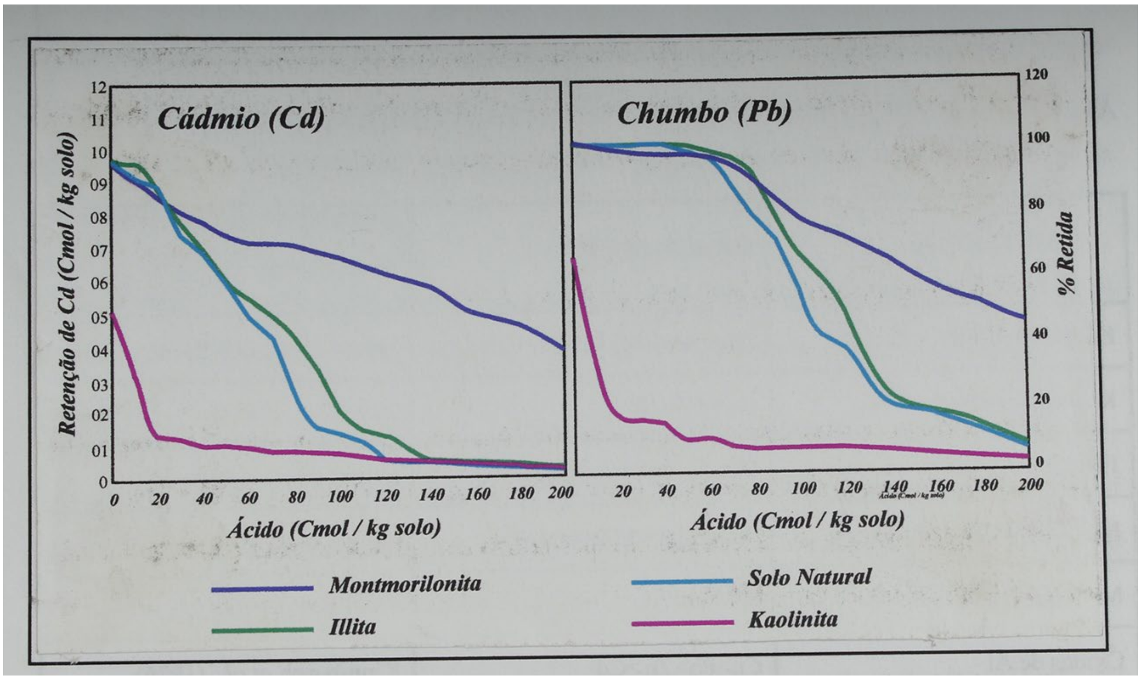

Figure 6-15. Pb and Cd retention by clay minerals. Source: YONG et al. 1993.

An analysis of surface samples and soil profiles in the Plumbum Co. pilot area present the following specifications:

1) the clay found in the pilot area is montmorillonite (BAHIA, 1996);
2) the presence of high levels of clay (46 to 87%), what classifies the soils as clayey to very clayey (EPA considers it abundant if more than 27% (BOULDING, 1994);
3) the high cation exchange capacity, from 23.7 to 53 meq/lO0g, significantly above the 20 meq/100g considered as high by EPA;
4) the high percentages of organic matter (2.9 to 10.9) in the samples in which the highest concentrations of Pb and Cd o occur (EPA considers values greater than 4.0 as high); and
5) the moderate to strongly alkaline soil pH in the area (7.9 to 8.7).

All these factors present conditions that are undoubtedly favorable to the adsorption process of Pb and Cd metals in the pilot area. Especially in the wetlands, where the highest concentrations of metals and organic matter occur.

6.6.2 Precipitation and solubilization process

The solubilization or dissolution of a substance in an aqueous medium is "the ability it has to dissolve until it reaches a certain threshold value" (BIRATA, 1992). Reaching this threshold value, the phenomenon of precipitation occurs, when insoluble solids are formed and separated from a solution.

In the subsurface, the oxygenation of water promotes the solubilization of metals. In waterlogged or compacted soils, the degradation of organic substances is compromised by the absence of oxygen and the anaerobic processes in general increase the pH, causing the precipitation of several metals (POMPÉIA, 1994).

Solubilization and precipitation are processes controlled by changing the pH and Eh of the medium. According to MESTINHO (1997), with increasing pH, many metals can be precipitated.

A study by YONG et al (1993), using the method of selective sequential extraction, quantified the percentages of Pb and Cd in some clayey soils through precipitation and dissolution processes, having pH as an intervening parameter. It showed that (Table 6-19) Pb precipitates exclusively between pH 6 and 8, ranging from 70.4 to 100%, respectively; while solubilization occurs at 100%, between pH 1 to 5. As for Cd, precipitation does not occur with pH variation; however, solubilization was 100% throughout the pH range.

TABLE 6-19: PRECIPITATION AND SOLUBILIZATION ORIGINATING FROM pH

PROCESSES	pH							
	1	2	3	4	5	6	7	8
% of Pb Precipitation	0	0	0	0	0	70.4	99.7	100
% of Pb solubilization	100	100	100	100	100	29.6	0.3	0
% of Cd Precipitation	0	0	0	0	0	0	0	0
% of Cd solubilization	100	100	100	100	100	100	100	100

Source: YONG (1993)

From the data collected from the Plumbum pilot area, we conclude that the wetland represents the best area for the assessment of solubilization and precipitation processes, as it contains:

a) the emergence of leached and/or solubilized water from the contaminated slag with levels of 3.13 mg/L of Pb and 0.013 mg/L of Cd;
b) expressive concentrations of 8,200 µg/g of Pb and 117 µg/g of Cd in surface soils; and
c) surface water pH with basic values ranging from 6.8 to 8.3.

These results suggest that this is an area conducive to Pb and Cd precipitation.

However, compared with the studies by YONG et al. (1993), it can be deduced that in the pilot area Pb is precipitated and Cd is solubilized. However, this hypothesis is contradicted by the high concentrations of Cd retained in the surface layers of the wetland, which suggests that other processes, mainly of a biological nature, may be occurring and favoring the precipitation of Cd.

6.6.3 Complexation processes

This process is considered by many authors as the most important mechanism for retaining heavy metals, given the complexity involved and its close connection with the biological environment.

It is a chemical reaction that "occurs between metals and organic and inorganic ligands, which facilitates the transport of metals and the mobility of various organic contaminants in the subsurface" (MESTRINHO, 1997).

Inorganic ligands are common species of ions found in groundwater, while organic ligands are generally formed by humic compounds of natural origin (BORMA et al., 1996).

Heavy metals (Pb, Cd and Hg) are particularly prone to complexation (BOULDING, 1995), given their atomic structure having a favorable formation for bonding with polar molecules, such as water or ammonia (NH3).

Studies by SCHNITZER & KHAN (1972); STEVENSON (1982) apud SCHULIN et al. (1995), demonstrate that the stability of heavy metals Pb and Cd depends on the chemical characteristics of the organic matter (humic acids), allied to the pH variation (Figure 6-16).

The retention of Pb in the organic complex occurs from pH 2 and occurs completely from pH 4.7, while the retention of Cd occurs in smaller proportions in pH around 6.0 (SCHULIN et al., 1995).

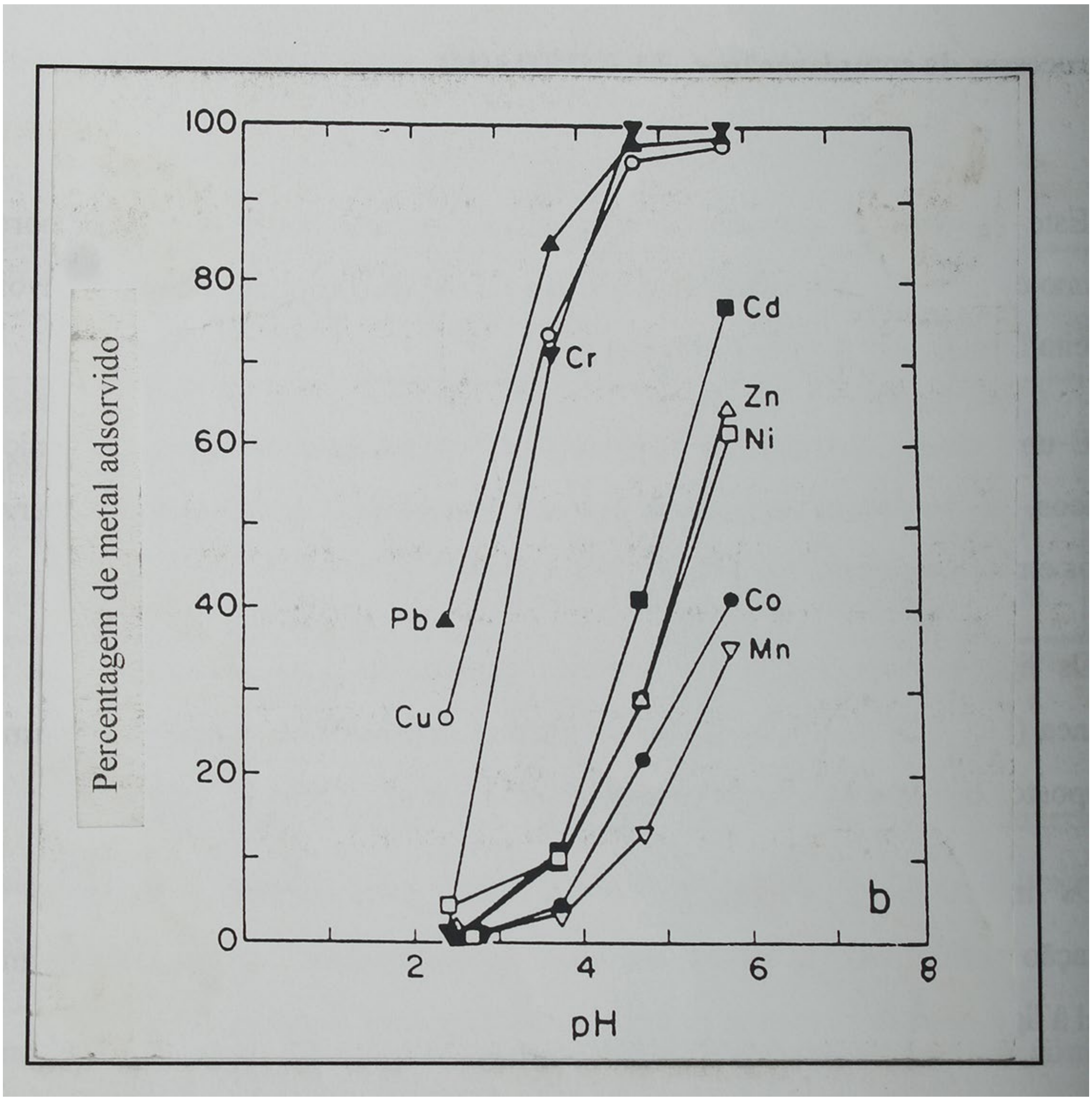

Figure 6-16. Effects of pH on the adsorption of heavy metals by humic acid. Source: SCHULIN et. al., (1995).

Comparing the studies of SCHULIN et al., (1995) with the values obtained in the study of the pilot area, we infer that, given the high percentages of organic matter present in the wetland of the pilot area and the alkaline pH values found, a larger process of Pb complexation is taking place.

6.7 Physical processes acting on the mobility of contaminants

Certain features of topsoil and the unsaturated zone naturally protect aquifers against pollution. They are the result of its strategic position between the surface and groundwater and the physical-biochemical environment, which facilitate the elimination and attenuation of pollutants.

The environmental conditions derived from the higher content of clay, organic matter and numerous bacterial populations are parameters that influence the processes of elimination and attenuation of contaminants for the aquifers (HIRATA, 1992).

Subsurface attenuation processes studied by GOWLER (1983) apud HIRATA (1992) and (1994), presents dilution, delay and elimination as mechanisms of self-purification of contaminants in unsaturated and saturated zones (Figure 6-17).

According to BOULDING (1995), filtration is one of the main mechanisms delaying contaminants and can occur through (see Figure 6-18):

- surface filtration, which is the hardening of a surface layer, making it difficult for larger particles to pass through it;
- tensioning, when contaminated particles of the same size are agglutinated between the porous spaces and the solid particles; and
- filtration resulting from the interaction of physico-chemical processes between the contaminant and the solid surface.

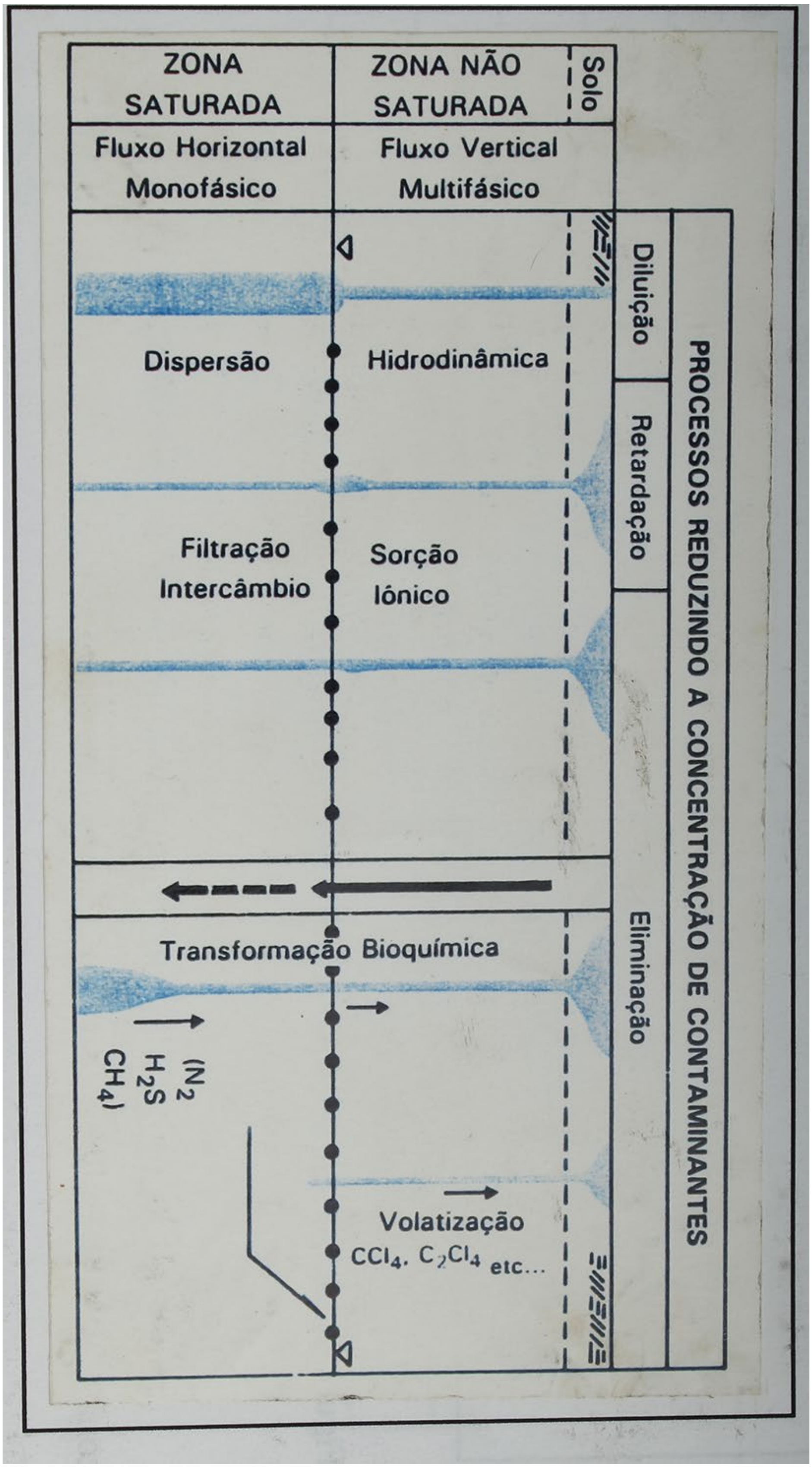

Figure 6-17. Physical processes that regulate the concentration of contaminants. Source: GOWLER (1983) apud HIRATA (1992).

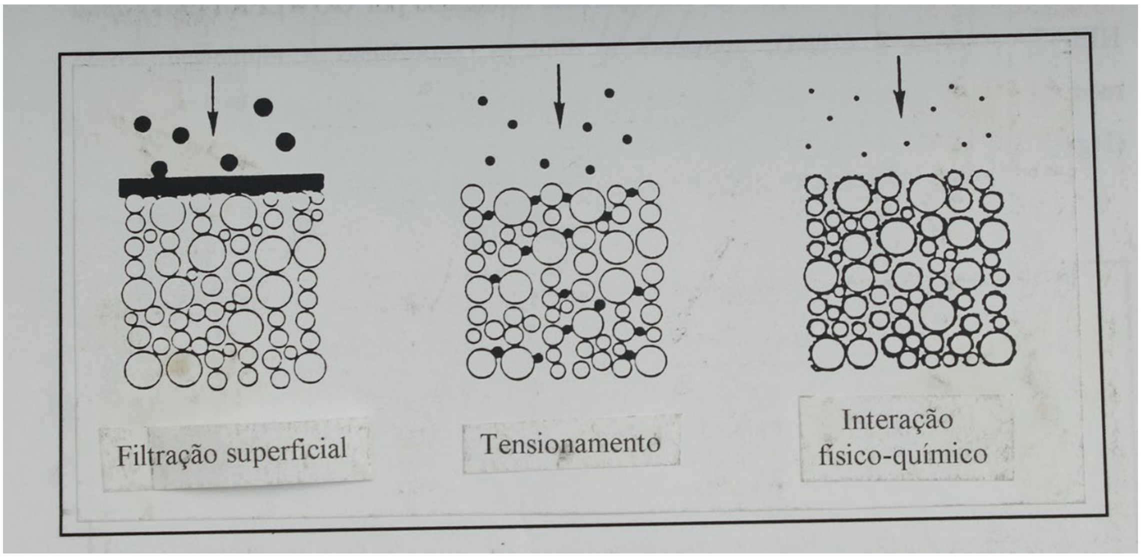

Figure 6-18. Filtration mechanisms that limit particle migration. Source: PALMER & JOHNSON (1989a); MCDOWELL-BOYER et al., apud BOULDING (1995).

From the parameters obtained from the PPS-02 soil profile located in the wetland, we infer that (Table 6-20):

1) the Pb and Cd concentrations in the PPS-02 profile are similar to the lag process described by GOWLER (1993) apud HIRATA (1992) and (1994). This attenuation mechanism presents high concentrations of metals in the surface soil, significantly reducing concentrations in the unsaturated zone and returning to low levels of concentration in the zone of variation of the hydrostatic level;
2) the cation exchange capacity, the organic matter and the texture of the soil in the subsurface attenuate the migration of contaminants and, possibly, help in the development of delay mechanisms, which is the result of the physicochemical interaction between the clay texture that surrounds the medium with high cation exchange capacity and montmorillonite clay.

TABLE 6-20: COMPILATION OF THE PARAMETERS OF THE PPS-02 SOIL PROFILE.

Profile	Depth (cm)	Pb (µg/g)	Cd (µg/g)	CTC	% of MO	% of Arg	% of Silt
01/02	0 - 10	1,800	38.0	44.3	2.9	78	10
02/02	10 - 30	1,300	18.1	41.0	0.7	74	14
02/03	30 - 50	821	12.4	35.6	0.9	71	16
02/04	50-70	307	3.7	38.6	1.1	46	14
02/05	70 - 90	175	1.7	39.0	0.9	60	16
06/02	90-110	<5.0	<0.5	23.7	0.4	62	16
02/07	110-130	<5.0	<0.5	53.0	0.9	69	16
02/08	130 -150	<5.0	<0.5	20.0	0.3	72	12
02/09	150 -170	182	2.2	41.7	0.9	72	13
02/10	170 -190	157	2.1	40.4	0.6	71	16

6.8 Discussion of results and conclusions

The conceptual model of contamination for the pilot area at the Plumbum site was based on the mechanisms of transformation and transfer of pollutants in the soil-water system. This model is composed of three basic steps, including a) entry of the pollutant into the system; b) system output, and c) its internal transfers and transformations (POMPEIA, 1994).

Using these mechanisms, we sought to understand the behavior of the pollutants in the pilot area, delimited from their source to the interactions going on in soil and water. This study was designed to identify the contamination of the source of pollution (slag), the means involved (surface water, soil and groundwater), environmental pollution indicators (Pb and Cd) and established parameters that interfere with retention or mobility of metals (pH, MO, CTC, soil texture and clay type).

These mechanisms can be schematically represented for the Plumbum site (Figure 6-19), and present the following development:

1) entry into the system, through inadequate slag deposition;
2) exit from the system, through leaching and solubilization of metals by rainwater;
3) transfers and transformation, through the chemical processes of precipitation and solubilization, adsorption and complexation, In addition to the physical process of retardation that interacts in the system.

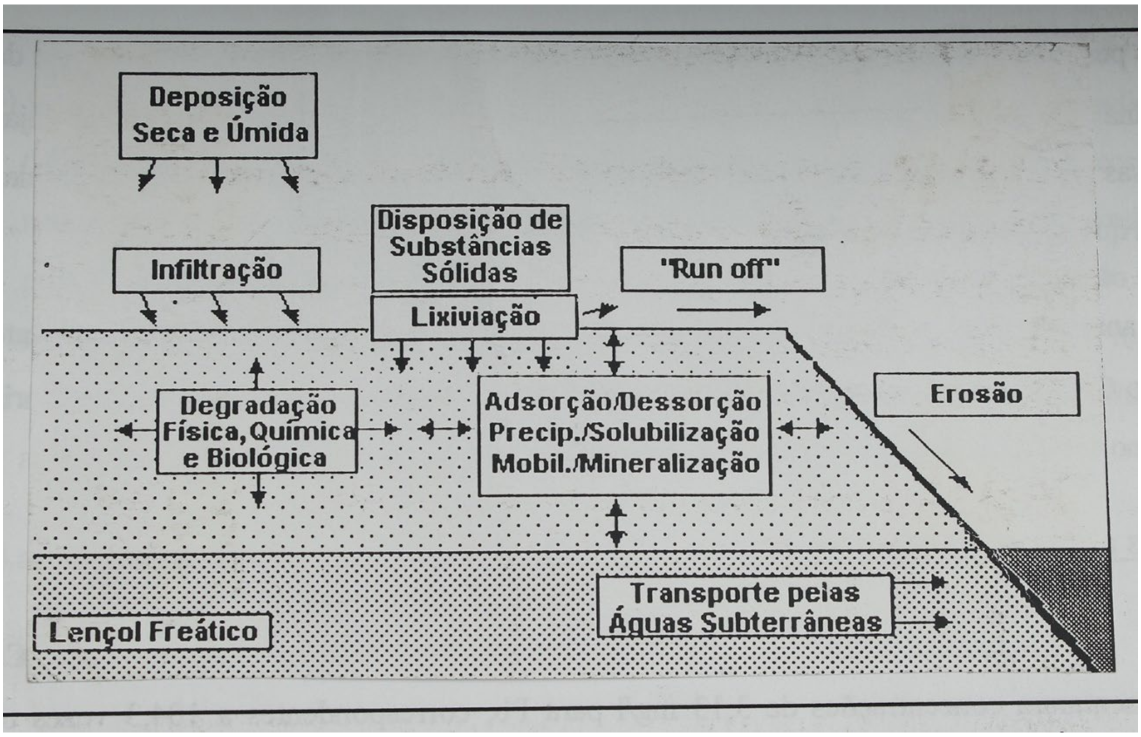

Figure 6-19. Interaction mechanisms of pollutants in the pilot area. Source: Adapted from POMPEII (1994)

The conclusions about the contamination of Pb and Cd metals in the pilot area was based on the hypotheses formulated in the conceptual model of the contamination. This method was chosen because of the difficulties to compartmentalize the assessment of each researched section, given the interactions of the chemical and physical processes acting in the surface water-soil-groundwater system. The conclusions of this study are as follows:

1) Characterization of the source of pollution.

"There is a source of pollution".

The source of pollution identified in this study is the inadequate deposition of the slag at the Plumbum site. This conclusion is based on:

a) the chemical composition of the slag, which contains around 35 g/t of Cd and 3% of Pb, therefore, prone to the transfer of these metals;
b) a previous study carried out by TAVARES (1990), in soils around the houses located in the vicinity of the metallurgical plant, concluded for the contamination with Pb and Cd in children living at homes contaminated with the slag, with the rates decreasing in slag-free areas; and
c) the chemical analyses of leaching and solubilization for the slag carried out initially by CRA and Plumbum, and confirmed in this study with the characterization of the slag as a hazardous waste (Chapter 6.2 - Characterization of the polluting source).

"The waters arising from this source are polluted."

The water overflowing from the slag dam presented concentrations of 3.13 mg/1 for Pb, corresponding to 104.3 times the maximum values recommended by the Subaé River Framework, and 0.013 mg/1 for Cd, corresponding to 13 times the maximum values of this same frame. There is no doubt, therefore, that the water is also contaminated with the slag.

2) Characterization of the contamination pathways.

"Surface waters are polluted."

in the wetland area, the surface water is contaminated. However, upstream and downstream this area, the levels found for Pb and Cd are very close to the maximum limits established by current legislation. This fact is related to the following factors:

a) only in the points located in the wetlands of the pilot area, surface water showed concentrations of Pb and Cd above the established in the Subaé River Framework. This location presents concentrations up to 260.3 times the maximum value allowed for Pb and 84 times allowed or for Cd.

b) the water accumulated upstream of the dam and downstream of the wetland (SWAP points - 01, 06 to 10) presented concentrations very close to the maximum levels for potentially harmful substances (concentrations found for Pb were lower than 0.05 mg/ 1 and for Cd less than 0.005 mg/1, while the maximum levels according to the Subaé River framework for Pb is up to 0.03 mg/1 and for Cd up to 0.001 mg/1), as the analytical method presents a detection limit higher than the regulatory levels.

c) the concentrations of metals indicate that:

- there is marked contamination of surface water in the wetland area;
- this contamination is the result of leaching and slag solubilization processes;
- Pb and Cd contained in surface water is retained in the wetland through the chemical processes of precipitation, adsorption and complexation;

- these processes are given especially to the sub-aqueous environment that characterizes wetlands and, above all, the basic pH, which favors the precipitation of metals, their adsorption by clays and the formation of organic complexes with OM;
- there is a risk of contamination of animals that graze freely on the contaminated site, especially cattle, which use the contaminated waters of the marshy area for their water supply; and
- very likely, there is no contamination at the upstream and downstream points of the wetland.

The conclusion from these results is that the wetland located in the pilot area retains Pb and Cd metals from surface waters, while the drainage water flowing to the Subaé River probably is not contaminated with the metals Pb and Cd. However, it is important to point out that only one sampling was carried out, in a period of regular surface water level. This leads us to believe that these results cannot be extended to dry seasons or high rainfall.

"Soils are contaminated".

The soil where the slag is deposited present very high concentrations of Pb and Cd, as shown from the analysis carried out in the following points:

a) the sample collected 7 km from the pilot area presents concentrations for the reference standard (<5.0 pg/g for Pb and <0.5pg/g for Cd) far below the limit recommended in the literature, such as concentrations defined at 15 to 20 ppm for Pb in claystone and 2.6 ppm for Cd in marls (MALAVOTA, 1994) and the values established by the Dutch model of 0.8 ppm for Cd and 85 ppm for Pb (CETESB, 1997);
b) the soil sampling upstream of the dam (PPS-01) shows Pb concentrations of 50.6pg/g and Cd concentrations of 1.0pg/g. As

expected, these concentrations are far below the values found downstream of the dam, which is justified by the lack of slag deposition in this area. These concentrations are considered by some countries as a reference standard, therefore presenting no risk of contamination;

c) soil samples from the wetland and landfill showed concentrations up to 8,200 ppm for Pb and 117.0 ppm for Cd. These values are well above the concentrations established by several countries in the world for intervention values for industrial areas (Canada and Germany adopt for Pb and Cd respectively, 1000 and 20 ppm) and indicate the need for some type of remediation for the area; and

d) the high concentrations of Pb and Cd, combined with high percentages of MO and CTC and montmorillonite clay on the surface of the wetland and landfill, confirm the action of the chemical processes of adsorption and complexation. These processes occur through the intervention of the basic pH, characterized as the main inducer in the retention of metals.

We conclude therefore that, wherever there is a deposited slag, there will probably be soil contamination, thus enabling the risk of contamination spreading especially to children. The results obtained at the reference point indicate that there is no contribution of the underlying rock (shale) in the increase of Pb and Cd concentrations in the studied area.

Therefore, the inadequate deposition of slag in the urban areas of the town by the public administration of Santo Amaro is currently the main means of contamination for the population. In addition, the cattle that feed on the contaminated grass from the damming zone and drink the polluted water from the wetlands can spread the contamination (bioaccumulation of metals) to the population consuming their milk and meat.

"Groundwater is polluted."

Groundwater is contaminated in the wetland area and at the beginning of the landfill area, given the following aspects:

a) the sample collected in the piezometer located upstream of the dam (GWSP -01) showed concentrations below the limits of the potability standard of the Ministry of Health. These results were as expected as there was no slag near the site;
b) the sample collected in the piezometer located in the wetland area (GWSP -02) showed concentrations higher than those established by the above-mentioned organizations, with values of 0.18 mg/1 for Pb and 0.007 mg/1 for Cd. These values are as expected, considering that the concentrations of Pb and Cd in the zone of the soil profile where the groundwater samples were collected (PPS-02.09 and 10) are, respectively, 157 to 182 pg/g of Pb and 2, 1 to 2.2 pg/g Cd;
c) the sample collected in the piezometer located in the landfill zone (GWSP -03) showed similar behavior to the wetland zone. However, the value for Pb (0.72 mg/1) is higher when compared to the wetland area, as the Pb concentrations in the soil of the PPS-03.06 profile are around 1,400 pg/g of Pb. As for Cd, although the concentrations found are around 20.4pg/g, the value found for the groundwater was slightly above the one for the wetland (0.008 mg/1 of Cd); and
d) the water from the well downstream of the landfill zone (GWSP-04) showed levels below the potability standards established by the Ministry of Health.

With the results from both the four collection points and the analyses carried out by CRA in the piezometers not found in the field, we can infer that the metals included in this study are limited to specific areas with higher concentration of metals in the soil.

This is related to several factors, especially the soil texture, which is characterized as one of the most important physical parameters in the attenuation of heavy metals. This parameter in the pilot area was classified as clayey to very clayey texture, which presents hydraulic conductivity equal to 10-6 to 10-9 cm/s and specific porosity around 5% O (MESTINHO, 1997). In addition. its coefficient of longitudinal and lateral dispersion are, respectively, equal to < lxl0-4 and <lxl0-6 m/day, according to BEST et al., (1993). These parameters classify the hydrogeological environment of the studied area as an aquiclude.

Considering that the aquiclude is a geological formation that can contain water, but without conditions to move it easily under natural conditions and in significant amounts (MESTINHO, 1997), and that the pilot area under investigation is affected by chemical processes such as adsorption and complexation, we infer that the groundwater presents significantly little movement in carrying the metals.

We conclude, therefore, that the pilot area is located in a system extremely conducive to the retention of heavy metals, and that the parameters pH, MO, CTC, soil texture and type of clay have been efficient in the process of trapping the metals, notably in the wetland area,

7 - REMEDIATION PLAN

“Prevention is better than cure” Csoil’98.

The term “remediation”, in English, refers to an educational approach, an “action or process of correction or mastery of knowledge or problem” (WEBSTER'S, 1995). However, it was introduced in the United States and Europe by influential voices as a “set of measures related to cleaning up sites degraded by industrial activities”, notably the disposal of toxic waste, which has caused soil and aquifer contamination (SÁNCHEZ, 1994).

BITAR (1997) defines remediation as treatment techniques to “eliminate, neutralize, immobilize, confine or transform contaminating elements or substances present in the environment and, thus, achieve the chemical stability of the environment”.

Used as a reference by the scientific community, USEPA defines remediation as a set of corrective actions applicable to a particular site contaminated with hazardous waste. In practice, these actions minimize the effects of contamination (BERTENFELDER, 1992), which means that it is difficult to recover a site.

Nearly two decades after the first regulations and the emphasis on technological research sponsored by the “Superfund”, the difficulties of recovering contaminated areas are evident. These conclusions stem from the complexity involved in the contamination of the sites, the techniques applied do not fully[32] achieve their objectives and, notably, the high costs of implementing the remediation.

The subject and its complexities were discussed at the “Sixth International Conference on Contaminated Soil”, held in May 1988, in Edinburgh, UK. This conference emphasized the difficulty for reaching more restrictive standards with current technology, the need to live with contaminated areas, and the urgency of using common sense to determine the sites with immediate risks. In addition, several proposals about techniques for the natural attenuation of contaminants, and for the reduction of costs were forwarded at the meeting..

Faced with these problems, several international organizations[33] conducting research on contaminated sites have presented proposals for cooperation and the exchange of scientific knowledge, and have forwarded methodologies and technologies for the remediation of soil and groundwater.

While these technologies and methods are discussed at governmental levels in developed countries, in Brazil, the remediation of sites contaminated with toxic waste is at the negligence stage (SÁNCHEZ, 1998). These areas come from former mining, chemical, explosives, metallurgical and ink industries, and from foundries and military bases.

This attitude, as already mentioned in the initial chapters of this work, is a consequence of the lack of specific public policies related to the issue,

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[32] In Germany, specifically in the State of Baden-Wurttemberg, research has been carried out to quantify the evolution of environmental impacts caused by remediation technologies. The study tries to evaluate the life cycle of remediation techniques already implemented in the State and, if reliable data and transparent decisions are obtained, make possible the selection of techniques with low potential for environmental impact. (BENDER et al., 1998).

[33] At the conference, the Committee on the Challenges of Modern Society (NATO) presented a study called “Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-up of Contaminated Land and for Groundwater”, containing information on the exchange of technologies between twenty-four countries. The Concerted Action on Risk Assessment for Contaminated Sites (CARACAS), formalized by several members of the European Union, with the purpose of elaborating risk assessment methodologies for the European countries and encouraging multinational cooperation between European scientists and contaminated soil researchers.

the inability of environmental agencies to control the risks to public health, and the omission of the private sectors.

It is important to point out that currently there are several in progress, especially by scientific community, in the field of risk assessment and management for sites contaminated with industrial solid waste (BERNARDES JUNIOR, 1995; CUNHA, 1997 and HASSUDA, 1997), and on techniques for remediation (ROEHRIG et al., 1996 and SHINOBLE et al., 1997). However, the survey and characterization of contaminated sites in Brazil initially require the implementation of specific policies guiding the survey of potentially contaminated areas, specific technical standards for the characterization of these sites and guidelines for their recovery.

7.1 Main remediation techniques

Research on contaminated sites coexists with two large groups of remediation techniques (USEPA, 1990 and 1994). The one carried out ex-situ, characterized by techniques promoting the removal of the soil for decontamination and subsequent replacement at the place of origin or disposal in an appropriate landfill. And the in-situ technique, which is performed at the contamination site, characterized and widely used to remove contamination from soil and groundwater.

The remediation technique to be implemented in a contaminated site depends on the target to be reached. SMITH et al., (1995), present criteria and approaches with the main objective of remediation, including reduction in the volume of the contaminant, restrict mobility in the contaminated environment, and decrease its toxicity. These procedures were distributed into the following groups:

1. Immobilization treatment.

They are in-situ techniques to reduce the mobility of contaminants in the soil matrix or in the transport of contaminants in groundwater, through the following mechanisms:

- reduction of fluid infiltration in the contaminated environment through the use of barriers;
- reduction of fluid infiltration by modifying the permeability of the contaminated matrix;
- reduction of solubility and, consequently, the mobility of the contaminant in groundwater; and
- controlling the flow of contaminants in water to allow effective collection and treatment (SMITH, et al., 1995).

An expressive number of publications have described these applications, among which the most used ones are:

- **Encapsulation systems** to reduce surface and water infiltration, control gas and odor emission, improve aesthetics and promote surface stabilization of the waste;
- **Vertical barriers** to reduce the movement of contaminants into groundwater (Figure 7-1);

• Horizontal barriers - are considered emergency techniques to reduce the mobility of contaminants;

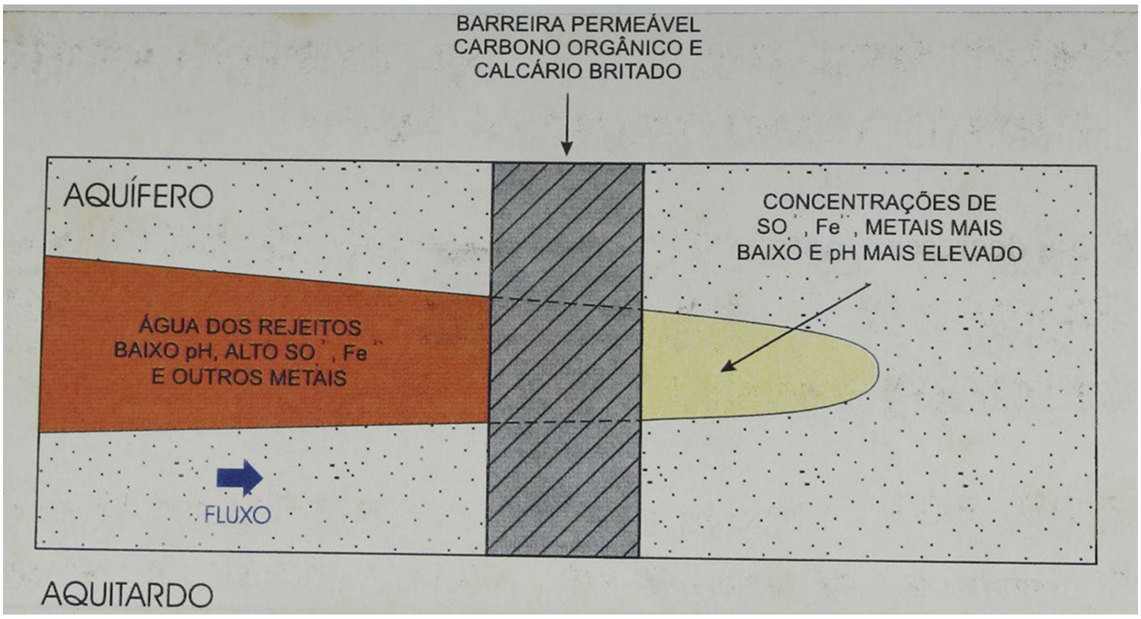


Figure 7-1. Encapsulation technique using vertical barriers, proposed for the control of the contamination plume, developed from a tailings basin of Titanio do Brasil (Tibras) Co. Source: SHINOBE et al., (1997).

- **Solidification/Stabilization (SS)** – a combined method of waste treatment widely used in the United States to decrease toxicity through the exchange of materials or leached waste (BELTENFELDER, 1992; GRUBE, 1992). The first phase (solidification) involves retaining the waste within a solidified matrix while the second (stabilization) converts the contaminated waste to more immobilized forms through chemical reactions. The main SS techniques involve the microencapsulation of polymers, pozzolanic portland cement, pozzolanic fly ash or lime, microencapsulation with thermoplastics, sorption and vitrification.

2. Toxicity-reducing treatment

These are in situ techniques applied to reduce toxicity by chemical and biological processes. They usually are used to convert the metallic contaminants from the solid waste matrix to a less toxic form. The main chemical treatment technologies are:

- **Chemical oxidation** - reactions that change the oxidation state of atoms through the loss of electrons. The predominant reactions are precipitation and solubilization, used basically for organic compounds;
- **Chemical reduction** - a process in which the oxidation state of an atom tends to decrease. The main reactions are precipitation and solubilization, used for both organic and inorganic compounds;
- **Chemical neutralization** - reactions that regulate the concentrations of hydroxide and hydrogen ion solutions, used for treating solids that are excessively acidic or basic.

The biological processes used in the remediation of contaminated areas are obtained through the decomposition of organic molecules into simpler molecules, such as CO_2, CH_4, inorganic salts and water. This process involves reactions of adsorption, oxidation, reduction, bioleaching, bio-extraction, biosorption and reduction or biological oxidation. The main technologies used for biological treatments are:

- **Bioaccumulation** - the process of transferring metals from the contaminated matrix to the biomass, as they can accumulate in selective living organisms or non-living biomasses;
- **Biological oxidation-reduction** - a technique used to select microorganisms through the reduction or oxidation of metals;

- **Methylization** - a process by which organisms attack the methyl group (-CH3) to form inorganic metals.

3. Treatment by concentration and separation

These are mostly ex-situ technologies stemming from ore treatment techniques. The most common ones are physical separation processes, pyrometallurgical and hydrometallurgical separations. In-situ technologies include soil washing processes and electrokinetic extraction for groundwater. The main problem involved in the implementation of these technologies is the high costs and the achievement of a desirable level of results.

The main ex-situ separation techniques are flotation, magnetic separation, gravimetric separation, classification by sedimentation velocity and sieving.

The main in-situ separation techniques are:

- **Soil washing** – a set of methods used without excavation of the contaminated material, used to remove contaminants from the substrate by the injections and extraction of the aqueous solution in this substrate. There are several treatment methods for contaminated liquid, including soil recirculation (biological treatment), oxidation, reduction and precipitation.
- **Electrokinetic treatment** - process involving the removal of metals and other contaminants from the soil and groundwater with the application of an electric field in the subsurface.

7.2 Proposed remediation technique for the pilot area

Several control techniques for the remediation of areas contaminated with lead and cadmium have been proposed around the world. This is related to the great potential for toxicity that involves these contaminants and a significant number of sites contaminated with these metals in urban and rural areas, many of them causing bioavailability and the risk of contamination.

The main reasons guiding the implementation of remediation measures on the Plumbum Co. site are:

a) control the source of contamination;
b) apply remediation techniques that achieve short- and long-term efficiency in pollution control;
c) study the technical and economic feasibility of applying the technique; and
d) protect human health and the environment.

To achieve these goals, the use of wetlands to control the contamination of the Plumbum site looks like the most appropriate approach, given the highest concentrations of heavy metals accumulated in the wetlands of the pilot area.

Wetlands have been intensively studied as a pollution control measure, both for domestic waste and for industries in reducing acidity and retaining metals (BRIX, H. 1994, COOPER, 1994 and JOHNSTON, C.A. 1994), besides representing the lowest cost in the installation and monitoring of the system (Photo 7-1).

In this context, the main functions usually attributed to wetlands are: the control of water quality through biogeochemical transformations and retention of pollutants; flood mitigation as an additional resource to hold water; groundwater recharge, serve as habitat for wildlife.

Photos 7-1 and 7-2 The first picture shows the wetland area with the deposition of slag in the surrounding area. Below, the vegetation of the area, especially the reed or cattail (*Typha angustifalia* L.) that reaches around two meters tall.

As for the control of the source of pollution, the disposal of slag as a landfill in urban (Photo 7-2) and rural areas of the town of Santo Amaro da Purificação account for the main route of contamination. This practice has to be totally abolished, considering that the contaminants leached from the slag are retained in the soil, and compose the risk of contamination for children living in the surroundings.

To control the contamination in the Plumbum Co. area, therefore, immediate measures are here proposed, such as:

a) do not use the slag for any activity, until studies on its decontamination make its use possible;
b) collect all existing slag in landfills carried out by the town administration and deposit it upstream of the slag damming;
c) place signs showing the toxicity of the residue, correctly fence the entire area, establish surveillance so that people never cross to the other side, do not destroy the monitoring wells, and animals do not use it as pasture;
d) install a wetland in the valley where the deactivated tailings basin is located, given the large amount of slag incorporated in the soil, as a control measure for metals that migrate towards the Subaé River;
e) do not use these lands as a landfill area or for any inert material;
f) implement a monitoring network to measure heavy metals in surface and groundwater; and
g) install a rain gauge to measure the acidity of rainwater.

These measures should last indefinitely, possibly for a long term.

8 - FINAL CONSIDERATIONS AND RECOMMENDATIONS

This work investigated the contamination with heavy metals of the slag, soil and surface and underground waters of a pilot area located in the waste deposition site of the Plumbum Mining and Metallurgy Co., located in Santo Amaro da Purificação-Ba. Based on the panorama presented and discussed above, we conclude and propose that:

1) The Slag is currently the main source of soil and surface and groundwater pollution. This conclusion comes from the leaching and solubilization tests, which characterized it as a toxic waste.
2) Landfills carried out by the town of Santo Amaro administration paving the streets of the urban and rural areas with the lag represent the main route of contamination.
3) It is possible that these landfills have contaminated the child population living in these areas.
4) The use of the slag by the State Highway Department (DERBA) as a basement for paving the road between the Bacraft Paper Co. and the Plumbum Co. represented an expressive increase in Pb and Cd concentrations in the region. This dangerous procedure will bring, in the mid and long term, a risk of contamination for the animals that feed on the grasses in this area.
5) The surface soil downstream the slag dam in the pilot area is contaminated with lead and cadmium, as can be seen from the high concentrations of Pb and Cd found in the chemical analysis for total metal in the soil samples from the pilot area.

6) The surface water of the pilot area is contaminated only in the wetlands, as can be seen from the high concentrations of Pb and Cd found in this zone through chemical analyses for total metal.
7) Groundwater in the wetland area and at the beginning of the landfill area is contaminated with Pb and Cd. This fact is attested by the result of the concentrations of these metals in samples from two monitoring wells installed in the wetlands and landfill areas.
8) The values found in the support parameters used in the research, the basic hydrogenic potential, the high percentages of organic matter, the high percentages of cation exchange capacity, the montmorillonite clay and the clayey and very clayey soil texture, favored significantly the processes of retention of metals in the soil.
9) The high concentrations of metals in the surface soils of the wetland and in the landfill of the pilot area are related to the chemical processes of precipitation, adsorption and complexation.
10) The wetland works like an effective dam in retaining the contaminants. It is necessary that this area be better understood, as it is a low-cost control technique and initially the most adequate to control the existing contamination in the soil and waters of the researched site.
11) The Plumbum Co. site represents a chronic and prolonged risk of contamination. The control of the current source of pollution (slag) must initially be carried out with the maintenance of the slag on the premises of the company until research into economically viable decontamination techniques for its reuse is carried out.
12) The lack of specific public policies for areas contaminated with industrial waste has effectively contributed to the contamination of the environment, putting the populations that live in these areas at risk. This fact became evident when the project was abandoned without

presenting a recovery plan for the area and later when a paper factory was installed on the same facilities of the Plumbum Co.

13) It was not possible to estimate the stock of pollutants released by Plumbum into the ecosystem, as the company did not measure the pollutants emitted as particulate, liquid effluents and contained in the slag in its production phases.

14) The technical reports made for the CRA agency, and the works published in conferences during the development of the study were essential for the environmental agency to prevent the continued use of the slag by the DERBA department and the local government.

15) To complement the research on the contamination of the Plumbum site, other studies are necessary, including:

- analysis of the contamination with heavy metals like Zinc (Zn), Arsenic (As) and Mercury (Hg) - in the slag, soil and water, considering that these metals present high concentrations in the tailings from the processing plant in Boquira;
- study on the efficiency of “wetland” as a control technique in the retention of heavy metals, given the risks of acid rain in the region and possible bioavailability of the metals retained in the soil;
- research on remediation techniques to decontaminate slag and to study its economic feasibility;
- continued research on the risks of contamination in children living in the vicinity of the Plumbum Co., including the people living in the areas paved with the contaminated landfills carried out by the Stown of Santo Amaro public administration;
- continued research on groundwater contamination, with the installation of deeper and multilevel wells, to determine the effective area of groundwater contamination. In addition to the use of a geophysical method to check a possible contamination plume;

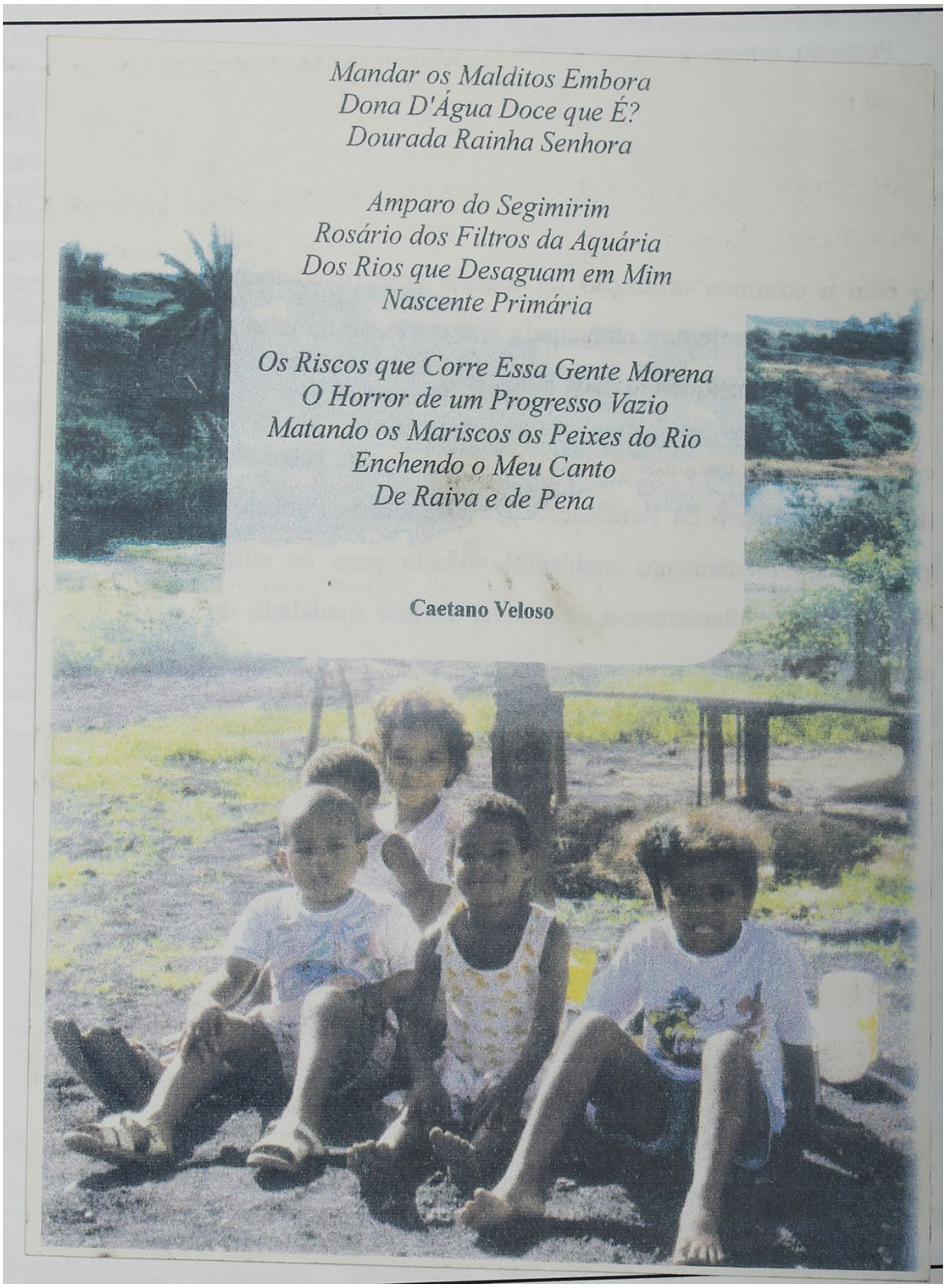
- biological studies on resistant and adapted species to the “wetland”, and their role in retaining heavy metals; and
- research on the contamination of heavy metals present in the sediments of the Subaé river channel, and on the increase in these concentrations in the sediments of the mangroves at the mouth of the river.

16) It is essential that research be carried out in the areas of alluvial deposits near Plumbum, as this area has undergone an intense process of landfill with slag during sand mining activities. This area presents a greater risk of migration of metals towards the Subaé River, given its proximity of the river and its textural composition.

17) It is necessary to develop a remediation program, in the short, mid- and long terms, for areas contaminated with industrial waste, involving not only the Government of the State of Bahia, but also the companies, universities and affected communites.

18) The implementation of an environmental education program focused especially on the causes and consequences of contamination from the Plumbum Co. and its effects for current and future generations.

When Caetano Veloso wrote verses about the pollution of the Subaé River (Figure 8-1), he denounced to the world the environmental degradation caused by the contamination with heavy metals released to the environment by the Plumbum Co. and the suffering of the population of his hometown. The song undoubtedly established the beginning of the environmental management process for the Subaé River Basin.



Mandar os Malditos Embora
Dona D'Água Doce que É?
Dourada Rainha Senhora

Amparo do Segimirim
Rosário dos Filtros da Aquária
Dos Rios que Desaguam em Mim
Nascente Primária

Os Riscos que Corre Essa Gente Morena
O Horror de um Progresso Vazio
Matando os Mariscos os Peixes do Rio
Enchendo o Meu Canto
De Raiva e de Pena

Caetano Veloso

Figure 8-1. Children exposed to slag landfill in urban areas of Santo Amaro da Purificação[34].

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[34] **Translator's Note:** For the reader not acquainted with the local religious and cultural sincretism, the patron saints of the town are Saint Amarus and Our Lady of the Purification. In his verses, Caetano Veloso, the singer, composer and son of the land, plays with the words in a passionate prayer to *Oshun*, the African- American Lady of the rivers: *Purify the Subaé (River) / Ban the accursed people / Oh, Lady of the Sweet Waters / Thou, Golden Queen, Protector of the Sergi-mirim / Crown 'n Purifier of the Aquaria / 'n of all the rivers flowing through me / Thou, Source of the waters / Deliver the dark-skinned people from the danger / 'n from the horrors of an empty progress / that kills the river's fish and shellfish / Flooding my song /With rage 'n sorrow.*

The measures taken by the Government of the State of Bahia in this regard, including the creation of a framework for the waters of the Subaé River Basin, and projects for the implementation of a sanitary sewage system, expansion of the water supply service and installation of a sanitary landfill, represented only basic sanitary sewage services. Important as they were but ineffective in controlling the contamination caused by the toxic residues released by the Plumbum Co.

This fact is confirmed by the continuous use of the contaminated slag material by public bodies (the State Road Department-DERBA and the local administration), as there was a lack of specific policies for the management of industrial toxic waste.

Therefore, it is expected that the results and conclusions obtained in this research will subsidize the CRA agency, the public administration in Santo Amaro da Purificação, and the Public Prosecutor's Office to effectively start an environmental management program for the sites contaminated with toxic waste and, consequently, promote better quality of life for all affected communities.

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Part II

Evaluation of the Efficiency of a Wetland in the Control of Pollution with Heavy Metals: the Case of Plumbum Co. in Santo Amaro da Purificação/Ba

Sumário

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ABSTRACT

The purpose of this investigation was to evaluate the efficiency of a wetland (wertland) that occurs on the premises of a lead industrial plant located in Santo Amaro da Purificação, Bahia, as a measure to control contamination from a slag dam contaminated with heavy metals.

Initially, an annual survey was proposed with weekly sampling of rainwater and surface water from the wetland, in order to assess the efficiency of the wetland, by surveying the concentrations of metals from the leaching and/or slag solubilization processes in their entry and exit points from the flooded system and concentrations and potential availability of the metals retained in the sediments of the floodplain.

The following parameters were selected: for rainwater, pH and volume; for surface water, the concentrations of the metals Lead (Pb), Cadmium (Cd), Zinc (Zn), Copper (Cu), Aluminum (Al), Manganese (Mn), Iron (Fe), Magnesium (Mg) and Calcium (Ca) and support parameters pH, Eh, conductivity, Dissolved Oxygen (OD) and temperature. For the soil and sediment of the wetland, the concentrations of metals like Pb, Cd, Zn and Cu e, determination by analyses of the sequential extraction of the total removed by the system in its different phases and the potential availability of heavy metals.

However, a modification of the investigation strategy had to be made due to a court decision that determined the covering of the slag and closing of the access to the wetland. The work was then divided into three phases, considering the surveys carried out before, during and after the coating.

The data collected in the five months before the coating showed that the metals cadmium, lead, copper and zinc have been retained by the wetland and that this system was 100% efficient for the copper and zinc metals, 82% for the lead and 73 % for cadmium. The support parameters that influence the removal of these metals were the pH, between neutral to alkaline, and Eh, in the surface water oxidation range, besides the high cation exchange capacity of the montmorillonite present in the sediment. As for the potential availability of metals, cadmium, lead and zinc present high values, while copper is preferentially concentrated in the residual phase.

The second stage of the survey carried out during the slag coating showed that there was little migration of metals from the wetland area, although the company did not comply with the technical standards for slag coating.

In the third stage, a survey was carried out at the exit of the wetland and the drainage near the Subaé River. The analyses showed the great availability of cadmium in the flooded system, a mechanism triggered by the erosion of the contaminated soil disposed on the slag and the great solubility of cadmium.

It can thus be concluded that the wetlands are efficient in retaining metals. The reduction of its area is undesirable, as it tends to decrease its efficiency, as a surface water pollution control system. It is recommended to build a new wetland downstream of the existing one.

Keywords: Wetlands, sequential extraction, heavy metals

CHAPTER 1: INTRODUCTION

Areas contaminated[1] by industrial waste constitute some of the most serious socio-environmental problems of the modern world. This is especially so because of the lack or difficulties in the application of specific policies for these areas, allowing for the contamination of soil and water and, consequently, the availability of toxic metals or organic compounds in the food chain, generating risks for the environment and for human health.

The management policies for contaminated sites formalized by most developed countries establish corrective actions among their dominant approaches, that is, the development of remediation measures in a planned and systematic way after the identification and diagnosis of the problem.

However, in developing countries, including Brazil, the dominant approach to the issue of contaminated sites is still negligence[2]. This approach is characterized by the non-recognition of the problem and is mainly linked to the priorities adopted by the jurisdictions involved.

The recovery of these degraded areas has been one of the main concerns in industrialized countries, especially in recent decades. This fact comes from the awareness and pressure of communities to achieve a better

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[1] According to the Contaminated Area Management Manual (CETESB 1999), contaminated areas are sites "where there is proven pollution caused by any substance or waste that has been deposited, accumulated, stored, buried or infiltrated, and which determines negative effects on the goods to be protected, which are: the health and well-being of the population; the fauna and flora; the quality of soil, water and air; nature/landscape protection interests; territorial planning and regional and urban planning; and public safety and order".

[2] "Neglect is a characteristic response of jurisdictions where there is still no public acknowledgment of the problem. This may be known to a restricted group of specialists, but it does not have repercussions on public opinion or is not seen as important by the decision-making administrative levels or by the political elite. Under the claim of not causing concern among the population, the problem may even be camouflaged, ratifying the fact that not having an explicit policy is a form of public policy, in reverse." SANCHEZ (2001).

quality of life, the survey of environmental liabilities for privatization of state-owned companies or transactions between private companies, the difficulties of economic evaluation in the incorporation of conglomerates and the advancement of scientific research on the availability and bioaccumulation of toxic metals and organic compounds in the food chain.

Given these conditions, a number of management instruments have been used in corrective policies for contaminated soils. Among them, the Contaminated Areas Management program, developed by the Environmental Sanitation Technology Company (CETESB), representing the Government of the State of São Paulo in partnership with the *Deutsche Gesellschaft fur Technische Zusammenarbeit Gmbh (GTZ)*[3] stands out. This program has already developed, as a management tool, the first stage of the Contaminated Areas Management Manual (CETESB 1999), the proposal for the Analytical Protocol for the preparation of soil samples for the determination of metals (QUINÁGLIA 2001) and the Guiding values for soils and groundwater in the State of São Paulo (CETESB 2001).

In disagreement with these initiatives, the Government of the State of Bahia does not develop any specific program for the management of Contaminated Areas, not even when referring to abandoned areas.

However, the Federal University of Bahia, since the 1970s, has been promoting one of the largest epidemiological surveys on the effects of lead and cadmium on the populations surrounding the lead metallurgy of the Plumbum Mining & Metallurgy Co. in Santo Amaro da Purificação, installed in 1960 and abandoned in 1993. These surveys found not only a large environmental liability attributed to the company, but also the lack of

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[3] GTZ stands for Technical Cooperation Society, a German government agency promoting technical cooperation in specific projects within the topic of Contaminated Areas and to train CETESB to act in the management of these areas.

commitment of the public and private sectors with the goods to be protected[4], after the contamination was diagnosed and widely publicized by the media.

In view of the confirmation of contamination in the population surveyed and the existence of several exposure routes, the author carried out a first survey on the contamination of soils and surface and groundwater at the Plumbum Co. site, to identify levels of contamination and assess the migration of contaminants (ANJOS 1998).

This study followed recommendations from the Contaminated Areas Management Manual (CETESB 1999). As a first step[5], we sought to determine the characteristics of the physical and anthropic environment of the site, the history of the enterprise, the identification and evaluation of potentially contaminated areas and the confirmatory investigation of contamination, through the identification of sources, routes and mechanisms of transformation and transfer of pollutants in the soil-water system at the Plumbum Co. site. The development of these stages supported the proposition of corrective strategies and prioritization of actions with the public authorities and the community.

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[4] According to the National Environmental Policy (Law 6,938/81), the following are considered assets to be protected: the health and well-being of the population; the fauna and flora; the quality of soil, water and air; nature/landscape protection interests; territorial ordering and regional and urban planning: and security and public order.

[5] According to the Contaminated Areas Management flowchart, this step is correlated to the Contaminated Areas Identification process, which establishes interspersed steps of prioritization, registration, classification and preliminary assessment of contaminants.

These previous studies found that the highest concentrations of heavy metals are accumulated in a wetland[6], downstream of the lead and cadmium contaminated slag produced by Plumbum Co. during its 33 years of operation.

Wetlands are considered “kidneys” of the global water cycle because they consistently improve water quality. Briefly, they are areas of low slope covered with temporary or intermittent water, which can develop naturally or built by man. Currently, they are intensively used all over the world as a technique for controlling the pollution of domestic and industrial waste.

The wetland originated from a landfill for channeling rainwater from the enterprise and reached an extension of about 90m[7].

In the area, the following characteristics were found: basic pH; clayey to very clayey soil texture, presence of montmorillonitic clay, high cation exchange capacity, high percentage of organic matter, concentrations of metals in the soil surface layers up to 8,200 µg/g of Pb and 117 µg/g of Cd and predominant vegetation of *Typha sp*. (ANGELS 1998).

The preliminary results demonstrate that, possibly, the geochemical processes of precipitation, sorption and complexation have been effective in retaining lead and cadmium in this wetland.

The purpose of this investigation was to study the retention of contaminants in this wetland. To assess the effectiveness of Plumbum's wetland as a pollution control measure, a one-year weekly survey of control parameters was planned. In the survey, physicochemical parameters were

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[6] All areas defined as wetlands, humid areas, swamps, swamps, swamps, swamps, mangroves, among others were encompassed as wetlands in 1956 by the U.S. US Government Fish and Wildlife Service. (TINER 1999).

[7] Wetlands can be natural or built, the main differences between them are that in constructed ones, you can choose plant species, soil composition, there is effective control of what enters and leaves the system (hydrological project) and, depending on size, can be installed, in practically all urban or rural areas.

quantified and evaluated for rainwater and surface water, in addition to analyzing the concentrations of heavy metals that enter and leave the wet system. Along with this survey, chemical analyses was carried out, by sequential extraction, in the sediments of the wetland to determine the concentrations of metals potentially available to the system.

During the execution of the investigation, there was a significant change in the physical conditions of the area, since, in compliance with a court order, the company covered the slag dam with soil and, in this process, filled part of the wetland.

Therefore, the investigation had to be reformulated to assess the efficiency of Plumbum's wetland and the effects of slag coating. In its reformulation, the work had three distinct phases: the first, before coating, tried to evaluate the wetland as a technique for controlling contamination from the slag; the second stage, carried out during the execution of the covering project, evaluated the technical containment project applied by the Plumbum Co., its execution and interference in the wetland system; the third stage, developed after the coating, tried to evaluate the efficiency of the project developed by the Plumbum Co., having as control the study from the first stage.

CHAPTER 2: OBJECTIVES

The general objective of this investigation is to evaluate a system comprised of a toxic waste dam (slag) and a wetland area, including the current retention or removal capacity and the potential availability of lead (Pb), Cadmium (Cd)), Zinc (Zn), Copper (Cu), Cobalt (Co), Chromium (Cr), Nickel (Ni), Aluminum (Al), Manganese (Mn), Iron (Fe), Magnesium (Mg) and Calcium (Ca) in the flooded area, using supporting parameters and chemical analyses for contaminated slag, rainwater and surface water, in addition to wetland sediment. As for the specific objectives, they are as follows:

a) Investigate the influence of rainwater pH on the system composed of the slag dam and the wetland;
b) Investigate the metals contained in the source of contamination represented by the slag;
c) Investigate the temporal and spatial distribution of concentrations of metals contained in surface water entering and leaving the wetland;
d) Evaluate the efficiency of the wetland in retaining metals, taking as reference the levels of liquid effluents applied by Conama Resolution 20/86;
e) Evaluate the current levels of retention and potential availability of metals contained in the wetland sediment, specifically, in the exchangeable phases of the soil, in the phases associated with carbonates, Fe and Mn oxides, in the organic matter and in the residual fraction of the sediment (chemical analyses by sequential extraction);

f) Apply the results of the analyses as a planning tool to propose the remediation of the Plumbum Co. site;
g) Evaluate the slag coating technical project carried out by the Plumbum Co., its execution and efficiency as a pollution control measure;
h) Evaluate the Plumbum Co. wetland as a technique to control surface water pollution from leachate and/or slag solubilized;
i) Propose an alternative remediation project for the Plumbum Co. site; and
j) Provide information to the Public Prosecutor's Office and the Environment Commission of the House of Representatives in relevant actions and the Santo Amaro da Purificação City Hall in actions to control pollution and promote well-being and public health.

CHAPTER 3: HYPOTHETICAL MODEL

Figure 3.1 represents a hypothetical conceptual model of a wetland as a metal-retaining system, modified from the global phenomenon of water circulation between the earth's surface and the atmosphere — hydrological cycle — and from the models of metal transfer within the wetland, as discussed by MITSCH and GOSSELINK (1993), KADLEC and KNIGHT (1996), KADLEC (1998) and WOOD and SHELLEY (1999).

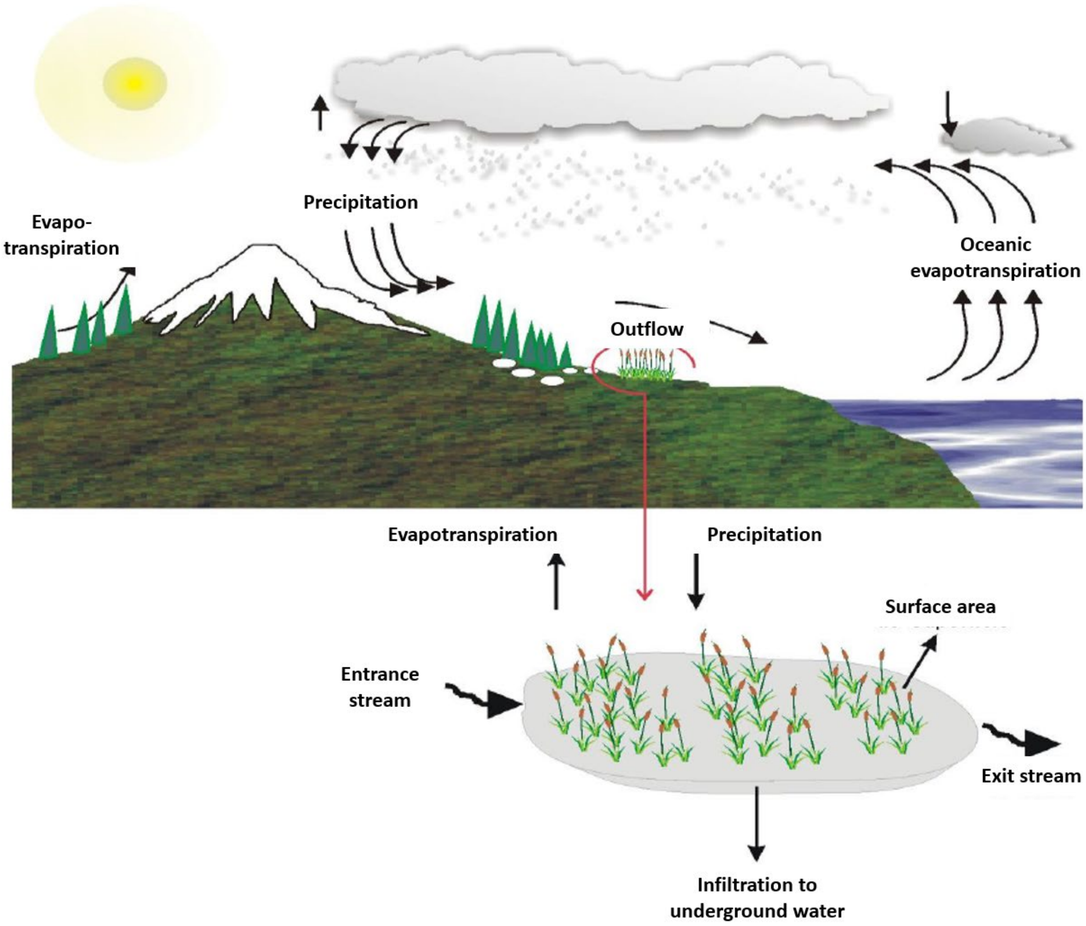

Figure 3.1 – Hydrological cycle (modified from Rebouças 1999) and detail of hydrological components for constructed wetlands, based on KADLEC and KNIGHT (1996).

Mathematical models of metal transfer were developed from constructed wetlands, predominantly for the treatment of domestic effluents, according to studies developed for mass balance, having as premises the qualification and quantification of toxic elements at the entrance of the system, the processes involving the biogeochemical cycles that occur within the wetland and the qualification and quantification of chemical species at the exit of the system.

Figure 3.2 illustrates a proposed model of water flow and metal transfer in the wetland at the Plumbum Co. site. The model is based on the natural conditions presented by the system and, as it is a system without a hydraulic project capable of dimensioning the volume and flow of effluents, it was not possible to carry out a mass balance, a common practice in constructed wetlands.

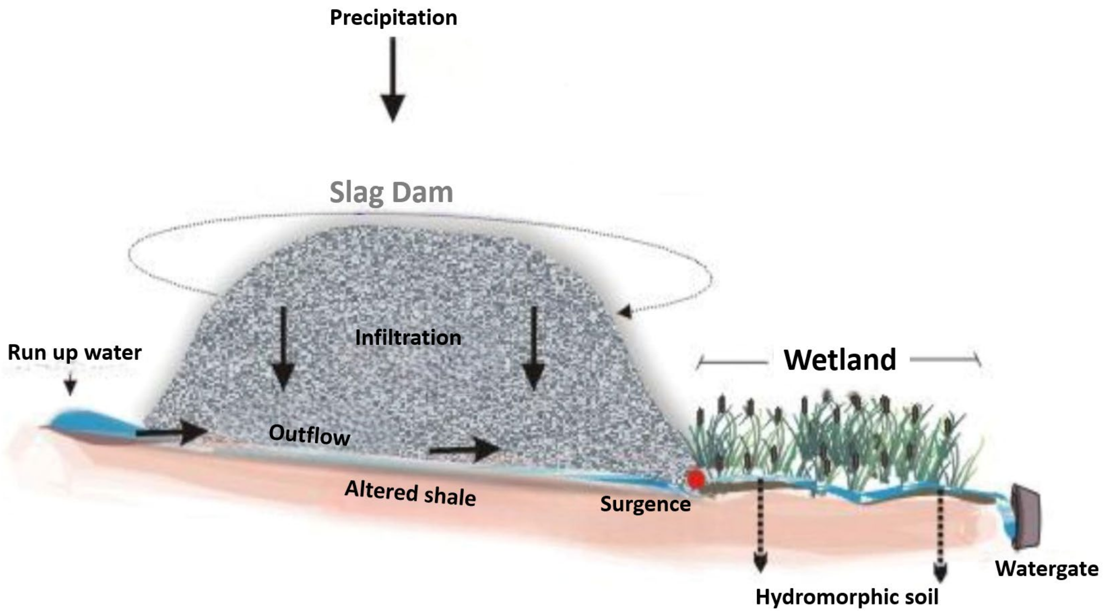

Figure 3.2 - Water flow model proposed for the Plumbum wetland

In fact, Plumbum's wetland is artificial, but it was not designed to be a wetland, let alone to have a metal retention or effluent treatment function. It became a flooded area because of a railroad embankment, which was equipped with a discharge pipe. It is, therefore, an unintentionally built wetland that, fortuitously, helps to prevent pollution of the Subaé River and its estuary.

The hypothetical conceptual model suggested for the Plumbum Co. site (Figure 3.3) takes precipitation (rainwater) as its natural source of energy, responsible for the leaching and/or solubilization processes of metals at the source of contamination (slag dam). The contaminants transport route is the surface water, responsible for the leaching and/or solubilization processes of the metals contained in the slag and for the precipitation, sorption, complexation and redox processes of the metals in the hydromorphic soil of the wetland.

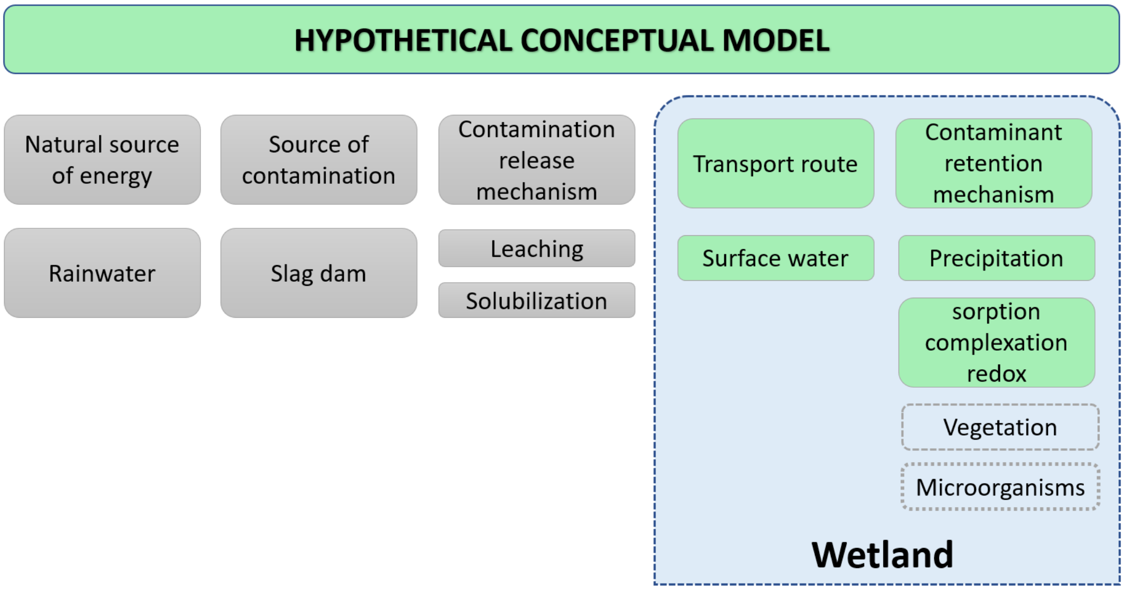

Figure 3.3 - Hypothetical conceptual model for the Plumbum slag and wetland system

It is worth noting that the processes of retention of metals in the wetland also involve vegetation and microorganisms. These parameters, however, were not included as part of this investigation, in view of their complexity and because they are outside the methodological approach proposed for the development of this work.

CHAPTER 4: MATERIALS AND METHODS

The methodology developed for this investigation tries to study the effects produced by rainfall in a system composed of a slag dam containing heavy metals and a small wetland developed downstream of the dam (Photo 4.1).

The interventions carried out by the Plumbum Co. during the development of the investigation, covering the slag, resulted in the landfill of the fixed point of emergence through which the monitoring of the leached water from the slag (P1) was carried out. This fact conditioned the reformulation of the investigation plan in view of the need to make the surveys compatible before, during and after the slag coating.

Photo 4.1 – Plumbum wetland with predominance of Typha sp. (cattail).

To evaluate the specificities of this area, the following procedures were carried in the field:

- topographic mapping (1:3000 scale);
- rainfall survey;
- survey of physical-chemical parameters of surface waters;

- sampling of surface water from the wetland area for metal analyses, and
- sampling of wetland sediment and surrounding soil.

For rainwater, pH and weekly rainfall were measured, while in the wetland area of Plumbum, surface water was sampled weekly for quantitative chemical analyses of the following metals: Aluminum (Al), Lead (Pb), Cadmium (Cd), Calcium (Ca), Cobalt (Co), Copper (Cu), Chromium (Cr), Iron (Fe), Magnesium (Mg), Manganese (Mn), Nickel (Ni) and Zinc (Zn).

In order to evaluate the mobility of metals in the surface waters of the wetland area, the following physicochemical variables were measured weekly for a period of one year: hydrogenion potential (pH), redox potential (Eh), dissolved oxygen (DO), temperature and conductivity.

As for the wetland sediments and surrounding soil, chemical analyses were carried out by sequential extraction, with the objective of evaluating the potential availability of Pb, Cd, Cu and Zn metals in the different geochemical phases of the sediment.

The research method contemplated for the area is characterized as an eminently quantitative approach[8].

Research planning at the Plumbum site involved specific procedures applied in methodologies for managing sites contaminated with industrial waste, unlike what was developed by MARKER et al. (1994), POMPEI (1994), SÁNCHEZ (1995), CETESB (1996), GLOEDEN et al. (1997), LEITE et al. (1997) and SÍGOLO (1997). These authors only address the main stages of site management plans.

However, a study carried out by BERNARDES JUNIOR (1995), CUNHA (1997), ANJOS (1998), GLOEDEN (1999) and SILVA (2001) in contaminated sites present methodologies with detailed steps and their prioritization. These studies demonstrate that, even due to the numerous variables found in the different contaminated sites (different chemical products, sources of contamination and physical, geochemical and biological

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[8] According to VARGAS (1985) apud BERTO and NAKANO (1998), modern science has used the combination of the hypothetical-deductive method proposed by Galileo to designate quantitative research. In this approach, quantitative research has the characteristics of systematic data collection, creativity, perception of the relevance of the collected data, systematic updating and the addition of new ideas and theories (GHAURI et al. 1995 apud BERTO and NAKANO 1998) .

aspects), the different procedures to identify, prioritize, investigate and evaluate are generally pre-established.

These sets of specific sequenced measures and procedures are widely discussed in CETESB (1999 and 2001) and SCHIANETZ (1999), with the purpose of identifying and assessing the impacts on contaminated sites, in addition to guiding and proposing corrective measures for the recovery of the area. and its proper use.

Thus, the following activities were considered essential to guide this study: a search for the pertinent literature; planning of field survey activities; selection of points for "*in situ*" measurements of wetland water quality parameters and sampling for metal analyses; selection and sampling of sediment and soil; implementation of a rain gauge to sample rainwater in the area close to the site; choice of chemical analyses methods to determine the concentrations of metals and the use of a statistical method to assist in the interpretation of the results obtained. For this study, field and laboratory data will be treated differently.

4.1 Methodology

The initial proposal for the evaluation of the system comprised by the slag damming and the Plumbum Co. wetland had as main objective to analyze the correlation between the pH and the volume of rainwater with the concentrations of leached and/or solubilized metals from the slag. The study was conceived to be carried out at two fixed points, entrance (P1) and exit (P2) of the wetland, in an annual hydrological cycle, scheduled to start in January 2001.

However, the initial proposal had to be modified to comply with the determinations contained in the records of Public Civil Action n. 302/97 of the Court of the District of Santo Amaro, Bahia. This Civil Action was initiated by the State Prosecutor's Office as a request for preliminary injunction and determined "the superficial encapsulation of the slag valley, that is, the hydraulic encapsulation complying with the requirements of soil and water pollution control contained in the NBR-1183 Norms. and 1264" (NETO 2001).

The works proposed by the Prosecutor's Office began in April 2001, through Morsa Engineering Co. However, with the progress of the work, it was found that it was not an encapsulation, but a surface coating outside the procedures established by the aforementioned standards.

The covering of the slag dam caused the landfill of the fixed point of emergence of the leached water from the slag (P1), making it imperative to change the methodology, which foresaw the survey of support parameters and chemical analyses of metals for a period of one year.

In view of the new conditions of the physical environment, the procedures for the methodological development of the study were revised, whose goals became: (i) the survey of metals and support parameters in the Plumbum wetland in order to evaluate the migration of metals to the river Subae; and (ii) analyses of the coating project as a technique for remediating the contaminated area.

The first stage (surveys prior to slag coating) was carried out in the first five months of the survey, until point P1 was grounded, to assess the removal and availability of metals from the Plumbum wetland as indicators of contamination.

The second stage, developed during the execution of the coating, was carried out in the months of June and July 2001 to evaluate the installation of the coating project and its interference in the behavior of metals in the wetland.

The third stage, developed after the slag coating project, was carried out from August to December 2001 to evaluate the efficiency of the slag coating and the monitoring of metals from the wetland to the Subaé River.

4.1.1 - Fieldwork

The field survey was carried out using standard procedures for the following surveys: location and sampling at the rainwater station; location of surface water collection points, their frequency and sampling; and the location and sampling of the wetland and soil sediment.

4.1.1.1 - Topographic map

A 1:100 scale topographic map of the area was prepared, comprising the Plumbum Co. facilities and its immediate surroundings. The survey was carried out by Purifica Project[9] with the objective of obtaining a topographic map compatible with the detail of the survey (Figure 4.1). This original map, in AUTOCAD format, was modified and adapted to a 1:3000 scale for this work.

4.1.1.2 - Survey of rainwater

Rainwater behaves as a critical agent in the functions developed by wetlands, being able to influence the amount of water during the seasons of the year and especially control the migration or retention of metals in the system.

In this way, the pH values and the volume of rainwater collected in the course of a year served as a basis for the evaluation of the changes that occurred between the first and third stages of the investigation. These values also allowed for the correlation of the concentrations of analyzed metals, at the entrance and exit of the wetland.

- **Location and installation of the sampling station.**

The choice of location for installing the rainwater sampling station prioritized: (i) proximity to the studied site; (ii) the implantation of the base in a deforested area; and (iii) the safety of the rain gauge, as Plumbum's facilities are abandoned and subject to theft.

The sampling station is composed of a type MI-028 rain gauge. The rain gauge was installed on December 27, 2000, so that the first sampling on January 3, 2001 would take place after a week of rainwater collection. This station has the following specifications, contained in Table 4.1:

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[9] The Purifica Project or Proposal for the remediation of areas degraded by the extraction of lead in Santo Amaro da Purificação was a project developed by the Polytechnic Schools of UFBA and USP, continuing the research developed by ANJOS (1998). The project was carried out with funds from the Financier of Studies and Projects (FINEP) in the amount of R$ 259,000.00. In addition to USP, the Research and Development Center (CEPED) and the Environmental Resources Center (CRA) participated as co-executor units.

Table 4.1 - MI-028 TYPE RAINFALL SPECIFICATION

Material	Stainless Steel 304 No. 26
Rabinet	Brass 378”
Clamp	Aluminum
Solders	Spot/tin
Capture area	400 cm^2
Mouth diameter	225.7 mm
Height	630 mm
rain capacity in millimeter	200mm
weight	3 kg
Calibrated beaker	Pyrex glass
Test tube capacity	25 mm
Beaker scale division	0.2 mm

- **Frequency and collection of samples**

Rainwater was sampled weekly, on Wednesday mornings, throughout 2001, using a calibrated Pyrex glass beaker. The beaker was washed with deionized water before and after collection of the sample.

- **Measurement of the physical-chemical parameter and volume of rainwater**

The analyses of pH, a non-conservative physical-chemical parameter[10], was performed "*in situ*" using a portable water quality meter, brand U 10 by HORIBA, and the equipment was calibrated using the standard solution specific to the physicochemical parameter sampled.

4.1.1.3 - Survey of surface water in the wetland area

The survey of sthe wetland’s surface waters was carried out for the determination of the physical-chemical parameters (in situ data collection) and of the heavy metals and support for quantitative chemical analyses, in stations of rigorously controlled location.

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[10] Non-conservative physicochemical parameters “are those that, temporarily, can vary rapidly and significantly, such as pH, Eh and temperature” (MESTRINHO 1997).

- **Location of sampling stations**

In the first stage, before covering, the survey was carried out at the points of emergence of water from the slag dam (point P-01) and at the exit of the wetland (inlet of the pipe in the landfill zone) (point P-02), (see Figure 4.2). In the second stage (during the slag coating), samples were collected only at point P-02. Finally, in the third stage (after the slag coating) the sampling was carried out at point P-02 and at a third point called P-03 located at the confluence of the Plumbum drainage with the Subaé River.

- **Frequency, collection and preservation of samples**

Sampling, both for in situ survey of support parameters and for chemical analyses of metals, was carried out weekly during 2001. Sampling of support parameters from surface waters was performed using a plastic collector cup belonging to the water quality meter (Photo 4.2). For this procedure, it was not necessary to preserve the samples, as the measurements were carried out "*in situ*".

For chemical analyses, samples were collected in 1000 ml glass flasks, and the samples preserved in 1% concentrated nitric acid.

- **Survey of physical-chemical parameters of surface waters.**

The analyses of support parameters, hydrogenion potential (pH), temperature, conductivity, dissolved oxygen and oxidation-reduction potential (Eh) were performed *in situ* using a water quality meter, model U 10 from HORIBA. To control the quality of the data collected, a monthly survey of the same support parameters was carried out using another water quality meter, the 230A from ANALYSER.

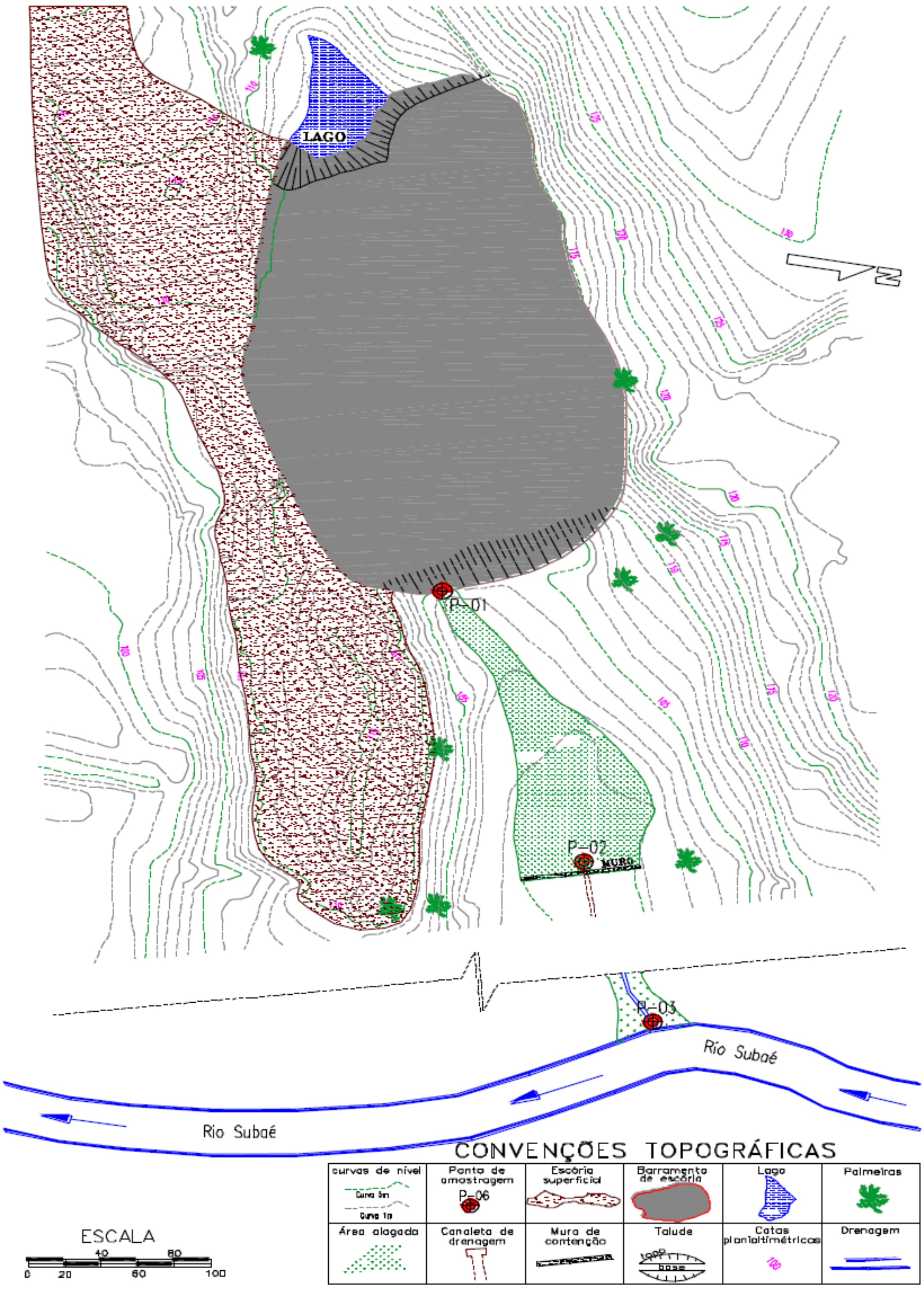

Figure 4.2 - Location of surface water sampling points

Photo 4.2 - HORIBA quality meter

The calibration of the equipment was carried out using standard solutions acquired from the company representing each equipment.

Twenty-two weekly samplings were carried out in the first stage, corresponding to the data obtained before the slag coating was carried out, 8 weekly samplings during the coating of the slag dam and 22 weekly samplings in the third stage.

- **Survey of surface water for metal analyses**

The sampling of surface waters for the total chemical analyses of the metals contemplated the same strategy established for the survey of the physicochemical parameters.

For 52 weeks, surface water samples for chemical analyses of metals were collected after measurements were taken for physical-chemical parameters.

The collection points were the same as for the physical-chemical parameters survey and the surface water collection was used to determine the levels of the metals Al, Ca, Cd, Cu, Fe, Mg, Zn, Mn, Co, Cr, Ni and Pb by quantitative chemical analyses. Sampling was carried out in accordance with the procedures of the Water Sample Collection and Preservation Guide (CETESB 1988). The samples were collected in polyethylene bottles, with a volume of 1 liter, preserved with 5 ml of concentrated HNO3 per liter and kept at a temperature of 04 °C.

4.1.1.4 - Survey of sediment in the wetland and surrounding soil

- **Sampling location**

Sediment and soil sampling was carried out at seven different points: five sediment samples within the wetland (AW - 01; 02; 03; 04 and 05), a soil sample (AW – 06) on the right bank of the wetland (Figure 4.3), in addition to a sediment sample from the control point, located in another wetland (AW – 00) located north of the Plumbum site, on the right bank of the road to the Pedra district (16 km) and upstream the Subaé River (Photo 4.3). This control point is outside the influence of drainage reaching the slag.

- **Frequency, collection and preservation of the sample**

The sediment and soil sampling was carried out in a single step and the collection followed the procedures of the Contaminated Areas Manual (CETESB 1999). The strategy used to prevent contamination of the samples was collecting them in the period in which the amount of surface water in the sediments was very low. In this way, the following procedures were considered in the elaboration of the sampling plan.

1. **Distribution of sampling points**

This procedure aimed to promote a survey of simple and representative data from the evaluated area, considering the investigation cost, in addition to estimating the distribution of contaminants present in the sediment and soil of the investigated area. Through the evaluation of pre-existing data, it was verified that the distribution of contamination in the area is concentrated in certain points, opting for a mesh with directed distribution of sampling points.

2. **Number of points sampled**

Considering the small extent of the wetland (90m long and more than 18m wide), 5 points arranged in two crossed sections were chosen.

3. **Depth and quantity and volume of sampling**

Soil and sediment samples were collected at a depth of 10 cm, homogenized and distributed in duplicates with a volume of around 1 kg.

4. **Sampler type and sample collection**

Mug auger for clayey soils and samples stored and preserved in polyethylene plastic bags.

5. **Sampling procedures**

Clean the area to be sampled; carry out the processing; place the sample in a plastic tray; homogenize and pack the sample in plastic bags and; decontaminate the equipment before the next sampling with deionized water.

6. **Sample identification**

Each plastic bag was identified with the sample number.

4.1.2 - Laboratory analyses

Laboratory work was carried out at the following institutions:

- Center for Research and Development of the State of Bahia (CEPED) carried out quantitative analyses for surface waters and reading the solutions for sequential analyses of soil and sediment (TESSIER method et al. 1979);

- Geochemistry Laboratory of the Geosciences Institute at the Federal University of Bahia, where procedures for sample preparation and separation of solutions for sequential extraction of soil and sediment were carried out;
- Technological Characterization Labs of the Department of Mining and Petroleum Engineering, where semi-quantitative analyses of the percentage of oxides present in the slag by X-ray Fluorescence were carried out; and
- Soil and Inorganic Chemistry Labs, respectively, at the Structural and Engineering Department of the Polytechnic School and at the Chemistry Institute at the University of São Paulo where analyses by sequential extraction of soils and sediments, using the new procedures standardized by the Community Bureau of Reference (BCR) were carried out.

4.1.2.1 - Analytical procedure for slag

The slag produced by the Plumbum Co. is a hazardous toxic waste (ANJOS and SÁNCHEZ 1997 and ANJOS 1998) and, for more than three decades, it was deposited in the soil of the municipality of Santo Amaro da Purificação without any environmental control measures.

For this study, samples were collected from two holes in the center of the slag dam, carried out by the Purifica project. The holes were seven meters and the following samples were analyzed to determine the oxides: Hole 33, samples AM02 – Prof. 1.00 to 1.99 m; AM03 – 3.00 to 3.99 m deep; and AM06 – 6.00 to 6.99 m deep; and Hole 34, sample AM02 – 1.00 to 1.99 m deep; AM04 – 3.00 to 3.99 m deep; and AM07 – 6.00 to 6.99 m deep.

The Technological Characterization Laboratory - LCT of the Department of Mining and Petroleum Engineering at the Polytechnic School of the University of São Paulo carried out the preparation and analyses of the slag by X-Ray Fluorescence.

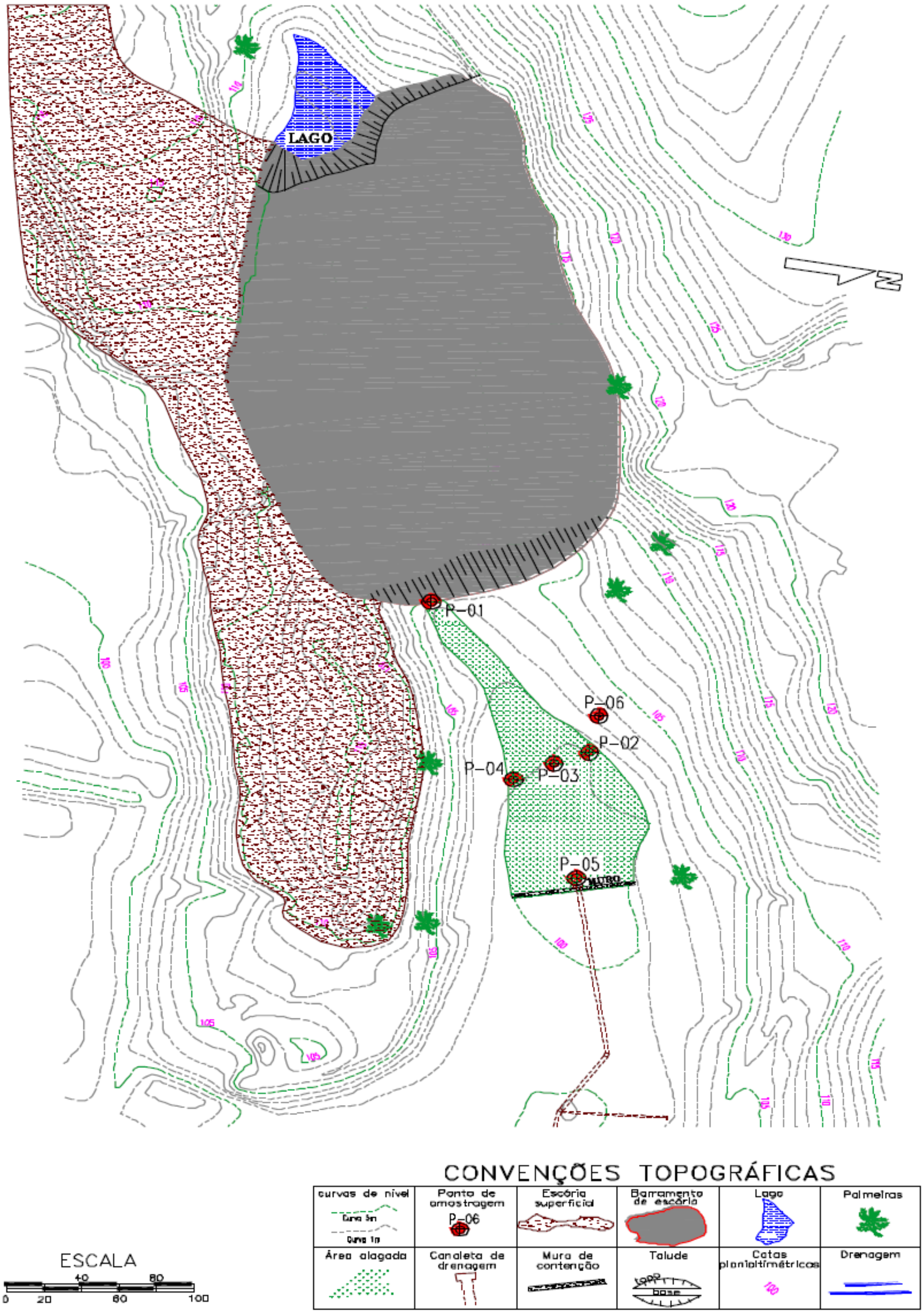

Figure 4.3 - Sediment and soil sampling points

Photo 4.3 - Wetlands used to control sediment metals

The procedures for making the tablet and subsequent reading on the X-ray, according to the LCT are shown in Figure 4.4:

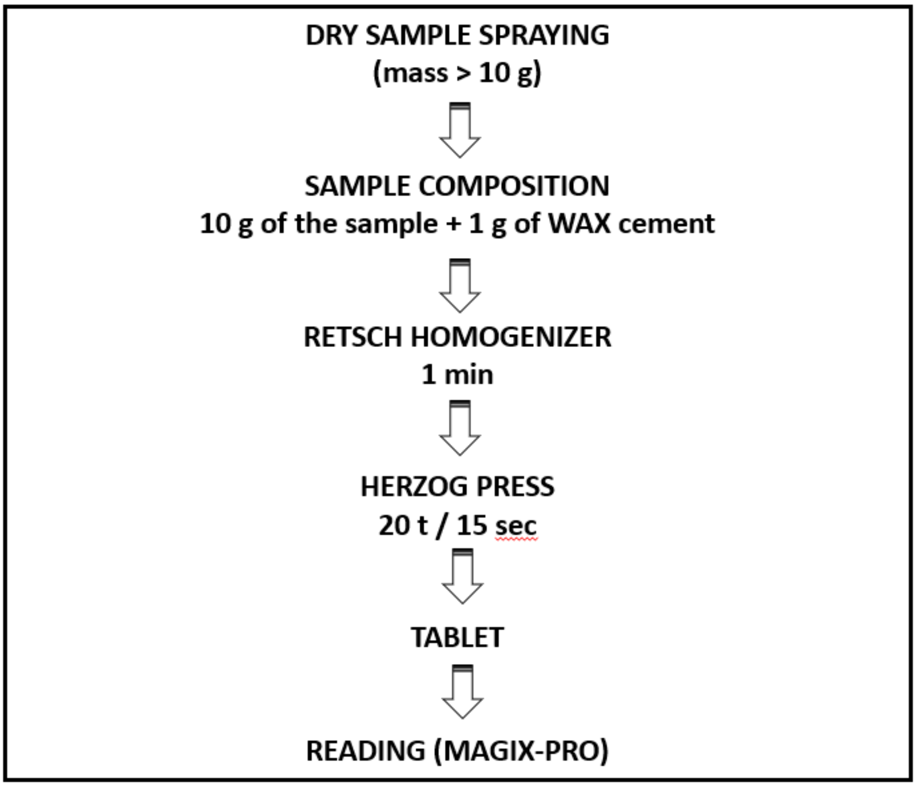

Figure 4.4 – Procedures for making the tablet and reading it on X-Ray.

4.1.2.2 - Analytical procedure for surface water

The analyses were carried out by CEPED, using the analytical method of Flame Atomic Absorption Spectrometry (FAAS) and Induced Plasma Atomic Emission (ICP-OES), complying with the procedures of the Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998. The outline of the procedure is shown in Figure 4.5.

The Optima 3000 DV Spectrometer and the Perkin-Elmer (ICP) were used under the following conditions:

- Torch Position/Readout – Axial
- Nebulizer - GemCone High Solids
- Expansion chamber – Cyclonic
- Detector - Segmented Solid State (SCD)
- Optics – Echelle (nitrogen purged)
- Coverage range – 167nm and 782nm

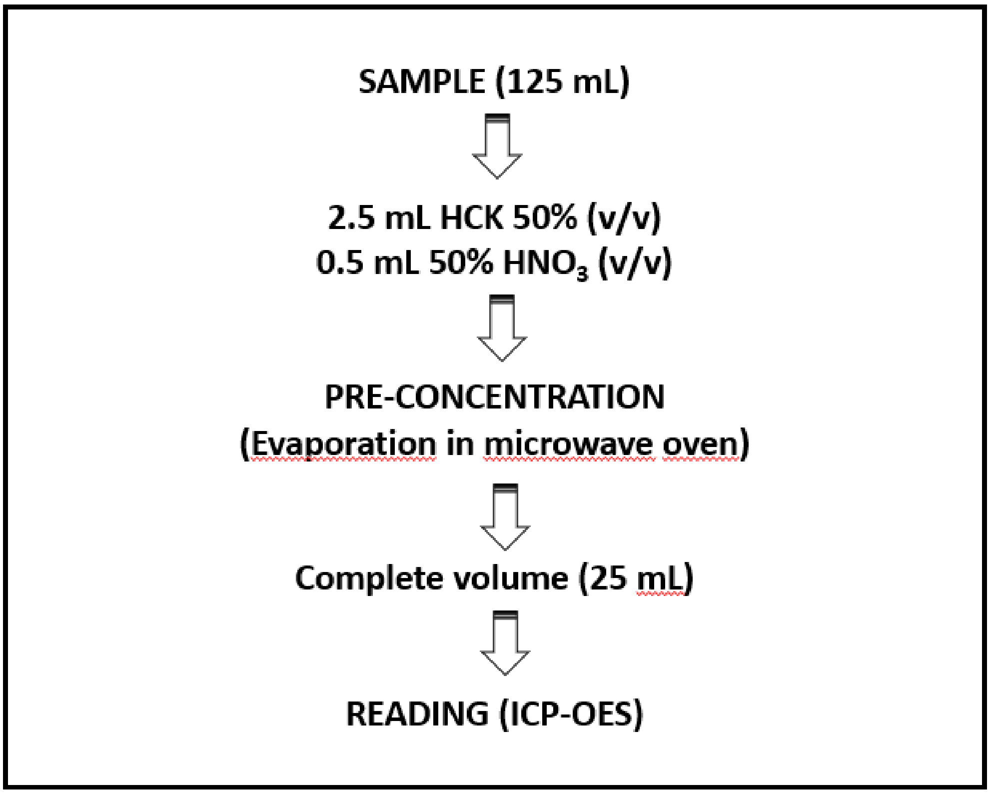

Figure 4.5 - Analytical procedures for reading metal concentrations

All samples analyzed for total metal were validated by a methodology that used yttrium as an internal standard to correct matrix interference. These corrections resulted from the optimization of parameters, such as plasma power and nebulizer flow (BANDEIRA 2002)

The results of the samples were obtained through the mean of triplicates and the instrumental detection limits (mg/L) of the ICP-OES used in the chemical analyses were the following: Aluminum 0.024; Cadmium 0.00024; Lead 0.0072; Cobalt 0.0024; Copper 0.0019; Chromium 0.00076; Iron 0.0013; Magnesium 0.0084; Nickel 0.0029; and Zinc 0.00062.

4.1.2.3 - Analytical procedures for sediment and soil

The preparation and analyses of soil and sediment samples for determination of metals were performed according to the procedures established by LAYBAUER (1995), MOZETO (1997), CETESB (1999), OLIVEIRA (2000) and QUINÁGILA (2001).

After collecting and preserving the samples carried out in the field phase, the following steps for analytical quantification were developed (Figure 4.6).

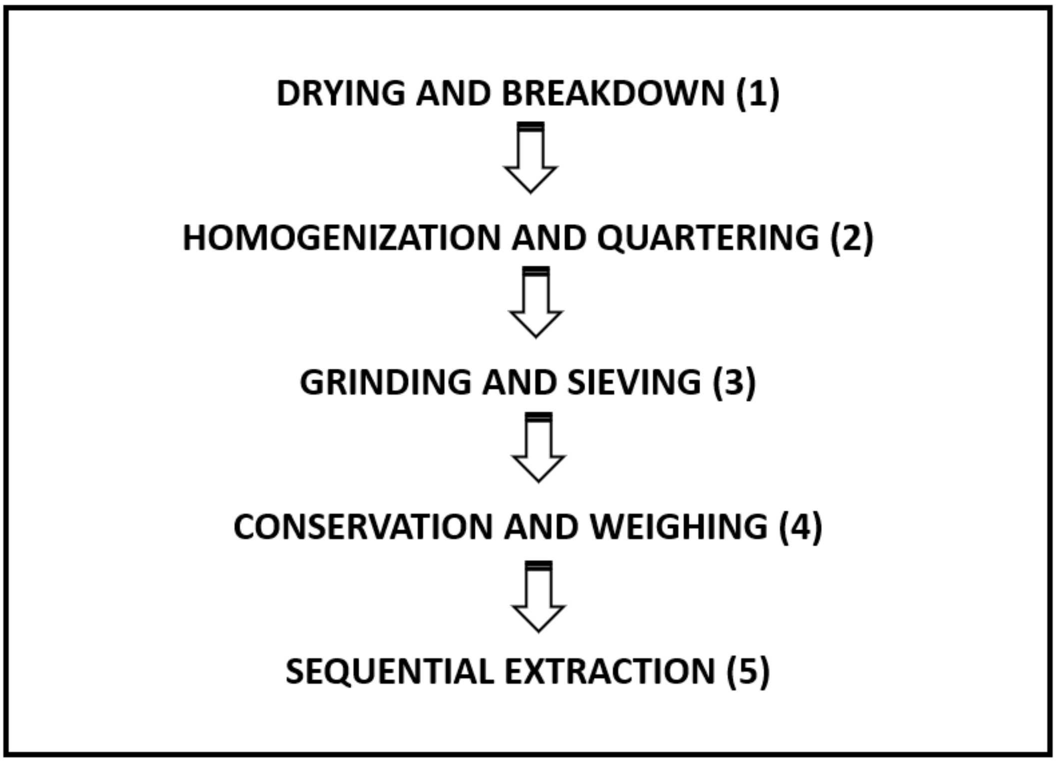

Figure 4.6 - Steps for preparation and analytical quantification of samples

The drying of 1 kg of sediment from each sample was done in an oven at 40°C, after which the material was disaggregated, removing the remains of roots and boulders that were not part of the sediment (1).

The sample was then homogenized in disinfected plastic boxes and quartered with a previously decontaminated spatula. Duplicate samples were placed in polyethylene bags, properly identified (2).

The quartered portion was ground in an agate mortar and the sample was macerated without excessive force, taking care not to alter the original size of the particles. After grinding, the sample was passed through stainless steel sieves with a mesh size smaller than 0.063 mm (3).

The portion of the sample smaller than 0.063 mm was placed in an identified plastic container and placed in the desiccator until weighing on scales with a precision of 0.1 mg (4).

To start the analyses by sequential extraction, the samples were placed in the centrifuge tubes and for each stage the reagents established in the analyses were placed (5).

Analyses by sequential extraction on a soil sample and six wetland sediment samples was performed at the Geochemistry Laboratory of the Institute of Geosciences at UFBA, to evaluate the amount of potentially available heavy metals in the sediment and contaminated soil of Plumbum.

The procedure adopted for the sequential extraction of metals in the Plumbum wetland was based on methods that used sediment samples, such as TESSIER et al. (1979), modified in Brazil by JORDÃO et al. (1990), NASCIMENTO et al. (1997), LACERDA et al. (1998) and OLIVEIRA (2000)[11].

The cited fractionation methods provide information regarding the chemical fractions and the proportion of the metal solubilized by a specific reagent. The main fractions are as follows (Table 4.2): exchangeable fraction, referring to metals weakly adsorbed to clays, organic matter and iron and manganese oxides; acid-soluble fraction of metals bound to carbonates; reducible fraction of metals bound to iron and manganese oxides;

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[11] Analyses by sequential extraction using the BCR methodology, developed on soil and sediment samples from the Plumbum wetland, were not performed in time for presentation in this thesis.

oxidizable fraction of metals bound to organic matter and sulfides; and residual fraction of the mineralogical matrix.

The solutions obtained in the exchangeable, carbonate, reducible, oxidizable and residual phases of the sediment and soil were sent to CEPED, where the concentrations of lead, cadmium, zinc and copper were analyzed by Flame Atomic Absorption Spectrometry method.

In the initial stage of the sequential extraction, the exchangeable phase, all metals weakly adsorbed[12] in clay minerals, hydrated oxides of manganese and iron and humic acids are released from the surface of the solids (NASCIMENTO 1997), in addition to metals found in interstitial waters, especially in sediments (JAAGUMAGI 2002).

In this phase, different types of reagents are used, including acid salts and strong bases, for example, KNO3 or MgCL2; or salts of weak bases such as ammonium acetates (NH4OAc) have been used in different analyses.

The phase linked to carbonates is easily soluble because it represents a group of minerals with a relatively simple structure (KLAMT and MEURER 1999). Metals associated with the carbonate phase are released through acids, such as acetic acid or sodium acetate (URE et al. 1993).

The reducing phase is correlated with Fe and Mn oxides and hydroxides. According to NASCIMENTO op cit., these oxides are thermodynamically unstable under anoxic conditions and are excellent receptors for heavy metals. At this stage, it is important that the reagents used to break the bonds between the metals and the oxides do not attack the silica minerals and the bonds between the metals and the organic matter (OLIVEIRA 2000).

According to URE op cit., the main types of reagents used for this phase include hydroxylamine chloride $NH_2OH.HCl$ in acetic or nitric acid, ammonium oxylate, and a mixture of sodium dithionite, sodium citrate and sodium bicarbonate.

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[12] Adsorption is a process that involves the accumulation or concentration of substances on the surface or interface of solids or liquids, and can be distinguished between physical adsorption, which involves weak intermolecular forces, and chemical adsorption, involving the formation of complex chemical bonds (NEDER 1998).

Table 4.2 - PROCEDURES FOR SEQUENTIAL EXTRACTION

FRACTION	METHOD
Exchangeable	20 mL ammonium acetate (1M), pH 7, stirring 2h, room temperature, spin 30min/3000RPM, solution in 50 mL flask.
Carbonates	20 mL sodium acetate (1M), pH 5, stirring 12 h, room temperature, spin 30min/3000RPM, 100 mL flask solution.
Reducible	40 mL NH2OH.HCL (0.1M) + CH3COOH (25%), pH 2, agitation 6h, heating to 96ºC (Photo 4.4), centrifugation 30min/3000RPM, solution in 50 mL flask (Photo 4.5).
Oxidizable	1st phase: 3mL HNO3 (0.02M) + 5 mL H2O2 (30%), pH 2, heating 85°C, stirring occasionally for 2 hours. 2nd phase: Insert 3 mL H2O2 (30%), pH 2, heating 85 ºC, constant stirring for 3 h. 3rd phase: Cool the solution, add 5NH4OAc (3.2M) in 20 mL of nitric acid, constant cold stirring for 30 min, solution in 50 mL flask.
Residual	Tri-acid decomposition 1st phase. 10 mL of HF+5mL of nitric acid (dryness); 2nd phase. 5 mL hydrofluoric acid + 5 mL nitric acid + 5 mL of perchloric acid (leads to dryness); 3rd phase. 5 mL of hydrofluoric acid + 5 mL of nitric acid + 2 mL of perchloric acid (leads to dryness); 4th phase. Dissolve the salts with hydrochloric acid solution (10 mL) to (6M).

Source: Modified from TESSIER et al. (1979)

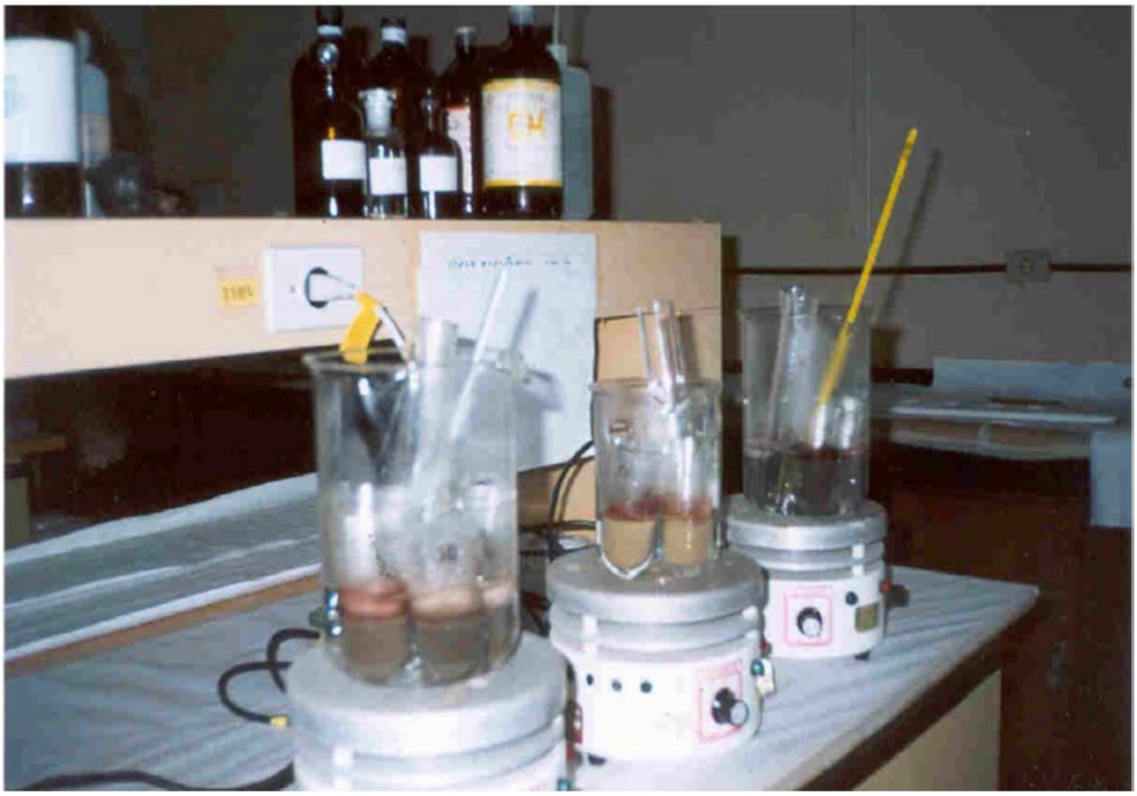

Photo 4.4 – Shakers with Beker containing the test tubes with the reducible phase solution.

Photo 4.5 – 50 mL flask with sample solutions being completed with deionized water.

The oxidizable phase is linked to organic matter and sulfides and the procedures adopted prioritize oxidizing conditions for the degradation of organic matter and associated sulfides based on hydrogen peroxide (H2O2). However, according to URE et al. (1993), no applied method seems satisfactory for separating this phase.

The residual phase corresponds to the analyses of metals in their mineral structure, this phase is characterized by the non-availability of metals. To release the metals, tri-acid solutions are used, with hydrofluoric, nitric and perchloric acids.

CHAPTER 5: LITERATURE REVIEW

5.1 What are Wetlands?

According to TINER (1999), wetland is a generic term used to define a universe of humid habitats, which are known under different names, such as swamps, marshes, wetlands, mangroves and similar areas subject to periodic or permanent flooding, which keep the soil sufficiently saturated for the establishment of macrophyte plants[13] and the development of hydromorphic soils[14]. These conditions influence the control of all biota (plants, animals and microorganisms) combined with the specificities of different hydrological regimes, climate and geomorphology (KADLEC and KNIGHT 1996).

The socio-economic importance of wetlands dates back to early times with the occupation of the delta of the Tigris and Euphrates rivers. This area, considered the cradle of humanity, is located in a huge and complex wetland, which during all these centuries has sustained thousands of families, especially with its agricultural production.

Some wetlands are among the largest productive natural systems on earth and are of vital importance for the conservation of the planet's biodiversity, among which we can highlight the mangroves, which occupy a large part of the Brazilian coast, the *igarapé* streams of the Amazon River and the wetlands of the Mato Grosso *Pantanal*.

Wetlands receive different names, especially in the United States and Canada and, due to their typological variability, they are called salt marsh, freshwater marsh, tidal marsh, alkali marsh, fen, wet meadow, wet prairie, alkali meadow, shrub swamp, wooded swamp, bog, muskeg, wet tundra, pocosin, mire, pothole, playa, saline, salt flat, tidal flat, venal poll,

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[13] Plants that germinate in water or soil and are periodically subject to anaerobic conditions due to excess moisture (TINER op. cit.).

[14] Hydromorphic soils are saturated soils, often close to the surface, which create conditions for the development of anaerobic reduction, which affects plant growth and promotes the fixation of hydrophytes (TINER op. cit).

bottomland hardwood swamp, river bottom, lowland, mangrove forest, and floodplain swamp (TINER op. cit.).

The first definition of wetland was published by Nathaniel Shaler in the 1890 U. S. Geological Survey, in an article called General Account of the Freshwater Morasses of the United States. In the article, Shaler uses the term swamp as flooded soils.

In 1956, the U. S. Fish and Wildlife Service (FWS) published a report entitled Wetlands of the United States, their extent and value for waterfowl and other wildlife. The study, known in the US government circles as "Circular 39", tried to standardize the various nomenclatures conceptualized as wet, humid, or swampy areas (MITSCH and GOSSELINK 1993 and TINER 1999).

LEFOR and KENNARD (1977) apud TINER (op. cit.), through extensive field sampling, carried out the first review on the definition of wetlands. According to the authors, a hydrogeologist would define a wetland as an area of fluctuation of the hydrostatic level, depending on the frequency and duration of floods or tides. A soil specialist would characterize it as a site with waterlogged soils and, when frequently flooded, affects crop production. A botanist would emphasize the occurrence of certain vegetation species, their communities and the humid conditions that promote their colonization. Thus, the authors conclude, definitions of wetland depend on the different areas of training or interest.

However, until the 1990s, the FWS based the definition of wetland on predominantly biological conditions. The FWS was responsible during the period from 1970 to 1980 for the most important investigation on the vegetation, soils and hydrology of wetlands, creating methodologies for identifying wetlands and criteria for regulating their use.

In the meantime, various definitions of wetland were applied to regulate different programs in the American states. Other countries, including Canada, Australia, and Zambia, have had their own definitions since the 1980s.

In 1998 scientists representing agencies from more than 90 countries interested in wetland conservation established a very broad definition called Ramsar wetland definitions. This international convention, besides extending the physical boundaries for wetlands, recognized that these ecosystems may contain other habitats as vital components to their development.

The Ramsar Convention[15] or Convention on Wetlands is an intergovernmental treaty, signed in 1971 in the City of Ramsar, Iran, which aims to promote and encourage the conservation and rational use of wetlands around the world.

According to the Ramsar Convention, wetlands are "all areas of marshes and peatlands or areas covered with water, whether natural or artificial, permanent, or temporary, with water that is still or flowing, fresh, brackish or salt. Marine areas are also considered wetlands, if the depth of low tide does not exceed six meters. It was also established that these wetlands may include adjacent riverside or coastal regions, as well as islands or extensions of marine areas deeper than six meters at low tide. As a result of this Convention, wetlands extend to a wide variety of aquatic ecosystems, including rivers, coastal/marine zones, and artificial wetlands such as lagoons, weirs and dams" (www.ramsar.org/).

The concept of wetlands in the Ramsar Convention is eminently political and comprehensive for environmental preservation, given that the introduction of wetlands in the Ramsar List represents new possibilities for international negotiation, such as those aimed at developing research, access to international sources of financing and creation of broader scenarios for intergovernmental cooperation.

Ramsar Convention signatory countries must promote the sustainable use of wetlands in their territory, provided that appropriate policies and laws are adopted, in addition to research activities intended to raise awareness of the population for the importance of these areas.

Brazil is currently the 4th country in the world in areas on the Ramsar List, with seven Wetlands considered Sites of International Importance – Ramsar Sites – equivalent to 6,356,896 ha.

According to RICHARDSON (1996), the value of a wetland is usually a subjective estimate, depending on its importance to the ecosystem and its

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[15] The Ramsar convention was established on 02/02/71. It is a multilateral agreement with global scope. This convention is also called "Convention on wetland or *Convention sur les zones humides* ou *Convención sobre los humedales*". Brazil ratified the convention in 1993 and the Ministry of the Environment established the term "wetlands" as the equivalent in Portuguese to define large natural humid ecosystems.

ecological functions. For this author, the main functions of a wetland are: a) hydrological flow such as discharge and recharge of aquifers, regulating water storage and regional climate control; b) biological productivity through primary and secondary production, storing and fixing carbon; c) in the biogeochemical cycle through the transformation processes of nitrogen, sulfur and phosphorus and in denitrification processes; d) in the decomposition of carbon and release or mineralization of nitrogen, sulfur and carbon; e) in the habitat of animal life and communities; f) in the control of floods and sediments; g) use as a water treatment, recreation and tourism system; h) in the capacity to preserve flora and fauna; and i) in historical, cultural and archaeological research.

However, natural or constructed wetlands to control water pollution are becoming a global technology. Surveys carried out recently indicated the existence of more than 6,000 wetlands built for the treatment of domestic waste in Europe and the United Kingdom, while in North America there are currently more than 1,000 wetlands controlling the pollution of industrial and domestic waste. On the other hand, in Brazil, Africa, Asia and Australia the number of wetlands built for waste treatment has increased rapidly (KNIGHT and KADLEC 2000).

In this research, wetlands, that is, all natural systems that fulfill the ecological functions established by RICHARDSON op. cit., the Ramsar Convention and the Ministry of the Environment (MMA). Meanwhile, constructed wetlands or wetlands will constitute constructed systems, natural or altered, used to control water pollution from industrial or domestic waste.

5.1.1 Built Wetlands

The technology for building wetland ecosystems began with the environmentalist movement of the 1970s, and had as its primary objective the production of habitats and the development of a natural and cheap technique for controlling water quality (KADLEC and KNIGHT 1996).

From that point on, the construction of wetlands as artificial ecosystems, using the basic principles derived from natural wetlands, has been used as an alternative technology in the control of water pollution. The recognition of this technology came from the first conference on the investigation and application of aquatic plants for water treatment, in 1986, in Florida/USA (SALATI et al. 1998).

Research on the construction of wetlands has taken a qualitative leap since 1988, after the Wetland Systems for Water Pollution Control Conference, in Chattanooga/Tenesee/USA. Since then, a large number of wetland construction models have been tested to control water pollution. Subsequently, the same conference was held in Cambridge/UK (1990), Sydney/Australia (1992), Guangzhou/China (1994), Águas de São Pedro/Brazil (1998) and Florida/USA (2000).

In 1990, the United States Environmental Protection Agency (USEPA) published a design manual called Constructed Wetland and Aquatic Plant Systems for Municipal Wastewater Treatment (USEPA 1990). The document was a development of a work carried out earlier at the Max Planck Institute in Germany and presented as its main technologies the Free surface water systems with emergent vegetation and the Free sub-surface water system with emergent vegetation (Figure 5.1).

According to USEPA (1990), built wetlands have the same positive characteristics as natural wetlands. In addition, its negative aspects are controlled, making it an effective low-cost alternative. In this way, wetland constructions for the treatment of liquid effluents can be built anywhere through a compatible hydraulic control project, considering the geographical limitations of plant species.

MITSCH and GOSSELINK (1993) presented the result of several studies on wetland construction based on the ecotechnological method. According to the authors, the design for surface and subsurface flow appropriate for wetland or series of wetlands seeks to control pollution at the source, maintain a wildlife habitat, maximize ecosystem longevity and be efficient with minimal costs.

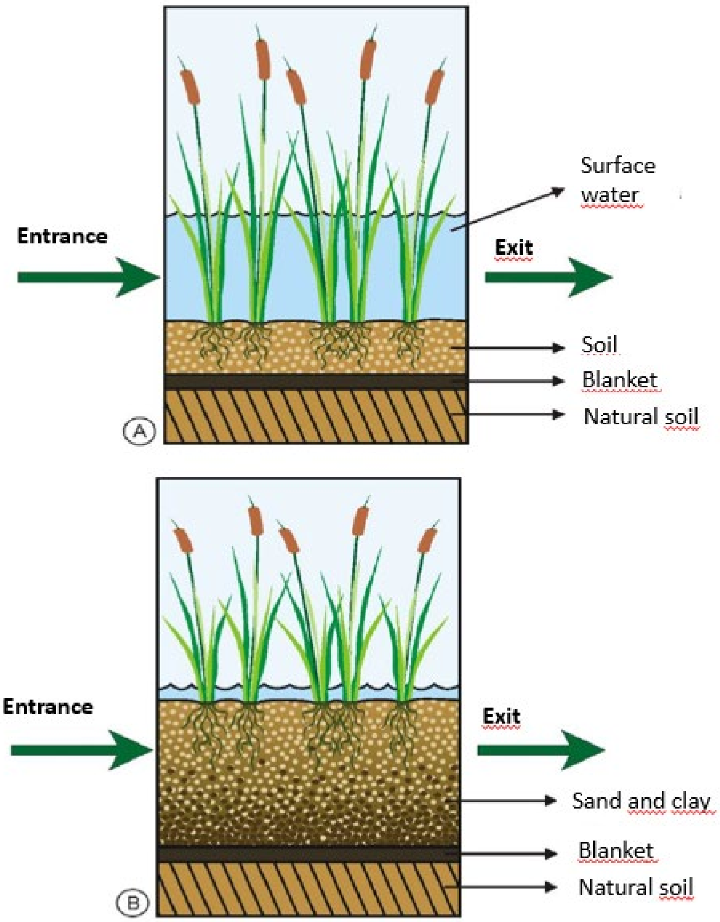

Figure 5.1– Types of wetlands used for waste treatment: a) surface flow; b) subsurface flow. Source: KNIGHT (1990) apud MITSCH and GOSSELINK (1993).

The surface flow system is generally not very effective in removing pollutants, while the subsurface flow system has been frequently used in Europe for the treatment of domestic liquid effluents, but its effectiveness has been questioned in controlling other pollutants. WEIDER et al. (1989) apud MITSCH and GOSSELINK (op. cit.) suggested that subsurface flow can be direct done directly in medium soil (root zone method) or directly in sand.

A new definition for constructed wetland was proposed by HAMMER (1992) apud KADKEC and KNIGHT (1996), characterizing the constructed wetlands as specific systems for treating water quality and the created wetlands as systems intended to restore habitats, that is, for recovery of degraded areas.

In the United States wetlands have been built for diverse purposes (KADLEC and KNIGHT 1996) and are part of the American government's environmental policy to prevent new losses of these systems or, in case it is unavoidable, to enforce the implementation of a new project compensated by the recovery of an equivalent area. However, given the limitations imposed by the regulations, the term constructed wetland was consolidated as the only terminology.

BRIX (1993) presented a study with constructed wetlands based on macrophytes, including the main constituents (solids in suspension, Biochemical Oxygen Demand (BOD), nitrogen, phosphorus and pathogens) and the associated residue removal mechanisms.

The constructive models addressed by BRIX (1993) are classified by VYMAZAL (1998), according to the life form and domain of the macrophytes, presenting the following types:

a) systems using floating aquatic macrophytes are usually built in long and narrow channels approximately 0.70 m deep;
b) systems using emergent aquatic macrophytes can be illustrated in the following three ways:
    b1) emergent macrophytes with surface flow: characterized by the surface flow of water with emerging plants;
    b2) emerging macrophytes with horizontal sub-surface flow: characterized by horizontal flow in substrate formed by rocks and emerging plants;
    b3) submerged fixed macrophytes: characterized by vertical flow in a soil layer over gravel in which emergent plants are cultivated;
c) system with submerged fixed macrophytes, where the water depth varies around one meter and the macrophytes are cultivated in a substrate with special soil;
d) DHS system (Water Depollution with Soils): wetlands built with so-called filtering soils, as they have superimposed layers of gravel and soil cultivated with rice. The filtering soils must present special characteristics, like a high coefficient of hydraulic conductivity and a high cation exchange capacity;
e) combined wetland systems are combinations of different types of wetlands to solve cases that depend on the quality of water resources, available area, interest in using the produced biomass and landscaping.

BRIX (1998) added the term “Green” to the traditional wetland construction system and proposed the following discussion. What is a clean treatment system? Bearing in mind that wetlands are considered cheap and clean technology systems, while high technology systems are only considered clean. To compare the different alternatives, the author proposes the following parameters: treatment performance in relation to effluent standards; emission of various pollutants into the atmosphere; waste production; recycling and reuse potential; energy consumption; use of chemicals; used area; and environmental benefits.

WETZEL (2001) proposes the construction of wetlands integrated to the ecosystem, considering the great diversity and heterogeneity of the flora and its emerging distribution. The author presents the following conclusions as advantageous implications for the project: a) the organisms are independent and integrated into the system; b) the photosynthesis process of macrophytes can be produced by organic matter; and c) natural wetlands export large amounts of organic matter in dissolved form.

Constructed wetlands are regularly being used to manage polluted water effluents for primary, secondary and advanced treatment of domestic and industrial waste (KNIGHT and KADLEC op. cit.), especially in Europe and the UK, as small constructed wetlands for domestic waste.

5.1.2 Hydrology of natural or constructed wetlands

Studies on the hydrology of wetlands demonstrate that the diversity of physical, chemical, and biological conditions has determined a high complexity for its understanding (RICHARDSON 1996).

The definition of natural wetland hydrology used for federal regulations and policies in the United States and established by the National Research Council (NRC) standard, has caused much confusion in its application (TINER 1999), due to a large number of factors to be considered.

According to WINTER and WOO (1990) apud TINER (1999), the factors that influence the hydrology of wetlands include the topographical position, the different types of soils, the geology of the area, precipitation, relationships with the depths of groundwater, surface water runoff and tidal movement.

RICHARDSON (1996) admits that the function of the hydrology of natural wetlands is determined by the type of wetland, topographical position (slope, proximity, width, small channels or lakes), extension of the area and its interaction with groundwater. While KADLEC and KNIGHT (1996) understand that the definitions of hydrological terms are, most of the times, ambiguous, adding that the hydrological conditions also influence the biota through the type of soil and nutrients.

According to MITSCH and GOSSELINK (1993), hydrology is the most important variable for the construction of wetlands and a determinant for their functioning. The authors propose that if the hydrological conditions are well defined, then the chemical and biological processes will develop accordingly. Parameters used to describe hydrological conditions include the depth of the system, the retention time of water in the system and the geomorphological basis.

Studies on different types of wetlands in the United States that do not suffer tidal effects concluded that the variation in the depth of groundwater, during the period of one year, presents different fluctuations, depending on the types of wetlands surveyed (TINER op. cit.).

The performance of constructed wetlands depends on the hydraulic design, combined with other factors such as precipitation, infiltration, evapotranspiration, hydraulic load pattern and water depth. These parameters are important in the water balance calculations and are expressed according to the following equation (KADLEC and KNIGHT op. cit.):

$$\mathbf{Qi - Qo + P - ET = [Dv/DT]}$$

where,

Qi = liquid waste influent flow (V/t)

Qo = liquid waste effluent flow (V/t)

P = precipitation (V/t)

ET = Evapotranspiration (V/t)

V = Volume of water, and

T = time

5.1.3 Vegetation of natural or constructed wetlands

According to KADLEC and KNIGHT (1996), due to the presence of water, the physical and chemical diversity present in wetlands results in the most varied form of life, from tiny viruses to large trees.

Genetic diversity and functional adaptation allow organisms and vegetation to use the constituents of industrial or domestic liquid waste for their growth and reproduction. These constituents produce chemical, physical and biological changes in pollutants and modify water quality.

The main functions of aquatic plants for treatment systems were noted by USEPA (1990). For roots and trunks in the water column, the main functions are the growth of bacteria on the water surface and the sorption and filtration of solids, while for trunks above the water surface, the functions are light attenuation, the reduction of the effects of wind on the water and the transfer of gases to the submerged parts of the vegetation.

The main species commonly used in the Northern Hemisphere in the effluent treatment system are bulrush, cattail (*Typha latifolia* or *Typha augustifolia*), commonly called cattail, sedges and spatterdoc (MITSCH and GOSSELLILNK 1993 and SHUTES et al. 1993).

The biosorption of metals using non-living wetland biomass has been extensively studied. KADLEC and KNIGHT (op. cit.) presented studies on the advantages and disadvantages of applying dozens of biomasses to different heavy metals and discussed the main factors caused by pH, temperature, initial concentration of metals, biomass weight and the presence of ions in the pre-treatment of biomass.

More detailed investigation on aquatic communities in natural wetlands is referred to in PORTIER and PALMER (1978), PENNAK (1978) and WPCF (1990a) apud KADLEC and KNIGHT (1996), while vascular plant species found in wetlands are referred to in MITSCH and GOSSELINK (1993) and GUNTENSPERGEN et al. (1989) apud KADLEC and KNIGHT (op. cit.)

In Brazil, water hyacinth (*Eichornia crassipes*), a macrophyte of the *Pontederiaceae* family and also known as baronesa, camalote or water hyacinth, has been intensively used in the treatment of industrial and sanitary effluents (ROQUETE PINTO et al. 1998).

Water hyacinth is native to Brazil and proliferates abundantly throughout the year, with a high rate of biomass growth (1 ton/ha/day of dry matter), bears a great capacity for survival in polluted water environments, and for absorption, through its roots, organic and inorganic toxic substances (ROQUETE PINTO op. cit.).

The depolluting action of water hyacinth is carried out by three mechanisms which are: a) the filtering action of the root hairs; b) absorption of pollutants, such as heavy metals, organochlorine compounds, organophosphates and phenols; and c) oxygenation of the water body through its aerial part (ROQUETE PINTO op. cit.).

Wetlands built by the Instituto Ecológico Aplicado, in Piracicaba/SP, since 1982, with the purpose of purifying effluents polluted by domestic and industrial waste, have shown satisfactory results with the use of rice and emerging plants as support vegetation for the implanted systems. Some systems have shown efficiency of up to 99% in the control of fecal coliforms (wetland from the Piracicaba City Hall treatment plant) and 96% of phenols (wetland from Cyanamidl) (SALATI et al. 1998).

The Ford Factory installed in 2001 in the Municipality of Camaçari in the State of Bahia, applies the wetland technique built for the biological treatment of its sanitary effluents, with cattail of the *Typha domingensis* species, the vegetation used in the removal plant of pollutants.

5.1.4 Types of Natural and Altered Wetlands

Natural wetlands are found in the most varied geomorphological conditions (Figure 5.2) and before the development of constructed wetlands they were already used for the treatment of effluents.

In some cases, wetlands can be modified to function as effluent treatment systems. However, the many design variables of constructed wetlands are generally pre-fixed, which can compromise their efficiency in treating effluents. Natural wetlands developed along narrow strips are considered relatively inefficient for treating the quality of the effluent, given to the short residence time of the water within the system (KADLEC and KNIGHT 1996).

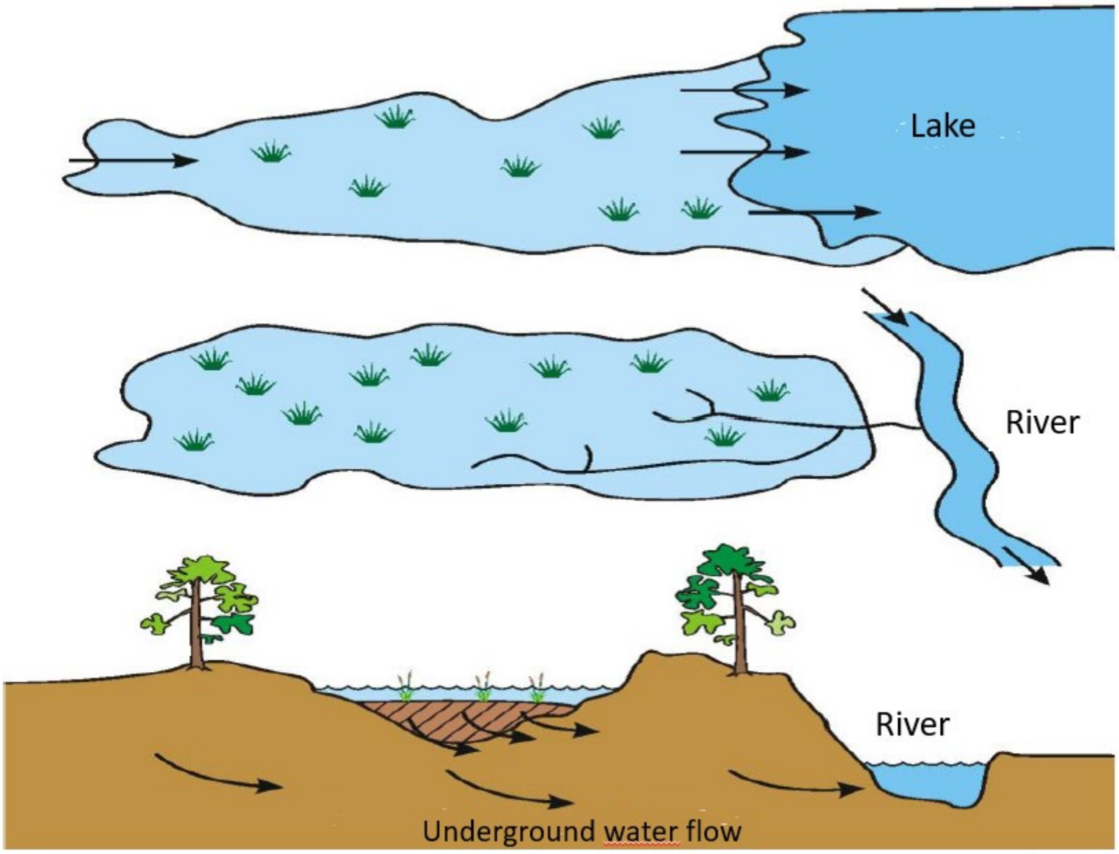

Figure 5.2. Types of natural wetlands. Source: KADLEC and KNIGNT (1996).

LUCA (1991) characterizes macrophytes and water hyacinth or *igarapé*[16] ponds as natural wetlands used in Brazil to remove nutrients, heavy metals, and solvents from effluents, in addition to retaining algae. Macrophyte ponds, also called ecological ponds, are composed of floating or fixed macrophytes and were developed without many technical criteria. The main problems in its operation are related to the low efficiency in the removal of nutrients, especially fecal coliforms, the proliferation of mosquitoes and the accumulation of sludge at the bottom of the lagoon, causing ecological succession.

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[16] The use of water hyacinth or *aguapé* ponds (commonly known as baronesa) to remove nutrients, organic compounds and trace metals has been used in high temperature regions. This system proved to be very effective in removing BOD5, nitrogen and phosphorus. However, there is a transfer of nutrients and metals to the plants that, if not collected when they die, will be adsorbed into the liquid medium. Another problem is related to the large consumption of O_2 in the system when dead (LUCA op. cit.).

Some natural wetlands may have components similar to those of constructed or altered wetlands, notably: the tributary entry system; the submerged area, the natural vegetation; the porous medium and the effluent outlet system (Figure 5.3).

A good distribution of the inflow, as well as a longer residence time of the water within the system, can determine a greater efficiency in the removal of pollutants, given to the larger area where the biogeochemical processes that control the retention of residues are manifested (KADLEC and KNIGHT op. cit.).

In some cases, the entry point of natural or altered wetlands can be used for monitoring water flow and quality as is done in constructed wetlands. However, the occurrence of more than one point of entry and/or exit of natural wetlands makes it difficult to monitor the system, making treatment more expensive (LAUTENSCHLAGER 2001).

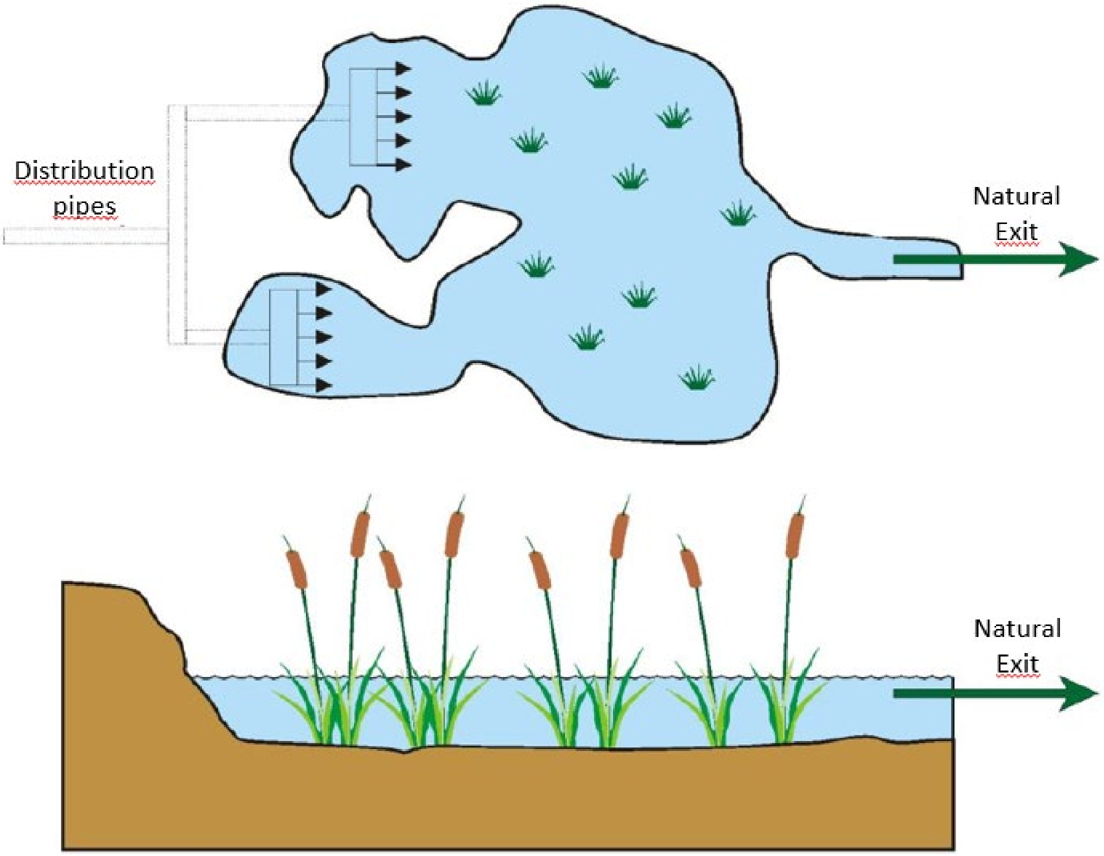

Figure 5.3 - Changed Wetland. Source: KADKEC and KNIGHT (1996)

Depending on the amount of effluents disposed in the system, wetlands will possibly need larger areas for an effective removal of pollutants, as a result of the lack of a project qualifying its efficiency and, consequently, increasing the costs for its implementation. and the need for a large area. According to these considerations, there is a direct relationship between the flow and concentration of effluents to be treated with the dimensions of natural, built or altered systems.

5.1.5 Main biogeochemical cycles in wetlands

One of the ecological functions of wetlands manifests itself through their role in nutrient storage and cycling. Abiotic (oxidation and reduction, precipitation and dissolution, hydrolysis and complexation) and biotic (involving microorganisms) processes, act as mass transfer mechanisms and, associated with aerobic or anaerobic soil conditions, produce chemical species (PO_4, NO_3, SO_4 and C) and release gases into the atmosphere (N_2O, H_2S, CH_4 and CO_2) (RICHARDSON 1996).

The best evidence that wetlands function as a filter and nutrient deposit comes from studies on the flow of urban and industrial waste into swampy ecosystem and its relationship with the nitrogen and phosphorus cycles. Studies have shown that the premature eutrophication[17] of many lakes is associated with the pollution process resulting from urban growth, industrialization, and agricultural activities (NOGUEIRA 1991).

These anthropogenic processes generate an addition of nutrients greater than the capacity of the system, causing an ecological imbalance in the biogeochemical cycles of nitrogen and phosphorus.

Nitrogen cycle

Nitrogen cycle is of fundamental importance in the development of plant species, in the eutrophication of water, in the oxygen content and in the assimilation of metals by aquatic vertebrates and invertebrates (KADLEC and KNIGHT 1996).

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[17] According to NOGUEIRA op. cit., “eutrophication is the natural or artificial process of adding nutrients to water bodies, as a natural aging process of lakes that would occur independently of human activities”. Artificial eutrophication is accelerated by anthropogenic processes, quickly causing the disruption of the ecological balance.

The main sources of nitrogen[18] for wetlands are sewage systems (releasing organic and ammoniacal nitrogen) and the atmosphere (nitrogen fixation in bacteria and algae) (PIVELI 1998).

The nitrogen cycle is a complex system of nitrogen fixation from the atmosphere to animal and plant life and return to the atmosphere through the process of denitrification.

The most important forms of nitrogen in wetlands are inorganic compounds, represented by ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitric oxide (N_2O) and nitrogen gas (N_2). The organic forms are urea, amino acids, amines, purines and pyrimidines, this being the initial step in the mineralization of organic nitrogen (LEWIS 1999).

The rate of ammonification[19] in flooded soils depends on temperature and pH. Under conditions where wetlands are not flooded, it is substantially reduced (KADLEC and KNIGHT 1996). According to BRIX (1993), constructed wetlands based on macrophytes present ammonification followed by bacterial nitrification and denitrification, as one of the nitrogen removal mechanisms.

Nitrification is considered by many authors as the main mechanism of change from NH^+_4 into NO_3^-, in the oxidizing zone of the soil. NH^+_4 is oxidized by bacteria and released by volatilization into the atmosphere, while in the reducing zone, NO_3^- is transformed into N_2 and N_2O through the denitrification process, which are released into the atmosphere. This complex mechanism produced in wetlands represents the main process that keeps nitrogen in global circulation (LEWIS op. cit.).

These studies present results on the effects of increasing or reducing nitrogen in constructed wetlands, its behavior in relation to physical chemical parameters and the macro and micro-biota, in addition to its effectiveness in controlling residues in the face of the variety of plants and types of constructed wetlands. (CRUMPTON et al. 1993, WATSON and DANZING 1993, GEISER et al. 1993, MANFRINATO et al. 1993, WARD PRUSTAY 1998, COOPER et al. 1998 and PLATZER 1998).

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[18] The element nitrogen has an atomic weight of 14.01 with five electrons in the last electron shell. With three available electron positions in the last layer, nitrogen can form compounds with several valences, with oxidation states ranging from –3 to +5.

[19] Ammonification is the initial step in the mineralization of organic nitrogen with the biological transformation of organic nitrogen into ammonia.

Phosphorus cycle

Like nitrogen, excess phosphorus in domestic and industrial sewage leads to the process of water eutrophication. Phosphorus is a macro-nutrient necessary for plant growth and is one of the main nutrients for biological processes. They are introduced into natural waters by the erosion of soils rich in phosphate and by discharges from sanitary sewage - especially superphosphated detergents used on a large scale in domestic cleaning -, industrial effluents (slaughterhouses) and from agricultural areas (pesticides) (PIVELI 1998).

Phosphorus is of great importance in the biogeochemical cycle, given especiially to the necessary proportion between nutrients, carbon, nitrogen and phosphorus (106C:16N:1P) in the ecosystem (PIVELI op. cit.). As effluents generally do not present this relation, their introduction through anthropic activities in natural ecosystems can cause imbalance of nutrients (KADLEK and KNIGHT 1996).

The efficiency in the ability to remove phosphorus is a difficult task and the use of natural or constructed wetlands constitutes one of the technological alternatives for the treatment of polluted waters (KADLEC and KNIGHT op. cit.).

Studies carried out by DAVIES and COTTINGHAM (1993) and WARD PRYSTAY (op. cit.) established the limit capacity of the system for the removal of phosphorus and demonstrated that the retention of this element in the different types of constructed wetlands presented an efficiency of 65 to 82 % of total phosphorus.

DAVIES and COTTINGHAM (op. cit.), KADLEK and KNIGHT (op. cit.) and RICHARDSON (op. cit.) present a simplified scheme of the biogeochemical cycle of phosphate with the main processes occurring during the fixation and release of phosphorus in humid zones, presenting PO4 (phosphate) and PP (particulate phosphorus) as the main sources of phosphate by precipitation, while by surface runoff it is PO_4.

According to DAVID and COTTINGHAM (1993), the exclusive use of macrophytes in the removal of phosphorus from waste is severely limited. Studies on the percentage of phosphorus in various wetland plant species is shown in Box 5.1. These studies verified an increase in phosphorus in plant species when the state of wetlands is changed from oligotrophic to eutrophic.[20]

Table 5.1 - LEVELS OF PHOSPHORUS IN THE TISSUES OF MACROPHYTES FROM WETLANDS

Species	Trophic status of water	Green Leaf (%)	Dry Leaf (%)	Detritus (%)	Reference
Cladium jamaicense	Oligotrophic	0.04	0.02	0.02	DAVIS (1990)
C. jamaicense	Eutrophic	0.08	0.04	0.12	DAVIS (1990)
Typha domingensis	Oligotrophic	0.14	0.05	0.02	TOTH (1990), DAVIS (1990)
T. domingensis	Eutrophic	0.20	0.07	0.16	TOTH (1990), DAVIS (1990)
Eleocharis sp.	Oligotrophic	0.18	0.08		WALKER et al. (1988)
Panicum spp.	Eutrophic	0.16			WALKER et al. (1988)
Sagittarius sp.	Oligotrophic	0.40	0.10		WALKER et al. (1988)
Utricularia spp.	Eutrophic	0.16			WALKER et al. (1988)
Salix spp.	Oligotrophic	0.12		0.10	CHAMIE (1976)
Pumila Birch	Oligotrophic	0.12		0.08	CHAMIE (1976)

Source: KADLEK and KNIGHT (1996)

However, according to BRIX (1993), the removal of phosphorus by wetlands has been carried out through precipitation and adsorption reactions with aluminum, iron, calcium, and clay minerals from the surface sediments of wetlands.

5.1.6 Efficiency of constructed wetlands

The efficiency of constructed wetlands is directly related to the percentage of nutrients or chemicals removed, retained, transformed, or

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[20] The oligotrophic level of water corresponds to 0.010 mg/L of phosphorus and 2.5 g/L of chlorophyll, while the eutrophic level corresponds to water with levels of 0.035 to 0.100 mg/L of phosphorus and 8 to 25 g/L of chlorophyll (PIVELI (1998).

decomposed by wetland ecosystems. Or simply the difference in percentage between the amount of waste entering the system (inflow or affluent) minus the amount leaving (effluent). This process is directly associated with the biogeochemical cycles (nitrogen and phosphorus) and the chemical transport processes (sorption, complexation, and oxidation-reduction) (MITSCH and GOSSELINK 1993).

The term efficiency or removal has been used, especially in constructed wetlands, to determine which constructive projects achieve a greater retention of substances, such as: “removal of trace elements in acid drainage” (EGER et al. 1993); “heavy metal retention in hybrid wetland systems” (OBARSKA-PEMPKOWIAK 2001) and “nutrient and heavy metal removal in constructed wetland systems in Arizona” (KARPISCAK et al. 2001). In terms of nutrients, there are: “removal of phosphorus from domestic waste by constructed wetland” (DAVIES and COTTINGHAM 1993); “Efficient Phosphorus Retention in Wetlands: Fact or Fiction?” (RICHARDSON and CRAFT 1993); and “state of the art and efficiency in waste treatment by constructed wetlands” (HUNT and POACH 2001).

However, the term “efficiency” has been applied when constructed wetlands are treated as an alternative technology, as compared to other conventional treatment systems for controlling wastewater pollution (BRIX 1998). Still, a few authors also use the term “removal efficiency” to determine the amount of waste retained in the system (KANTAWANICHKUL and ANH 1998, FUJITA et al. 1998 and NENCOVA et al. 1998).

The application of the term “removal” as a process inherent to the retention and/or transformation of nutrients was applied at the 7th International Conference on Wetland Systems in Water Pollution Control, held in Florida in 2000. The structure of this event presented three main subdivisions, with articles on the transformation and removal of phosphorus, nitrogen and pathogens, encompassing the relative processes, and mechanisms when using macrophytes, surface, sub-surface and combined flow systems, in surface runoff of agricultural systems, in the evaluation of impact on large ecosystems and removal indicator bacteria (REDDY and KADLEC 2001)

According to GEARY and MOORE (1998), the capacity to efficiently remove pollutants from wetlands can be determined using mass balance, which involves understanding all functions (hydraulic loading, transfer routes and evapotranspiration) of the wetland (KADLEC 1986 apud GEARY and MOORE op. cit.). However, KADLEC and KNIGHT (1996) developed a relationship that has been used to calculate the percentage of mass removed (1).

$$\% \text{ Mass removed} = 100\,(M1 - M2) / M1 \quad (1)$$

M1 = Mass of the pollutant entering the wetland

M2 = Mass of the pollutant from the wetland outlet

This relationship between masses has served as a parameter to determine the efficiency of natural and constructed wetlands for both nutrients and toxic metals.

The efficiency of constructed wetlands is correlated with the risks that established after their installation, including the impacts on ecologically important species; human exposure to contaminated water or food and maintenance of low-efficiency projects (LEWIS et al. 1999).

Researchers however have used wetlands as a remediation technique in contaminated areas, as they have been shown efficient in the natural attenuation of benzene compounds and bioremediation of organic compounds (MEANS and HINCHEE 1999).

5.1.7 Wetlands in Brazil

The term wetland in Brazil is represented by natural ecosystems called: mangroves, ponds, swamps, and igapós. These systems have common characteristics and properties, depending on geology, geomorphology, soil and climatic conditions. Meanwhile, the term built wetland is used for water purification projects and depends on the objective and the effluent to be treated, and can be divided into four categories: a) systems to purify large volumes of water; b) urban sewage treatment system; c) industrial water purification system; and d) urban and industrial water supply system (SALATI et al. 1998 and 1999).

The first attempt to use a wetland construction system in Brazil was developed by SALATI et al. (1982) apud SALATI et al. (1998), through the construction of an artificial lake using water hyacinth for depollution. Subsequently, research was directed towards the depollution of rivers using the phytopedological method (SALATI 1984, 1987 apud SALATI et al. 1999)

The main constructed wetlands were developed by the Institute for Ecological Application and had systems for controlling water quality. Among them, the projects for the Municipality of Piracicaba/SP, Cyanamid Química do Brasil in Iracemápolis/SP, Taboca Mininc Co. in Vila de Pitinga/AM, IRCOSA – Leather Industries in Caruaru/PE, Vila Romana Condo in Piracicaba/SP, and Companhia Vale do Rio Doce Co. in Barcarena/PA.

MANFRINATO (1989) apud SALATI et al. (1999) and MANFRINATO et al. (1993) presented a study on water purification and reuse techniques developed in the Piracibaca river. The study, initially named Edaphic-Phytodeupration Technique, deals with wetlands constructed for the treatment of large volumes of water. The study, developed from June 1986 to June 1987, analyzed the efficiency of two wetlands built for the pre-treatment of water.

These wetlands used combinations of aquatic plants and filtering soils cultivated with rice. The parameters studied in both systems were efficient, making it possible to improve the water quality from a Class 3 river to a Class 2 river, according to Conama Resolution 20/86.

LUCA (1991) discusses alternative systems for the treatment of liquid effluents and, among them, describes the ecotechnological method (Figure 5.4) as an economical and efficient system for the reuse of effluents and the removal of contaminants. This method is based on the purification capacity of the ecosystem, presenting a wetland with the same functions as an advanced sewage system.

According to LUCA (op. cit.), wetlands can efficiently control problems related to excess nutrients and micronutrients reaching water bodies, interacting as transformers of chemical products and, through a seasonal pattern of use, return nutrients to the ecosystem, as exemplified by successful projects in mining and aquaculture, where these marshes are highly efficient in removing BOD5, nitrogen and coliforms.

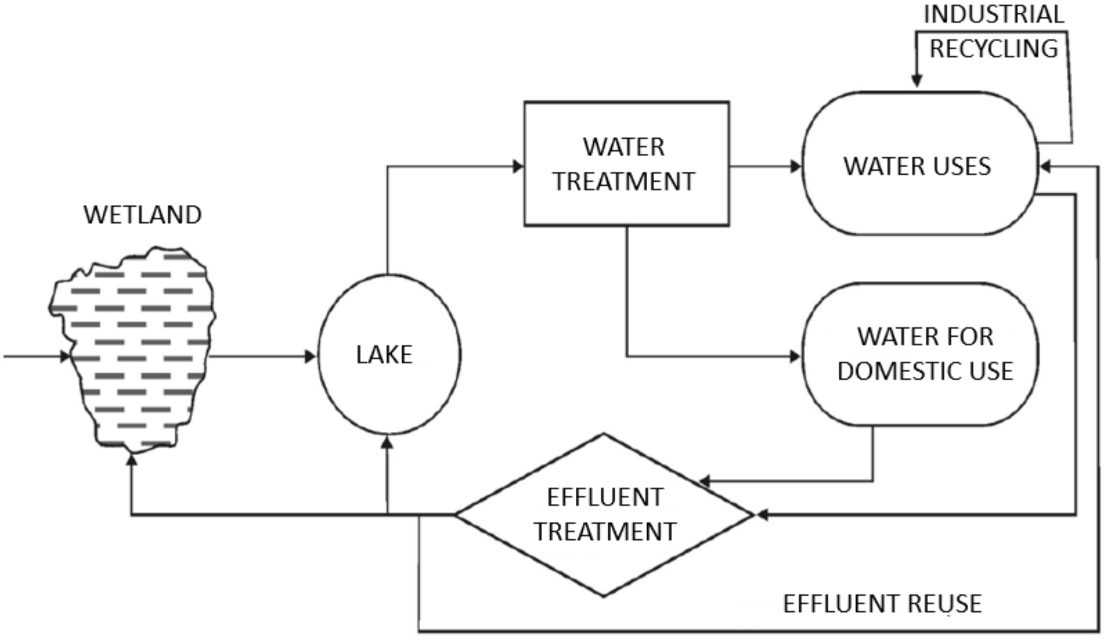


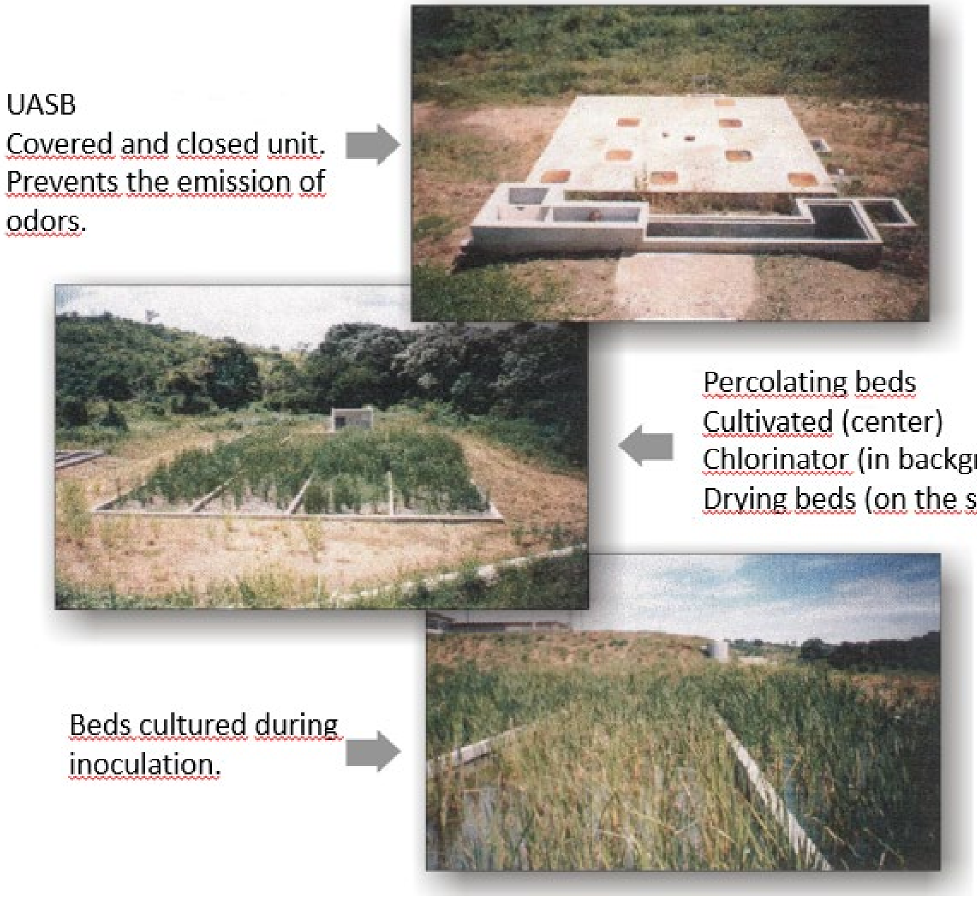
Figure 5.4 - Eco-technological method of effluent treatment and pollution control, Source: LUCA (1991).

ROQUETE PINTO et al. (1998) present a water treatment technique through a bio-technological process using water hyacinth. The size and cost of a water hyacinth system depends on several factors, including flow and effluent characteristics. The sanitary depollution system for secondary and tertiary treatment costs 80% less than a traditional secondary system.

VALENTIM and ROSTON (1998) developed small domestic water treatment systems for rural areas. The system is composed of a modified septic tank associated with cultivated beds of subsurface flow macrophytes, forming a primary+secondary system. The subsurface flow prevents the contact of people and animals with the water surface, preventing the proliferation of insects and inconvenient odors.

SILVA and SANTOS (2000) developed studies based on landscape ecology for the metropolitan region of São Paulo. This system used digital thematic maps of geology, geomorphology, soils, land uses and land cover and ultimately produced an integrated map for analyses of the spatial body. The integrated map demonstrated that the wetlands located in the metropolitan region of São Paulo present good potential for use and improvement of water quality.

TUNDISI et al. (1999) presented functioning mechanisms of floodplain lakes and flooded areas of the Amazon and Paraná rivers. In the study, the authors present morphological characteristics for the flooded areas and show the fundamental stages of the nitrogen and phosphorus cycles in floodplain lakes.



UASB
Covered and closed unit. Prevents the emission of odors.

Percolating beds
Cultivated (center)
Chlorinator (in background)
Drying beds (on the side)

Beds cultured during inoculation.

Figure 5.5 – Wetland at the Luis Eduardo Magalhães Public Hospital. Source: FONTES and HAANDEL (2001) apud MELO FILHO et al. (2002).

Two large wetland projects have been implemented in the State of Bahia. The first was designed by the Environmental Engineering Co. (Figure 5.5), as a treatment plant at the Luis Eduardo Magalhães Public Hospital, in the municipality of Itabuna. The project called UASB + Cultivated

Percolating Beds was designed for 1000 daily users and is composed of wetlands combined into three cells: a covered and closed unit preventing the emission of bad odors; one with cultivated percolating beds and drying bed; and a third with cultivated beds.

The second wetland project built for sewage treatment and water reuse has been used at the Ford Amazon Complex in the municipality of Camaçari and is intended to treat sanitary effluents from an estimated population of 500 people, for a flow of approximately 0.8 L/ s.

The project comprises primary and secondary treatment and is intended to produce water with a low organic load, pathogenic microorganisms and odors, but rich in nutrients. The effluent resulting from the treatment will be used to fertilize landscaped areas (MELO FILHO et al. 2002). The first stage is carried out through the conventional primary treatment and is intended to remove the material in suspension, thus avoiding clogging of the tubes of the DHS System (BRIX 1993). The second stage of the project consists of two identical modules that alternate every 15 days and a discharge filtering soil. According to the company, the cost/benefit ratio of this technique is low, as the factory does not pay sewage fees and does not need to consume water to irrigate the green areas (MELLO FILHO op. cit.).

5.2 Heavy Metals

Most of the 110 chemical elements found on the periodic table are metals[21]. The use of different criteria for definition of heavy metal has led the literature to present different numbers by different authors. According to HILLERT (1997), at least 70 elements are considered metals, while another 5 (five) are metalloids with metallic and non-metallic properties. While TOREM et al. (2002) stipulated the number of heavy metals at 59.

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[21] Metal is a material with high reflectivity and conductivity, which can be plastically deformed and reflects light unless the surface has been corroded. HILLERT (op. cit.) presents interesting considerations on what a metal is and what a heavy metal is. According to the author, the term metal also refers to metallic elements when these are combined with other elements, forming non-metallic compounds, such as salts and oxides, for example, copper sulfate and sodium chloride (table salt). He also states that when a metallic element is absorbed by the human body or the environment, it is not in its pure metallic form, but in combined forms. He adds that, depending on the temperature or under certain conditions, they may have metallic or non-metallic characteristics, such as arsenic. They can also be divided into light metal - metallurgists - (beryllium, magnesium, aluminum, titanium and their metal alloys) and heavy metal. The term heavy metals is used by policy makers to refer to metals with toxic potential, due to anthropic activities having significantly increased their concentrations in soils in urban and agricultural areas.

The term “heavy metal” has usually been referred to metals with a density greater than 5 or 6g/cm3 or with an atomic number greater than twenty (WILD 1993, MALAVOLTA 1994, AMARANTE 1977 and ELEUTÉRIO 1997). It generally encompasses metals, semi-metals and even metalloids such as selenium (MALAVOLTA 1994) and are frequently applied to the elements Pb, Cd, Mo, Co, V, Al, Cu, Hg, As, Ni, Zn.

Renowned scientists (KABATA-PENDIAS 1995, FORSTNER 1995 and SOLOMONS 1995) associate some heavy metals with their high toxicological potential, hence also called toxic metals (As, Cd, Hg, Pb, Sb, Ti and U). This is due to the specific functions of each of these elements in relation to human health. However, other researchers relate its assimilation by plant species and associate the deficiency and excess of trace elements called essential and non-essential (MALAVOLTA op. cit.).

According to NOVOTNY (1995), thirteen metals and metalloids have been recognized as potentially dangerous for human life and aquatic biota and have been included in the lists of priority pollutants “Priority Pollutants List (Blacklist)” of the environmental control agencies in the world, including Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Th, and Zn.

Heavy metals come from natural sources, such as mineral deposits, and in this case they are referred to as trace elements, which together constitute less than 1% of the composition of rocks in the Earth's crust (ELEUTERIUM op. cit.). Or as anthropogenic sources, among them the chemical and metallurgical industry, mining, agricultural pesticides, and domestic sewage stand out (Table 5.2).

In many parts of the world, particularly in the vicinity of urban areas and industries, high concentrations of heavy metals have been identified. Among them, the most dangerous for the terrestrial system stand out, As, Cd, Cu, Hg, Pb and Zn (SINGH 1997). These metals become dangerous for human health and the environment when they exceed certain concentrations/limit.

Table 5.2 - INDUSTRIAL ACTIVITIES THAT GENERATE EMISSIONS OF METALLIC POLLUTANTS

	Cd	Cr	Cu	Hg	Pb	Ni	Sn	Zn
Paper		🟩	🟨	🟥	🟦	🟧		🟫
Petrochemical	🟦	🟩		🟥	🟦		🟦	🟫
Chlorine and KOH industry (electrolytic)	🟦	🟩		🟥	🟦		🟦	🟫
Fertilizers	🟦	🟩	🟨		🟦	🟧		🟫
Oil refinery	🟦	🟩	🟨	🟥	🟦	🟧		🟫
Steel mill	🟦	🟩	🟨	🟥	🟦	🟧	🟦	🟫
Non-ferrous metal industries	🟦	🟩	🟨	🟥	🟦			🟫
Automotive vehicles and airplanes	🟦	🟩	🟨	🟥	🟦		🟦	
Glass, cement, ceramics		🟩						
Textile industry		🟩						
Leather industry		🟩						
Thermoelectric power plant		🟩						🟫

Source: TOREM et al. (2002)

However, according to TOREM et al. (2002), there are 17 heavy metals classified as the most toxic, due to the speed at which they are absorbed by organisms (Table 5.3) and, among them, 9 are the most important due to the high rates of introduction into the environment.

Soils present a high retention capacity for metallic ions and the mobility of these ions is strongly influenced by geoenvironmental conditions involving interactions between soil and heavy metals (BORMA et al. 1996).

The movement of metals in the soil depends on several factors, including the existence of a prolonged time of contamination, the change in pH and the saturation of the retention capacity of metals in the system (CETESB 1997).

Concurrently with the transport of heavy metals through the soil, reactions occur between metallic ions dissolved in aqueous solutions and the solid constituents of the soil. These processes, generally called soil-contaminant interaction, include chemical reactions, and physical-chemical and biological processes, which act to transfer elements from the liquid phase to the solid phase and are grouped as: sorption/desorption reactions; cation exchange; precipitation/dissolution and complexation (BORMA et al. 1996).

According to BOURG (1995), the main processes involving the mobility of heavy metals and the soil are determined by the interaction of chemical reactions between the aqueous medium (dissolved) and the solid. The reactions involving the dissolved medium are represented by organic (solubilization) and inorganic (complexation) complexes and those involving the solid medium are precipitation and absorption.

Table 5.3 - IMPORTANCE OF HEAVY METALS BY TOXITY LEVELS AND THE RATE OF INTRODUCTION INTO NATURE

Metals classified as very toxic according to how quickly they are absorbed by organisms		Critical metals due to their high rates in the environment	
(+)	Ag, Au	(+)	Ag
	Bi, Cd		Cd
	Co, C		Cu
	Hg, Ni		Hg
	Pb, Pd		Ni
	Pt, Sb		Pb
	Se, Sn		Sb
	Te, Tl		Sn
(-)	Zn	(-)	Zn

Source: TOREM et al. (2002)

Among the main sources of pollution, industrial and mining have developed sophisticated environmental control operations, even though the basic causes of pollution continue to occur (ALLAN 1995). An example of a typical operation of a mining-metallurgical process (MARSHALL 1982 apud ALLAN op. cit.) demonstrates that the extraction, processing and metallurgy processes produced much more waste contaminated with heavy metals than the final production of the metallic alloy. According to the author, the production of 280 thousand tons of metal in metallurgy results in the production of about 1500 thousand tons of slag, that is, a ratio of 1/5, not counting the solid, liquid, and atmospheric residues produced in the three stages.

Up until the 1980s, around 16 million tons of lead alloys were produced (Table 5.4). Comparing only the metal/slag ratios produced in the metallurgical phase, approximately 80 million tons of slag can be found, with high concentrations not only of lead, but also of other metals that are sometimes more toxic than lead.

Table 5.4 - GLOBAL PRODUCTION OF METALS WITH MINERAL ACTIVITY (x1000 t)

METAL	Pre-1850	1850-1900	1900-1940	1950	1960	1970	1980
Copper	45	13	49	2650	4212	6026	7660
Zinc	50	15	40	1970	3286	5469	5220
Lead	**55**	**25**	**51**	**1670**	**2378**	**3395**	**3096**
Nickel		200	1	144	327	639	759
Cadmium				6	11	17	15
Silver				6	7	9	11
Mercury				4	8	9	7
Gold				1	1	1	1

Source: Modified from NRIAGU and PACYNA (1987) apud ALLAN (1995)

However, it is indisputable that this production process results in liquid effluents containing organic and inorganic pollutants. Generally, the most used method for treating organic effluents is a biological process, while for inorganic compounds, the standard treatment includes the physical-chemical processes of precipitation, ion exchange, adsorption and solvent extraction (TOREM et al. 2002), in addition to constructed or natural wetlands that represent the most recent technique for controlling pollution caused by liquid effluents (KNIGHT and KADLEC 2000 and REDDY and KADLEC 2000).

5.2.1 - Heavy metals in surface water and soil

Water is the major transport vector for heavy metals in the lithosphere, in which solids present in the soil, surface and groundwater can carry expressive amounts of toxic metals, providing interaction with various water cycles and biogeochemical processes (BOURG and LOCH 1995) .

According to FORSTNER (1995), the interactions between solid and solution in the system are conditioned by pH, Eh, organic and inorganic complexes and transformation of microbiological species. These constraints produce physical (adsorption, sedimentation and infiltration processes), chemical (complexation and precipitation mechanisms) and biological (associated with the translocation of metals through the membrane of roots and stems of plant species) barriers that mitigate the risk of contamination to receptors.

The addition of chemical elements or compounds to natural waters, such as salts (NaCl; $CaSO_4$ and CaF_2), acids (HCl), bases ($FeOH_3$), macronutrients (N, P, C, O, Ca and Mg) and mincronutrients can cause serious environmental problems as each category represents different levels of importance for different forms of life (KADLEC and KNIGHT 1996).

According to TOREM et al. (2002), some factors tend to affect the toxicity of heavy metals in aquatic life, such as: the form of the metal in the water (dissolved or as particulate matter); the presence of other metals or substances such as the reaction of Na^+, Ca_2^+, K^+ and Mg_2^+ ions, which reduces toxicity when associated with Pb_2^+, Cu_2^+ and Zn_2^+ ions. However, the opposite effect can occur when pairs of metals are present, such as Ni and Zn, Cd and Zn, Cu and Zn and Cu and Cd, which together are more toxic than their individual toxicity.

In aquatic systems, cationic heavy metals tend to dissolution when the pH decreases, while with the increase in pH, the precipitation of cationic metals occurs up to a certain limit, when they are solubilized again (BOURG and LOCH 1995).

According to KADLEC and KNIGHT (1996), some micronutrients can be called essential metals (or beneficial to living organisms). Non-essential, toxic, or heavy metals that are generally not present in high concentrations in natural wetlands are usually lead, cadmium and copper.

High concentrations of metals in industrial and domestic liquid waste can cause biochemical transformations in micronutrients and lead the system to a biomagnification process, that is, an increase in the concentration of metals along the food chain to humans.

The use of constructed wetlands to remove toxic metals has multiplied around the world (KNIGHT and KADLEC 2000). However, its application has to be carefully examined as surface flow treatment systems allow the free movement of water into the adjacent environment and, in this way, contribute to the contamination of natural areas and the food chain.

5.2.1.1 Cadmium (Cd)

Cadmium is a non-essential element and highly toxic to plants and animals. When pure it is rarely found in nature, occurring as minerals of Greenockite (CdS) and Octavita ($CdCO_3$). Silvery white in color, elastic and ductile, it is found in the environment associated with oxygen, chlorine or sulfur. Transition metal with Zn and Hg, has atomic number 48, atomic weight 112.4, density of 8.642 g/cm3 (MOLAVOLTA 1994) and is classified as the 67th element in order of abundance.

The main sources of cadmium are sulfide minerals (Zn, Pb-Zn and Pb-Cu-Zn), from which it is removed in mining-metallurgical processes. Usually associated —and presenting geochemical behavior similar to— zinc, both have similar atomic structure and electronegativity (SMITH et al. 1995).

Cadmium is released into the air, soil and water by anthropic activity and the main sources of contamination are the production and consumption of non-ferrous metals by the automobile industry in pigments, stabilizers for plastics, batteries, as well as use in photo and lithography, rubbers and fungicides.

According to SMITH et al. (1995), depending on the values of pH and Eh, cadmium can present the following forms of stability: Cd+2 for low pH (0-2) and oxidizing Eh; $CdSO_4$, $CdCO_3$ and $Cd(OH)_2$ for oxidizing Eh and pH varying, respectively, (0-2), 8 and 14; CdS for Eh (low reducer) and pH ranging from 6-8; and Cd for Eh (high reducing) and pH ranging from 6-8 (Figure 5.6).

Cadmium can be found in soils and sediments in the following forms: exchangeable, reducible, carbonate, organic, crystalline network and solution. It exists in water as complexes of ions and hydrates or as humic substances (MOLAVOLTA 1994). It presents high concentrations in hydromorphic sediments, having as main transport mechanisms the processes of precipitation, sorption and complexation (SMITH op. cit.).

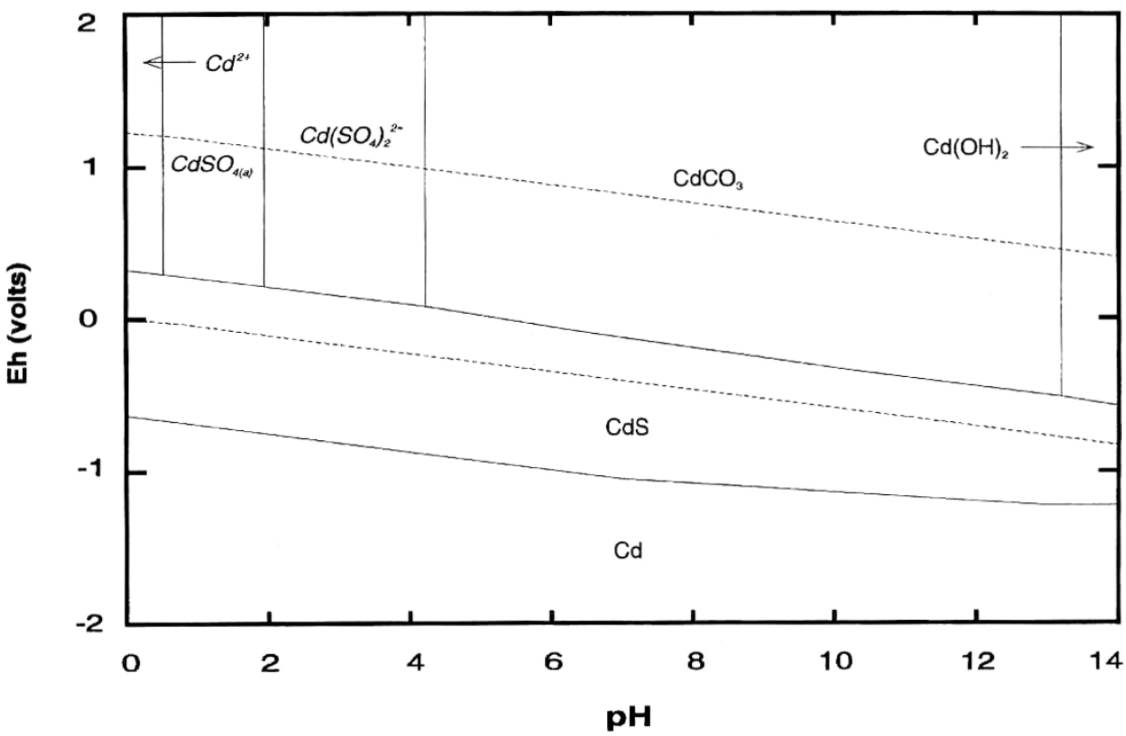

Figure 5.6 – Region of stability of cadmium species. Source: USEPA (1984) apud SMITH et al. (1995)

According to BOURG and LOCH (1995), the pH versus Eh diagrams generally give a view of the mobility potential of the different types of heavy metals, this because the aquatic system involves the transfer of electrons, developing reactions that are not necessarily fast.

Cadmium removal from water increases with pH ranging from 6 to 9. With pH below 6 little or no cadmium is removed. Cadmium sorption is often correlated with the Cation Exchange Capacity of clay minerals, carbonates, oxides and organic matter of soils and sediments. Whereas in surface water cadmium is present primarily as Cd+2 ions. In the presence of high concentrations of organic matter, a significant amount of Cd+2 ions is complexed (SMITH et al. 1995).

Cadmium is more mobile in the aquatic environment than most other heavy metals and can be removed from water by precipitation, sorption from the mineral surface and complexed with organic matter.

Cadmium is relatively immobile in the soil profile. In studies in areas contaminated by foundry, it is observed that in depths of 30-40 cm, the values are equal to those found in soils with low reference values (MALAVOLTA 1994). Areas close to non-ferrous metal mines and smelters often present severe Cd contamination in the soil, resulting in the uptake of the metal by plants, usually at low pH.

The application of phosphate fertilizers and the deposition of precipitated Cd from the atmosphere are important sources of Cd in cultivated soils, in addition to semi-solid material from sewage, which can be an important source of local contamination (WHO 1992). However, in urban centers, domestic waste incinerators are sources of Cd emissions, caused by the burning of plastics (TAVARES 1990).

Organisms such as shellfish, crustaceans and mushrooms are natural Cd accumulators. In horses and some domestic animals, there is an increase in Cd levels in the liver and kidneys, when exposed to contamination (TAVARES op. cit.). tobacco is an important source of cadmium intake for smokers, whereas for non-smokers this intake occurs through food (WHO 1992).

Prolonged occupational exposure to Cd has caused severe chronic effects, predominantly in the lungs and kidneys. Chronic kidney effects have been observed among the general population. Long-term inhalation exposure causes emphysema and other chronic pulmonary effects (TAVARES 1990).

Cadmium is absorbed by the lungs or the gastrointestinal tract and stored mainly in the liver and kidneys, where more than half of the Cd load will accumulate (WHO op. cit.).

The toxicity of cadmium in waste is determined by ABNT standards 10005 – Waste leaching and 10006 – Waste solubilization, with respective values of 0.5 mg/L and 0.005 mg/L. For surface water, CONAMA Resolution 20/96 establishes a value of 0.001 mg/L for Class 2 water bodies, while Ordinance No. 36 of the Ministry of Health establishes a value of 0.005 mg/L for potability (ANJOS 1998) .

For soils and sediments, some countries use intervention values[22]. In the Netherlands, the values for soil and sediments are 12 mg/kg for cadmium and 6 µg/L for groundwater (SCHUABETZ 1999). On the other hand,

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[22] Maximum permitted level, above which recovery actions are required (SCHIANETZ op. cit.) or threshold values used to induce immediate remediation measures (CETESB op. cit.).

Germany and the State of São Paulo in Brazil use research values[23] (soil multifunctionality). The values adopted in São Paulo are: 10 mg/kg of soil in agricultural areas and areas of maximum protection; 15 mg/kg soil in residential areas; and 40 mg/kg soil in industrial areas (CETESB 2001).

Studies on sediments from the estuary of the Subaé River show the following levels of contamination: TAVARES (1996) found concentrations between 0.07 to 0.25 µg/g of CD; and SANTOS (2002) obtained values between 0.02 and 1.29 µg/g of Cd in mangrove sediments also near the municipality of São Francisco do Conde.

5.2.1.2 Lead (Pb)

Lead is a soft, flexible and malleable metal, silvery gray in color, melts at 327.5 °C, has atomic number 82, atomic weight 207.19 and density of 11.35 g/cm^3 (MALAVOLTA 1994). It is a lustrous metal when exposed to air, flexible and can be shaped, rolled and pressed.

It has low mobility, persistence in marine sediments, forms salts such as organic acids, lactic and acetic acids, in addition to forming stable organic compounds such as tetraethyl lead and tetramethyl lead.

Tetraethyl lead has been considered the greatest anthropogenic source of this element in the environment, as it has been added to gasoline since the 1920s (TAVARES 1990). In Brazil, lead was replaced by alcohol in the 1980s.

Lead occurs in a variety of deposits, most notably those containing cadmium, zinc, and copper. The main lead mineral is galena, lead sulfide (PbS), also occurring anglesite, lead sulfate ($PbSO_4$) and cerussite, lead carbonate ($PbCO_3$).

All rocks in the Earth's crust contain Pb. The concentration in acid magmatic rocks and clayey sediments ranges from 10 to 40 ppm, while in ultramafic rocks and calcareous sediments it ranges from 0.1 to 10 ppm. Natural sources of lead (geological erosion and volcanic emissions) produce around 19,000t/year and anthropogenic sources (mining and smelting) are estimated at 400,000t/year (MALAVOLTA op. cit.).

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[23] They are threshold values for a simplified investigation that may indicate the need for a more detailed investigation in the assessed area (CETESB 1999)

Lead can be present in different ways depending on the pH and Eh values of the medium. According to the USEPA stability diagram they are as follows: PbO2 forms under high oxidation conditions in any pH range; $PbSO_4$, $PbSO_3$ and $Pb(OH)_2$ occur under conditions of low oxidation and pH, respectively, up to 6, from 6 to 10, and from 10 to 14; PbS at the interface between oxidizing and reducing environments and variable pH; and Pb in a reducing environment and variable pH (SMITH et al. 1995) (Figure 5.7).

The main parameters that influence lead availability in the environment include soil texture with increasing clay content and, consequently, greater cation exchange capacity; low pH influences solubility and availability mechanisms; and organic matter is effective in fixing lead (MALAVOLTA 1994).

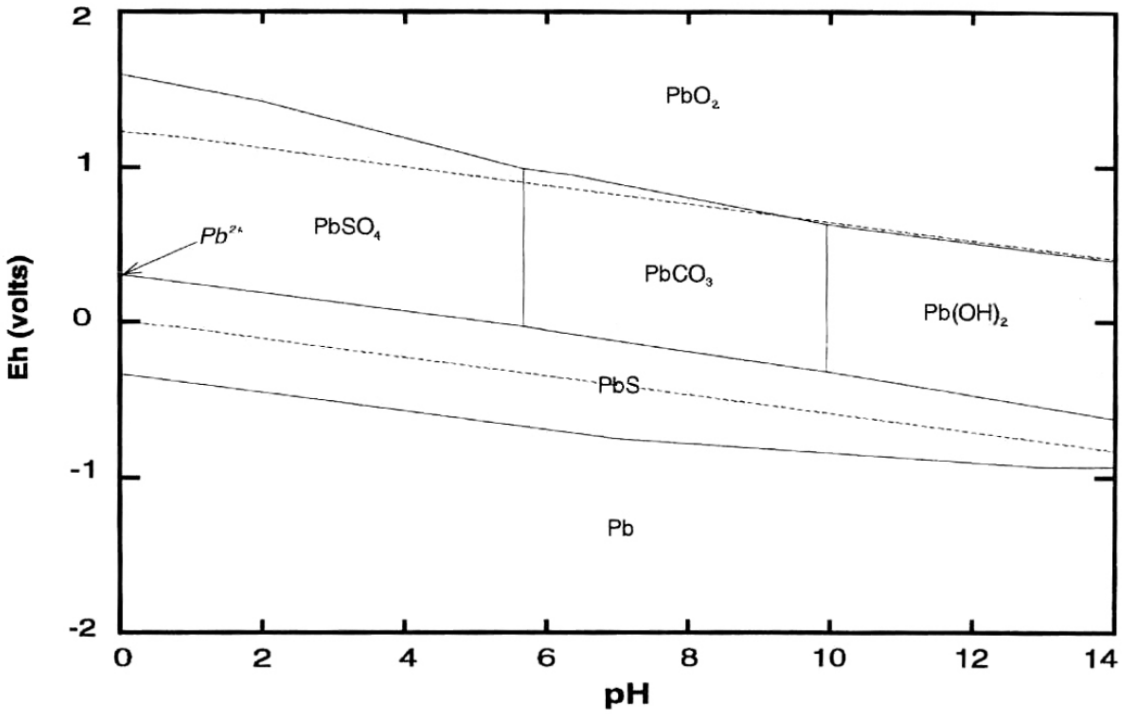

Figure 5.7 – Lead species stability region. Source: USEPA (1984) apud SMITH et al. (1995)

The montimorilonite and kaolinite clays bear the property of controlling the mobility of heavy metals, which present the following degree of mobility: Cd>Zn>Pb>Cu. However, the fate of lead in soils is initially affected by adsorption processes, ion exchange, precipitation, and complexation with organic matter (SMITH et al. 1995). The amount of lead in the water depends on the pH of the water and the levels of salts contained in the system.

Lead is an element that can be adsorbed by clayey soils at pH□6, phosphates, sulfates, carbonates, hydroxides, and organic matter. It has an affinity for organic ligands and the formation of these complexes increases its mobility in the soil in a similar way to cadmium.

In surface water lead occurs not frequently in the divalent Pb_2^+ form, rather than forming salts, and it combines with organic ligands to form colloidal and soluble complexes. For pH above 8.5, lead is solubilized at concentrations around 1 µg/L and with increasing solubilization the pH and alkalinity values decrease (KADLEC and KNIGHT 1996).

According to SMITH (1995), lead transport in surface water is low and its concentration in water depends on pH and total dissolved salts. For pH greater than 5.4 its solubility can reach 500 µg/L for water poor in calcium and magnesium and 30 µg/L for water rich in calcium and magnesium. Above 5.4 it can form lead bound to carbonates in the form of $PbCO_3$ and $Pb_2(OH)_2CO_3$. However, lead is carried by rivers, mainly in the indissoluble form of colloids or particles.

Lead is indispensable in many natural conditions because it forms insoluble salts and its ionic form is adsorbed by suspended particles. Thus, when a high concentration of lead is found in surface waters, it is possible that biomagnification is occurring in the aquatic biota.

Lead adsorption by organic matter and the cation exchange capacity of clays and organic matter, combined with an alkaline pH, have favored lead retention within the Plumbum wetland zone (ANJOS 1998). Studies carried out in dozens of wetlands built for lead removal show values ranging from –181% to 98% removal (KADLEC and KNIGHT op. cit.).

The effects of lead on humans depend on the intensity and duration of exposure. According to the Agency for Toxic Substances and Disease Registry (ATSDR), for neurological, metabolic and behavioral reasons, children are more vulnerable to the effects of lead than adults (Figure 5.8).

Lead affects many organs and systems. Among its effects, the following stand out: decrease in the Intelligence Quotient (IQ); effects on the nervous system, with deficits in cognitive functions; decreased sensory, involuntary nerve and kidney functions; and some epidemiological studies demonstrate the occurrence of premature births (WHO 1995).

Human exposure to lead occurs in the smoker population, through the ingestion of food and water. For children, the main routes are food, water, air, dust and soil. Absorption in humans via inhalation ranges from 4 to 200 μg/day (CETESB 1999).

Depending on the level of exposure, lead can result in diverse effects, ranging from sub-cellular and general body malfunctions, enzyme inhibition to morphological changes and death. Children are more sensitive than adults. Adults in general absorb 10% of the lead that passes through the digestive tract, whereas children absorb 50%, most of which is retained and accumulated in the skeleton, with a half-life of 20 years (WHO 1995).

In general, plant food products contain more Pb than animal products. In vegetables, Pb is higher in the roots, except for leafy vegetables, which retain dust, while foods of animal origin, such as meat, milk and eggs, have a low concentration of lead. However, viscera, especially kidney and liver, have very high concentrations.

Lead toxicity in waste is determined by ABNT standards 10005 – Waste leaching and 10006 – Waste solubilization, with respective values of 5.0 mg/L and 0.05 mg/L. For surface water, CONAMA Resolution 20/96 establishes a value of 0.03 mg/LPb for Class 2 bodies of water, while Ordinance No. 36 of the Ministry of Health establishes a value of 0.05 mg/LPb as potability (ANJOS 1998).

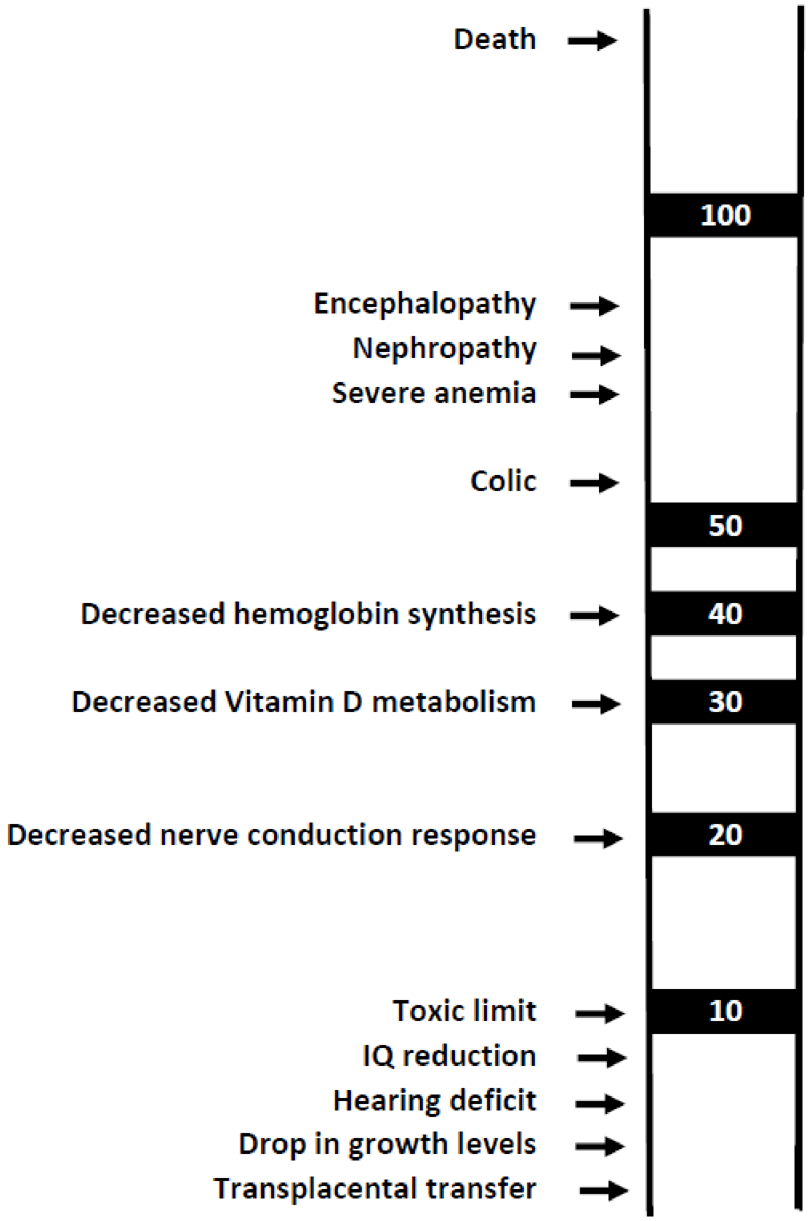

Figure 5.8 – Levels and effects of lead observed in children. Source: ATSDR (1990)

For soils and sediments some countries use intervention values. Holland determines for soil and sediments the value of 530 mg/kg of lead and for groundwater 75 µg/L (SCHUABETZ 1999). While the Intervention values adopted in the State of São Paulo are: 200 mg/kg of soil in agricultural areas and areas of maximum protection; 350 mg/kg soil in residential areas; 1,200 mg/kg of soil in industrial areas (CETESB 2001).

Studies on sediments from the estuary of the Subaé River show the following levels of contamination: TAVARES (1996) found concentrations between 29.80 to 310.00 µg/g of Pb; and SANTOS (2002) obtained values between 10 and 32 µg/g of Pb in mangrove sediments also close to the municipality of São Francisco do Conde.

5.2.1.3 Copper (Cu)

Copper is a reddish, ductile and malleable metal, a good electrical and heat conductor. It melts at 1082 □C, has atomic number 29, atomic weight 63.546 and density of 8.96 g/cm3. It occurs as a natural metal in various mineral forms, mainly cuprite and malachite. The most common valence state is Cu+2, and it can also assume the ionic forms Cu0 and Cu+ (MALAVOLTA 1994, ELEUTÉRIO 1997 and FIGUEIREDO 2000).

It is an essential element for plants, acting in association with enzymes in vital functions. It plays an important role in the synthesis of chlorophyll and acts in the synthesis of hemoglobin. Sediments and sedimentary rocks contain high concentrations of copper, which can be released in the form of ions in the primary and secondary mineral phases, and can be absorbed by organic matter, iron and manganese oxides or by clay minerals (ELEUTERIUM op. cit.) .

Copper, along with lead, is considered a metal of low mobility due to its attenuation capacity, resulting from the texture of the soil (clay minerals) associated with high pH. Clay soils (montimorilonite and koalinite) containing oxides and high pH are very effective in copper removal (SMITH et al. 1995).

According to SPOSITO (1984) apud SCHULIN et al. (1995), Cu_2^+ and Pb_2^+ are generally found in high concentrations in the dissolved fractions of organic matter and removed by the system through precipitation and coprecipitation processes. While Cd_2^+ and Zn_2^+ are removed in smaller proportions (Figure .5.9).

Copper occurs usually in surface waters as chelated compounds of Cu_2^+, occurring in the form of an insoluble complex with hydroxides and linked to carbonates and organic compounds, and may present relative solubility (KADLEC and KNIGHT 1996). In wetlands built for the treatment of liquid municipal waste, copper is effectively reduced, with efficiency of up to 96% (KADLEC and KNIGHT op. cit.)

Copper is retained in soil and sediments through adsorption and cation exchange mechanisms. However, it presents a lot of affinity for organic soluble binders, responsible for increasing its mobility in the soil (QUINÁGLIA 2001) and in acid mine drainage they are easily mobilized in the form of sulfides (FIGUEIREDO 2000).

There are few reported cases of acute copper effects. Among them are: gastric burning, nausea, vomiting, diarrhea, injuries to the gastrointestinal tract and hemolytic anemia. As a chronic effect, it is rarely reported, except for Wilson's disease, responsible for the accumulation of copper in the liver, brain, and kidney (QUINAGLIA op. cit.).

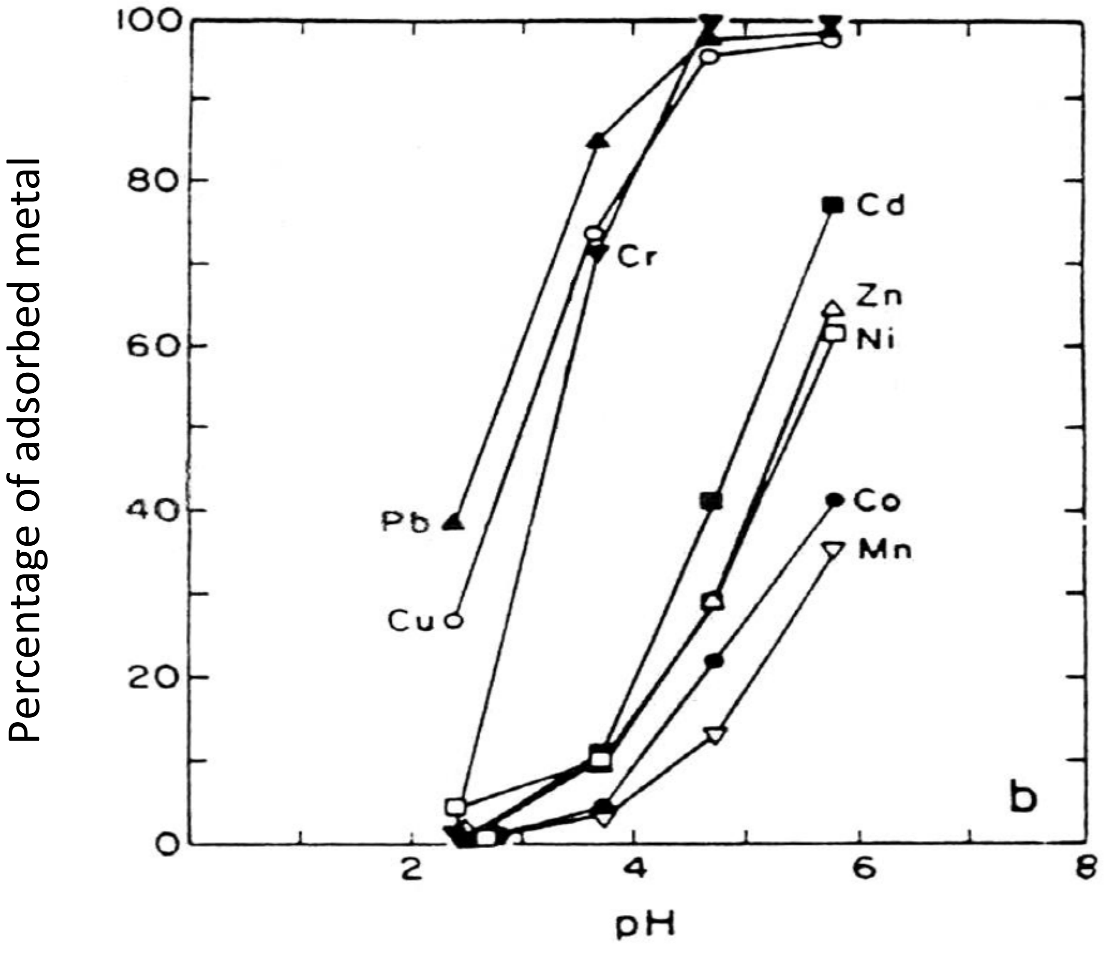

Figure 5.9 - Effects of pH on the removal of heavy metals by organic complexes. Source: SPOSITO (1984) apud SCHULIN et al. (1995).

For surface water, CONAMA Resolution 20/86 establishes a value of 0.02 mg/LCu for Class 2 bodies of water, while Ministry of Health Ordinance No. 1,469 establishes the value of 2000 µg/LCu as potability.

In the Netherlands, for soil and sediments the intervention value is 190 mg/kg of copper and for groundwater 75 µg/LCu (SCHUABETZ 1999).

Studies on sediments from the estuary of the Subaé River show the following levels of contamination: TAVARES (1996) found concentrations between 8.31 and 31.1 µg/g of Ass; and SANTOS (2002) obtained values between 38 and 83 µg/g of Cu in mangrove sediments near the municipality of São Francisco do Conde.

5.2.1.4 Zinc (Zn)

Zinc is an essential element for plant and animal life. It is a lustrous, ductile and malleable metal when heated. It melts at 419 °C, has an atomic number 30, an atomic weight of 65.39 and a density of 7.14 g/cm3.

It occurs in free and combined forms of ZnS (Blend), $ZnCO_3$ (Smithsonite), ZnO (Zincite) and Calamine, and the main occurrence of zinc in the world comes from the mineralization of zinc sulfides (ZnS), often associated with sulfides of other metals, mainly lead, cadmium, copper and iron (SMITH et al. 1995).

The main mineral provinces responsible for the source of zinc are: Pb-Zn (Vale do Ribeira/SP and Boquira/BA); Zn-Pb-Ag (Sullivan/Canada and Mc Arthur River/Australia) and Cu-Zn-Pb (FIGUEIREDO 2000).

Zinc occurs in surface waters as divalent Zn_2^+ ions where it forms ionic hydrides, carbonates and complexed with organics (KADLEC and KNIGHT 1996).

Sorption is the dominant fate of zinc in aquatic environments and occurs through iron and manganese oxides and hydroxides, clay minerals and organic matter. Zinc has been sorbed to pH below 7 and is readily transported in many surface waters due to mobility (SMITH et al. 1995).

In natural and constructed wetlands, zinc concentrations have been reduced by 77 to 91%, ranging from 5.6 to 230 µg/L.

Zinc is an essential and useful element for human metabolism. However, its role in the body is still not well known, having been generally attributed to enzymatic functions, protein synthesis and carbohydrate metabolism (ELEUTÉRIO 1997).

The main applications of zinc are: metallic alloys, such as brass (Zn-Cu) and galvanized iron (Zn-Fe) in roofs and gutters of homes; sacrificial electrodes (anode) to protect iron against corrosion; and in the electroplating industry in general, as a component of galvanized steel. Zinc compounds are also used as zinc sulfide in plastic manufacturing; zinc chloride in batteries; zinc chromate as a wood preservative; zinc carbonate, used as a supplementary diet for animals; and zinc borate, in the manufacture of fireproof materials (SMITH op. cit. and PETRONI 1999).

In soils and sediments, under conditions of pH equal to 7.7, zinc hydrolyses and is easily adsorbed by clay, carbonates or oxides. Under aerobic conditions Zn^{+2} is predominant at acidic pH and under anaerobic conditions it forms ZnS between pH 1 to 14 (QUINÁGLIA 2001).

Zinc accumulation does not cause profound deficiencies. For this reason, it is of low toxicity. The ingestion of zinc by excessive intake can cause gastrointestinal disturbances and diarrhea (ELEUTÉRIO op. cit., and PETRONI op. cit.)

In surface water, zinc is bound to yellowish fulvic acids, forming chelates (zinc fulvates) under a wide range of pH, which favors an increase in its solubility and mobility in the system (KIEKENS 1995 apud PETRONI op. cit .)

For surface waters, CONAMA Resolution 20/86 establishes for Class 2 water bodies, the value of 0.18 mg/LZn; while Ordinance No. 1,469 of the Ministry of Health establishes the value of 5000 µg/LZn as potability.

The Netherlands determines the following intervention values for soil and sediments: 720 mg/kg of zinc and 800 µg/L for groundwater (SCHUABETZ 1999).

Studies carried out by SANTOS (2002) obtained values between 78 and 116 µg/g of Zn for mangrove sediments near the municipality of São Francisco do Conde.

5.2.2. - Support elements

Some chemical substances work as a support in the analyses of contaminated areas. This is related to the factors that affect the concentration of metals in solution, that is, their relationship with the processes of removal or availability of heavy metals. Among the support elements, the following stand out: aluminum; calcium; the iron; manganese; and magnesium.

Aluminum occurs naturally in surface waters, in small and large concentrations, respectively in hydrated ions and complexed as silicates in colloidal form. It is generally found in surface waters due to its diffusion from the most varied anthropogenic sources (KADLEC and KNIGHT 1996).

Aluminum solubilization occurs with pH variation, as it is less soluble near pH 7. For low pH values, it increases solubility as $Al_2O_3H_2^+$ and $Al(OH)_2^+$ ions, while for high pH it forms ions ($HAl_2O_4^-$) (KADLEC and KNIGHT op.cit.).

According to MEURER et al. (2000), in the case of ions with different valence, usually those with higher charges are preferred in the exchange between ions, such as: $Al^{+3} > Ca^{+2} > Mg^{+2} > K^+$. Aluminum and hydrogen represent the exchangeable acidity, as they are considered sources of soil acidity. According to BOHNEN et al. (2000), ions such as aluminum (valence +3) are more strongly attracted to the vicinity of particles with negative charges, to the detriment of sodium and potassium (valence +1) and calcium and magnesium (valence +2). In this way, aluminum is more fixed in the soil, while the other cations tend to have greater mobility in the profile.

Calcium occurs on water surfaces as divalent ions and its concentration in rainwater ranges from 0.1 to 10 mg/L. Calcium concentrations in surface water depend on the soil, rock or source of pollution, and can reach concentrations of 0.3 to 70 mg/L (KADLEC and KNAGHT 1996).

According to SOUZA et al. (2000), calcium and magnesium, although they do not participate directly in redox reactions, have increased solubility, as they are displaced into the solution by iron and manganese.

According to COLLINS and STOTZKY (1989) apud SCHULIN et al. (1995), Ca_2^+ and Mg_2^+ can compete with species of cationic metals assimilated by microorganisms, influencing the toxicity of the environment.

The higher the concentrations of Ca2+ and Mg2+ the lower the concentrations of cationic metals.

Calcium is biologically active because it is used as a nutrient by vertebrates and invertebrates and plays an important role in the carbon cycle by forming calcium carbonate. The divalent calcium ion is the main component of calcium carbonate and, during photosynthesis, it is removed from surface water along with carbon dioxide (KADLEC and KNIGHT op. cit.).

Studies in constructed wetlands have shown that calcium removal efficiency ranges from minus 547 to 56% and, in wetlands with little decomposition, calcium has minimal mobility (RICHARDSON 1996).

Studies carried out by RIBEIRO (1985) in the clayey soils of the Recôncavo Bay demonstrate that calcium and manganese occur in high concentrations in the soil profiles. This is related to the input process of material introduced as a soil amendment to neutralize the soil through the continuous removal of H^+ and the precipitation of Al^{+3} in the form of $Al(OH)_3$, making it less acidic.

Iron is the metal occurring in the highest concentrations in the surface waters of natural or constructed wetlands, as it is frequently assimilated by plants and animals in significant concentrations that can reach up to 5000 mg/kg in some aquatic plants (KADLEC and KNIGHT op. cit.) .

Basically, in wetlands, iron can be present in surface waters in an oxidized state as Fe^{+2} (ferrous ion) or reduced to Fe^{+3} (ferric ion). The oxidation and reduction of iron in wetlands depends on the conditions of the redox potential. The ferric ion forms complex states with a variety of ligands such as ferric hydroxide ($Fe(OH)_3$), ferric phosphate ($FePO_4$) or insoluble adsorbed by organic matter (KADLEC and KNIGHT 1996).

According to SOUZA et al. (2000), the most important chemical alteration that occurs in flooded soils is the reduction of ferric oxides (Fe^{+3}) to ferrous oxides (Fe+2), causing an increase in the solubility of this element. According to the same author, the concentration of Fe^{+2} in the soil solution increases until it reaches a maximum, then decreases and varies according to pH and organic matter content.

According to SOUZA (op. cit.), the reduction of ferric oxides (Fe^{+3}) to ferrous oxides (Fe^{+2}) represents the most important chemical alteration that occurs in the flooded soil and, consequently, the increase in iron solubility.

Iron concentration in surface waters can range from 50 to 200 μg/L in natural aquatic systems, while wetlands constructed for supply systems shows that iron can be removed from 84.6 to 100% (LEWIS et al. 1999).

Manganese is an essential element, which chemically behaves similarly to iron – and its occurrence is rarer – in surface waters. In photosynthesis, it is used as an enzyme for respiration and nitrogen metabolism in plants and animals (KADLEC and KNIGHT op. cit.).

In surface waters manganese typically occurs as Mn^{+4}, as it is relatively unstable to Mn^{+3} as insoluble oxides and hydroxides. In environments where low redox potential and low pH predominate, it occurs in the Mn^{+2} form (KADLEC and KNIGHT op. cit.).

According to SOUZA et al. (2000), low values of Eh increase the availability of iron and manganese and, under anaerobic conditions, microorganisms use oxidized soil compounds as electron acceptors, obeying a reduction sequence, in which nitrate has the highest affinity to receive electrons, followed by manganese oxides, iron oxides and ending with sulfate.

Manganese occurs in concentrations below 100 μg/L in surface waters. The reduction of manganese concentration in wetlands has been extensively researched, with removal reaching up to 98%.

5.3. Metals in soils

Soils have been characterized as natural obstacles for contaminants. This is especially related to the sorption, solubilization, precipitation and complexation reactions involving the soil and the contaminant, in addition to the control of parameters such as: pH; Eh, soil texture; percentage and type of clay minerals; percentage of organic matter; CTC; oxides and hydroxides and Fe and Al; and free $CaCo_3$ (SOLOMONS 1995, KABAT-PENDIAS 1995, BOULDING 1995, ANJOS 1998 and MEURER et al. 2000).

For some authors, the mobility of metals fundamentally depends on the pH behavior (YONG et al. 1993 and BORMA et al. 1996). This is related to the main processes of retention and availability of metals being dependent on the pH of the soil solution.

According to BUNZL et al. apud SCHULIN et al. (1995), the half-life for sorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Ca^{2+} with organic matter is very fast in an aqueous environment, where a time of around 5 to 15 seconds was observed for the process to take effect. While the toxicity of metals in microorganisms, according to WELP and BRUMMER (1989) apud SCHULIN op. cit. decreases in the following sequence: $Hg^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+}$.

The geochemical phenomena controling the retention of heavy metals, according to BOURG and LOCH (1995), are the sorption and precipitation processes and, when dissolved, the complexation influences the transport by dispersion and advection. For all phases, pH and Eh conditions are the “Master” variables in controlling pollutants in the aqueous phase. According to the authors, the solids that control the fixation of metals are clay minerals; organic matter; oxides and hydroxides of Fe, Mn and Al by sorption; low sulfide solubilization; and precipitation for phosphate and carbonate minerals.

Many wetland soils are characterized by a lack of oxygen caused by flooding. The low level of dissolved oxygen results in the accumulation of organic matter in the soil which reduces the activity levels of microorganisms and organic decomposition (KADLEC and KNIGHT 1996). These conditions characterize wetland soil and sediments as hydromorphic compartments. These soils are usually saturated or flooded long enough to develop anaerobic conditions that favor the growth and regeneration of hydrophytic vegetation (KADLEC E KNIGHT op. cit.).

Soils and sediments of natural wetlands generally have the characteristics of other soils, except for their reduced atmospheric exposure and consequent reduction in aerobic conditions. Wetland flooding can concentrate or dilute chemical constituents in the soil, depending on the chemistry of the flood waters, the chemical and physical nature of the soil and the surrounding environment (KADLEC and KNIGHT op. cit.).

According to RODGERS Jr. et al. (1999), this hydromorphic soil condition favors the main pollutant removal mechanisms in constructed wetland systems, such as: sedimentation; filtration; sorption; vegetation metabolism; carbonate precipitation, co-precipitation; sulfide reduction; hydrolysis and oxidation of metals, decomposition of organic matter and microbial metabolisms. And the main parameters that control the retention or availability of metals in constructed wetlands are: o Eh; the pH; the CTC; the texture of the sediment; and water hardness (RODGERS Jr. op. cit.).

Among these mechanisms, according to the same author, the reduction of sulfide constitutes the main form of metal removal in constructed wetlands. This process takes place in the sub-surface in the anaerobic environment of the wetland and is driven by the decomposition of organic matter under reducing conditions, promoting the removal of metals.

Knowledge of the physical and chemical properties of the soil and sediment of constructed wetlands is of fundamental importance in the planning and design of these zones, as these properties affect plant growth and the assimilation of some constituents of liquid waste.

According to SOIL SURVEY STAFF (1998) apud TINER (1999), the definition of soil was revised to “a natural mass composed of solids (minerals and organic matter), liquids and gases, which occurs occupying spaces and characterizing horizons or layers that are distinguished of the starting material through the loss, transfer or transformation of energy or the ability to support plant roots in the natural environment”.

Some wetland soils like vertisols are problematic, as they present high plasticity, expansion when wet and contraction when dry. According to TINER op. cit. these soils form microtopography of low hills and shallow depressions.

The types of soils found to a large extent in the Recôncavo Bay area, particularly in the Plumbum site, are vertisols[24] and combisols, rich in montimorilonite clay (BOYER 1971, RIBEIRO 1985 and BAHIA 1996). These soils originate from green shales, with clayey to very clayey composition (ANJOS 1998).

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[24] The vertisols and combisols show great similarity in most properties, the main difference being the occurrence of A, Bi and C horizons and the formation of deep cracks and cracking surfaces in the combisols.

Montmorillonite clay is part of the smectite group[25], of the 2:1 type and present flat surfaces with thicknesses from 10 to 16 m. This mineral has the property of swelling when in a wet state and returning to normal thickness when in a dry state. This variation causes the formation of cracks, favoring the entry of mineral ions as well as fine particles of organic matter (BOYER 1971).

According to RIBEIRO (1985), montmorillonite is a neighboring mineral of mica that has weak connections between the leaflets, which allows the penetration of water. It has a peak close to 14 A° when stacked and its variety depends on the presence of different ions within its structure.

The high cation exchange capacity of montmorillonite is mainly responsible for the retention capacity of heavy metals in the soil, especially at low pH values. It has the highest specific surface among all soil minerals (BOURG 1995), around 700 to 800 (m_2/g), and chemical composition $(OH)_4Al_4Si_8O_{2}0.xH_{2}0$, and consists of a structural unit formed by a layer of gibbsite between two silica groups and water molecules added to the crystal (VARGAS 1977).

However, studies carried out by RIBEIRO (op. cit.) in the clayey soil of the Recôncavo Bay area, near the town of São Sebastião do Passé, characterized montmorillonite as a transformation mineral with all species of the smectite group. This mineral occurs as interstratified[26] and, as it can possibly explain the low CEC found in the area, which does not match the expected CEC for the smectite group.

In addition to montmorillonite, organic matter represents another parameter with great influence on the mobility of contaminants, having the ability to immobilize metals by complexation reactions or cation exchange and often behaves more efficiently than clays. This is related to its very high specific surface (700 m^2/g) (AMARANTE 1997).

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[25] According to KLAMT and MEURER (2000), the main minerals that are part of the smectite group are montmorillonite, beidelite and nontronite; they are minerals of the 2:1 type and present isomorphic substitution of Al^{+3} by Fe^{+2}, Mg^{+2}, Zn^{2+} and other cations in the octahedral lamina, giving rise to the negative charges that will manifest on the mineral surface. Smectites can expand and have a high cation exchange capacity (80 to 120 cmol/Kg) and a large specific surface area (800 m^2/g). Given to the great expansiveness of the layers, it allows the entry of hydrated cations, water molecules and polar organics.

[26] According to KLAMT and MEURER (2000), stratified minerals frequently occur in soils simultaneously presenting the structure of two or more distinct minerals, such as, for example, mica-ilite, illitamontmorillonite and mica-illite-vermiculite.

Chemical analyses carried out on the surrounding soil and sediments from the Plumbum wetland area revealed the following characteristics: the soils showed concentrations for Pb and Cd ranging, respectively, from 2,000 μg/g to 38 μg/g on the surface and < 5.0 μg/g and < 0.5 μg/g at a depth of about one meter, while the wetland sediments show higher concentrations for Pb and Cd, varying, respectively, from 8,200 to 117 μg/g (ANJOS 1998).

The hydromorphic sediment has the highest CEC value, 47.1 meq/100g, while the soil surrounding the wetland has a value of 44.3 meq/100g. As for the OM, the sediment has a value of 10.9% and the soil 2.9%, in addition to pH around 8 for both the soil and the sediment.

An expressive amount of chemical and biochemical processes are taking place in the Plumbum wetland and are the result of interaction processes involving water, mineral and gaseous phases, as well as organisms and plants. The main mechanisms that occur in this flooded system are sorption[27] and precipitation, in addition to complexation[28] (ANJOS op. cit.).

These mechanisms are closely related to the sub-aqueous environment that characterizes the wetlands, especially to the basic to alkaline pH, as it favors the precipitation of metals, their sorption by clays and the formation of organic complexes with organic matter (ANJOS op . cit.).

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[27] Sorption is generically used to refer to the various retention mechanisms of ions and molecules by the solid phase (MEURER et al. 2000). It is a phenomenon encompassing physical and chemical adsorption (BORMA et al. 1996) and according to SCHACELFORD (2000), it also includes adsorption by exchange. Physical adsorption has the following characteristics: they are measured by attractive forces such as "Van Der Waals"; usually very reversible; and the adsorbed molecule is free to move over the surface of the solid. Chemical adsorption results from: the relatively strong contribution of attractive forces; molecules are not free to move over solid surfaces; and are relatively reversible. While adsorption by exchange is characterized by: electrostatic attractive forces (exchange of ions); ions with large charges are more strongly attracted than ions with low charges; and may or may not be reversible depending on their concentrations (SCHACHELFORD op. cit.). According to the same author, sometimes it is difficult to determine one or the three types of adsorption that are taking place due to the interrelationships involving chemical and physical processes. The main mechanism of sorption reaction with clay particles is isomorphic substitution, which represents the main cause of the cation exchange capacity of montimorilonite and the oxides of Al, Fe and Mn.

[28] Complexation is the combination of the central cation with one or more ligands. Organic matter in the soil contributes between 20 to 70% of the CEC of most soils and, due to its high reactivity, regulates the availability of metals (Cu, Mn and Zn) (SILVA et al. 2000). The complexation with metals is carried out through stable bonds with the MO and when these bonds occur at two or more points of the organic molecule, it forms a metallic complex generically known as a chelate. According to SCHACHEELFORD (op. cit.), the aptitude in the transition from metallic ions to complex ions is very regular and follows the following order: $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$ and $> Zn^{2+}$.

5.4 Surface water from wetlands and physical-chemical parameters

In interaction with the aerobic and anaerobic sediments of the wetlands, surface water develop the most varied biogeochemical transformations involving nitrogen, phosphorus, iron, sulfur and carbon (MITSCH and GOSSELINK, 1993). These transformations are conditioned to the greater or lesser input of nutrients into the systems, which thus determine varied chemical compositions for water in wetlands (KADLEK and KNIGHT, 1995).

Water storage in natural or constructed wetlands is mainly determined by the input (Inflow) and output (Outflow)[29] of the system, associated with the basic characteristics of each wetland. These factors define the water residence time within these zones, implying a greater or lesser interaction with the environment and triggering physical-chemical, biological and microorganism processes, responsible for the retention or availability of waste induced in the system.

The removal of pollutants in the wetland depends, among other components, on the surface or sub-surface flow, the soil matrix, the hydraulic conductivity, the interactions between the effluent and the matrix and the variation of physical-chemical parameters (BOVOR and SCHULZ 1993).

The physicochemical parameters can change quickly and significantly and must be averaged in situ to indicate any periodic changes. The main characteristics of each parameter to be measured in the surface waters of the Plumbum wetland are presented below:

Water temperature

Water temperature influences not only biological processes, but also biochemical and chemical reactions and the solubility of gases dissolved in water. According to PIVELI (1998), temperature is an important environmental parameter in the control of water quality. The increase in temperature causes an increase in the speed of reactions, reducing the

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[29] KADLEK and KNIGHT (op. cit.) used the terms Inflow and Outflow to characterize water inlet (source) and outlet areas, both for natural and constructed wetlands. TINER (1999) noted that there are different terms used in the literature for directional flow and that the terms Inflow and Outflow are used for hydrological studies and classification of wetlands.

solubility of gases dissolved in water, in particular oxygen, the basis for aerobic decomposition.

This parameter is useful to determine the conditions of the thermal potential of the waters in the treatment of wetland (KADLEK and KNIGHT 1996). However, studies developed by GRIFFIN Jr et al. (1999) showed that seasonal variation in liquid waste temperature has little or no effect on the removal of Biochemical Oxygen Demand from a constructed wetland.

Hydrogenionic Potential (pH)

According to KADLEC and KNIGHT op. cit., pH reflects the hydrogen ions contained in wetland waters. Some types of natural wetlands have a high pH between 6 and 8, while wetlands where high decomposition of organic matter occurs the pH can be very low between 3.5 and 5.5. This parameter is strongly related to the amount of calcium contained in the system and for Ca >20 mg/L there will be an environment with neutral water.

pH and Eh are considered the “master” variables of geochemical processes controlling the solubilization of heavy metals (BOURG and LOCH 1995). The pH controls the precipitation of metals through its ability (concentration of H+ in water) to attack minerals in rocks, soils and sediments, inducing leaching and/or solubilizing their constituents (SOLOMONS 1995, KABAT-PENDIAS 1995 and BORMA et al. 1996).

According to DEAN AND BOSQUI (1972) apud SOUZA (2001), the order of precipitation of metals in diluted solution, with increasing pH is (Table 5.5):

Table 5.5 - METAL PRECIPITATION ORDER

ION	pH	ION	pH
Fe^{3+}	2.0	Ca^{2+}	6.7
Al^{3+}	4.1	Cd^{2+}	6.7
Cr^{3+}	5.3	Co^{2+}	6.9
Cu^{3+}	5.3	Zn^{2+}	7.0
Fe^{2+}	5.5	Hg^{2+}	7.3
Pb^{2+}	6.0	Mn^{2+}	8.5

Source: DEAN and BOSQUI (1972) apud SOUZA (2001)

Studies by BORMA et al. (1996) indicate that the mobility of heavy metals in clayey soils depends fundamentally on the pH behavior. In the study, the authors name the main interferences caused by pH in contaminated clayey soils, highlighting, among them:

a) sorption and desorption reactions, precipitation, solubilization and complex formation are dependent on the pH of the soil solution;
b) for high pH values, precipitation mechanisms prevail, whereas as the pH decreases, the precipitates redissolve releasing metallic ions, with cation exchange prevailing;
c) for pH values in which cationic exchange prevails, the retention capacity of metallic ions is directly influenced by the clay minerals present.

Conductivity

Conductivity is determined by the presence of dissolved substances that dissociate into anions and cations. Its value depends on the type and concentration of ionic species, valence and mobility of the ion and temperature of the medium. Electrical conductivity also measures the ability of water to transmit electrical current. The unit used is the micromhos/cm equivalent to microsiemens/cm (BRANCO 1991).

Water conductivity is a function of the total quality of ions in a surface water sample. Total salts in wetlands are measured by conductive species (calcium, magnesium, potassium, sodium, bicarbonate, nitrate, and chloride) and can be altered by physical and chemical processes in natural or constructed wetlands. A survey carried out by several authors in different types of wetlands found that the conductivity can vary from 60 to 940 µmho/cm (KADLEC and KNIGHT 1996).

Dissolved Oxygen (DO)

Oxygen dissolves in natural waters coming from the atmosphere, due to the difference in partial pressure. This mechanism is governed by Henry's Law, which defines the saturation concentration of a gas in water as a function of temperature (PIVELI 1998).

Some natural wetlands have very high or very low levels of DO as a function of temperature variation, the amount of dissolved salts and, especially, biological activities (KADLECK and KNIGHT op. cit.). The mechanisms of oxygen transport in wetlands depend on the diffusion of oxygen in the oxidizing surface soil with the roots of plant species.

According to KADLEC and KNIGHT (op. cit.), dissolved oxygen in wetlands can present a limit of zero to more than twice the theoretical solubility. Surface waters present a vertical DO gradient that is very high at the water/air interface and very low at the water/sediment interface. Some natural wetlands are low in DO and have very low redox potential in sediments.

Redox Potential (Eh)

Wetlands are ideal environments for chemical transformations due to the variation in the oxidation state that naturally occurs in wetland soils. Free oxygen decreases rapidly with soil depth due to metabolism from the consumption of organic matter in the soil. This decline is called oxi-reduction potential (Eh), and present distinct environments in aerobic conditions (available dissolved oxygen) Eh greater than 300 mV, anoxic between 300 to –100 mV and anaerobic (poor in available oxygen) when Eh is less than –100 mV (SIGG 2000) (Figure 5.13).

Redox potential is measured in mV and has an equivalent scale for classifying redox equilibrium with ρε (redox intensity) (Figure 5.13). It is essential to recognize that the redox potential is based on the concept of thermodynamic equilibrium and that it will only be properly measured at equilibrium (SIGG op cit), as it determines the characteristic of the environment, whether reducing or oxidizing, controlling numerous chemical processes that occur in nature, for example, a rapid decrease in the redox potential of water and sewage can cause an anaerobic biological process.

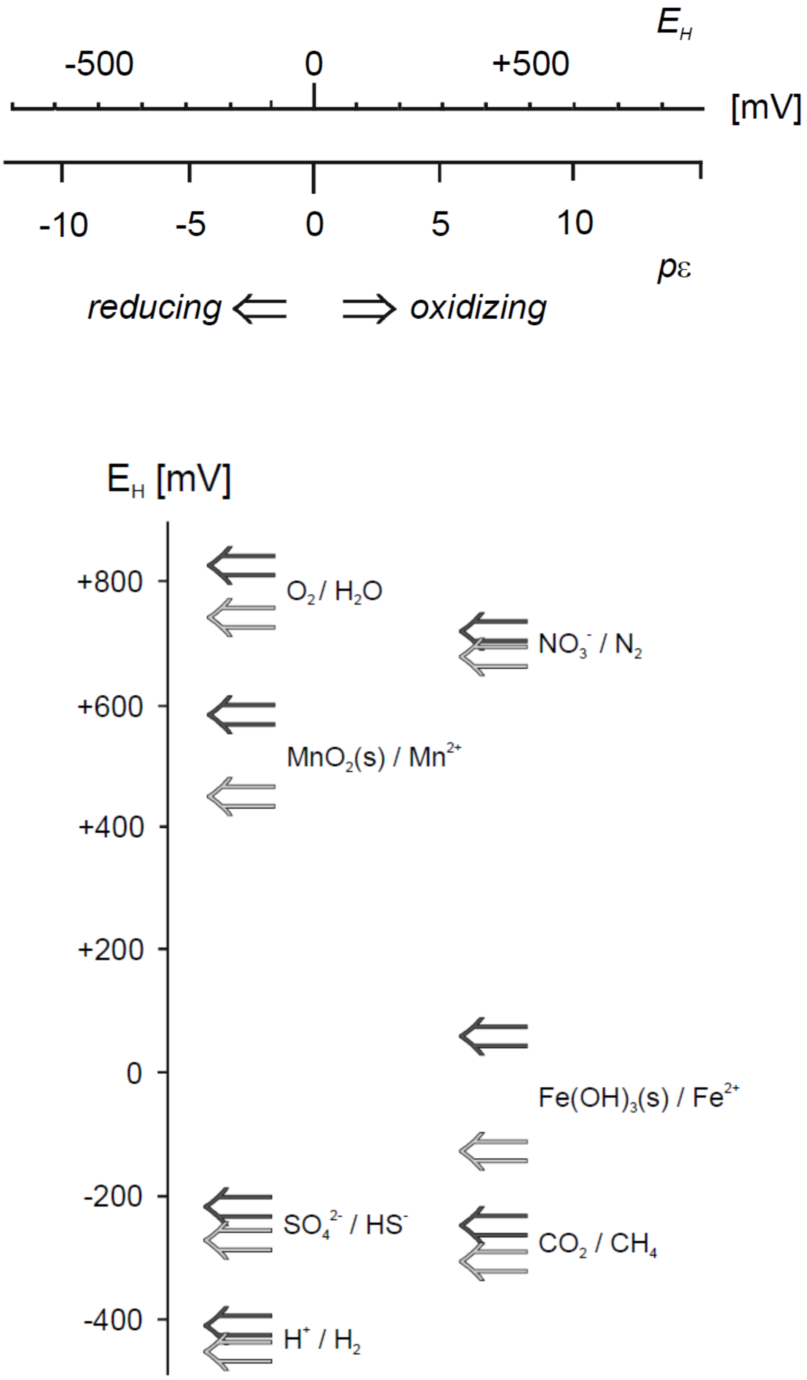

Figure 5.10 – Redox potential in a natural system. Fonte: SIGG, 2000.

The redox potential in natural waters is limited by negative variations for reduction of H_20 to $O_2(g)$ and positive variation for oxidation of H_20 to $O_2(g)$ (-400 mV to 800 mV) at pH ranging from 7 to 8 (Figure 5.10) (SIGG op. cit.).

The redox potential can be measured in the water and soil of wetlands, as it represents a quantitative measure of the tendency of the soil to reduce and oxidize substances (MITSCH and GOSSELIND 1993).

Natural or constructed wetlands are poor in oxygen, which contributes to low values for this parameter. This fact is due to the consumption of oxygen by the decomposition of vegetation and the action of microorganisms (KADLEK and KNIGHT 1996). Oxy-reduction in the root zone can help in the oxidation and immobilization of natural or anthropogenic toxic substances (LEWIS et al. 1999).

5.5 Analyses by sequential extraction

Historically, the geochemical analyses of soils has made a relevant contribution for the most diverse purposes. Among them, the following stand out: the tracing of some specific chemical elements of economic interest; surveys for Forensic purposes and; in the study of environmental impacts as one of the procedures for measuring risk and damage to the environment (JARDIM 1999).

From the 1960s onwards, analytical procedures for soils and sediments gained momentum due to the need to initially elucidate aspects inherent to contamination, whether natural or anthropogenic. Subsequently, investigation on ecotoxicity, reference standards for contaminated soils and estimation of the availability of toxic metals in the environment favored the sophistication of analytical procedures, from remote sensing by satellite to multielement analyses by Plasma Atomic Emission Spectrometry (ICP -MS) (JARDIM op. cit. and CHUI et al. 2001).

Thus, with modern analyses techniques it is often possible not only to quantify an element, but also to show the way in which it is presented. This type of analytical procedure is often described as speciation[30] or speciation analyses (URE et al. 1993).

Chemical speciation is used in analyzes for the sequential extraction of metals in the soil as an operational procedure, in which reagents or extractors are used for physical isolation of the soil solution (URE op. cit.). This type of speciation is often equated with the quantification of elements in specific phases of the soil or sediment matrix.

However, some authors, including YONG et al. (1993), question the perfect selectivity of the used reagents, i.e, whether they destroy just the connections between the contaminants and the selective geochemical phase. In this way, the results of the sequential extraction can be interpreted as a semi-quantitative evaluation of the partition of the contaminants between the geochemical phases or as a good qualitative indicator. (OLIVEIRA 2000).

TESSIER et al. (1979) developed the first complete analytical procedure for sequential extraction of metals. The procedure had the purpose of evaluating the differences between total metal and metal concentrations in the various forms found in the soil. It is important to point out that until then there was already a series of simpler procedures involving a smaller number of phases.

Sequential extraction, as described by TESSIER (op. cit.), employs a series of five extracting solutions for the selective removal of metals in the chemical fractions of soils, making it possible to quantify the proportion of metal that is solubilized by a specific reagent. This set of steps has become more useful and informative for understanding the mechanisms of immobilization, release, and transport of metals.

Five soil chemical fractions were selected from previous research and grouped by TESSIER (op. cit.). The forms: interchangeable (POSSSELT et al. 1968 and VAN DER WEIJDEN at. al. 1977 apud TESSIER op. cit.); carbonate (GUPTA and CHEN 1975, STOVER et al. 1976, CHESTER and HUGHES 1967 and PERHAC 1974 apud TESSIER op. cit.); reducible

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[30] Chemical speciation is defined as “the process of identifying and quantifying the different species, forms or defined phases, in which an element occurs in a material” (URE 1990 and URE op. cit.). RUDD et al. (1998) apud GARDOLINSKI (1998) defined terms commonly used in research on speciation in soils and sediments: fraction refers to the portion of metal present, which is extracted by a specific reagent; phase is the metal species, or group of metal species, that a particular reagent is intended to extract; and species corresponds to the ions, complexes, oxidation states and compounds of individual metals.

(JENNE 1968 apud TESSIER op. cit.); oxidizable (GUPTA and CHEN 1975 apud TESSIER op. cit.) and; residual (Table 5.6).

TESSIER's procedure (op. cit.) has been adapted and modified by several researchers, notably SOLOMONS and FÖRSTNER (1980), LUM and EDGAR (1993), MEQUELLATI et al. (1993), FORSTNER (1985), KERSTEN and FÖRSTNER (1986), TOWNER (1986) and CHESTERS (1986) apud URE et al. (1993).

These modifications make the isolation of the oxide and hydroxide phases of Fe and Mn more specific, following the example of SOLOMONS and FORSTNER (1980) apud URE (op. cit.), while the modification of MENQUELLATI et al. (1993) apud URE (op. cit.), which isolates the organic phases before the carbonate phase.

Although many other sequential extraction methods exist, the procedure by TESSIER et al. (1979) has received more attention and been the subject of investigation for the development of protocols for contaminated soils. From there, several relevant studies and protocols followed, such as YONG et al. (1993), URE et al. (1993), USEPA (1992, 1994 and 1994a) and QUINAGLIA (2001).

Variations of extractors in other studies have intensified, especially due to the specificity of the soil and sediments, the type of aggregated toxic waste and the surrounding environmental conditions.

YONG et al. (1993) presented research results on the retention capacity of heavy metals (Pb, Cu, Zn and Cd) by the analytical method of selective sequential extraction in some clayey soils (kaolinite, illite, montmorillonite and natural soil). Studies have shown that these heavy metals can be retained by four clayey soils, at different intensities, in the various soil phases (exchangeable, carbonate, reducible, oxidizable and residual).

Table 5.6 – SEQUENTIAL EXTRACTION PROCEDURES.

FRACTION	METHOD
EXCHANGEABLE	8 ml (1 m $MgCl_2$, pH 7) or (1M NaOAc, pH 8.2), room temperature for 1 hour.
CARBONATIC	8 ml (1 m NaOAc pH 5 + HOAc) at room temperature and time needed for extraction.
REDUCIBLE	20 ml (0.3M Na2S2O4 + 0.175M Na-citrate + 0.025M H-citrate) or (0.04 m $NH_2OH.HCl$ in 25% (v/v) HOAc), Temperature 96±3 °C with occasional stirring.
OXIDABLE	**1st Step** - (3 ml 0.02M HNO_3 and 5 mL 30% H_2O adjusted pH 2 with HNO_3), Temperature 85± 2 ºC, occasional stirring for 2 hours. **2nd Step** - Add (3ml to 30% H_2O_2 adjusted pH 2 with HNO_3), Temperature 85±2 ºC with occasional stirring. **3rd Step** - Add (5 ml 3.2M 20% NH_4OAc (v/v) HNO_3), diluted with 20 ml, stirring continued for 30 minutes.
RESIDUAL	HF-$HClO_4$ digestion, 50 ml polyethylene tubes, centrifugation at 10,000 rpm for 30 minutes.

Source: TESSIER (1979)

Analyses by selective sequential extraction, carried out by YONG (op. cit.), demonstrated that heavy metals can be retained in all phases of clayey soils. The study showed that the retention of heavy metals depends on the soil pH solution, the soil constituents (clay types and percentages) and the type of heavy metal. For high pH values in the soil solution, the retention mechanism of heavy metals by precipitation prevails, while at low pH values in the solution, the cation exchange mechanisms become dominant (YONG op. cit.).

In 1993, the Commission of the European Communities Bureau of Reference (BCR) published a report called Improvements in the determination of extractible contents of trace metals in soil and sediment prior to certification (EUR 14763 EM), to standardize analytical values between laboratories in the European Community (URE et al. 1993). The strategy envisaged by the BCR for preparing the protocol provided for the following priority actions:

1) review of procedures through the relevant literature and consultation with European soil and sediment specialists;
2) an experimental study of sequential extraction of seven samples of sediments and one of soil previously prepared for the analyses of their total contents of trace elements was carried out by four reference laboratories. The procedures adopted were TESSIER et al. (1979) modified by FORSTNER (1985), SOLOMONS and FORSTNER (1984) and MAGUELLATI et al. (1983) apud URE et al. (1993);
3) soils and sediments were certified regarding the concentrations of the extractable forms they possess and that the concentrations measured at regular time intervals remained stable; and
4) test protocol procedures for soil and sediment extraction.

The sequential extraction procedures suggested by the BCR are as follows for 1 μg of sediment (fraction < 63 μm) (ERU op. cit.):

a) exchangeable phase: 0.11M HAc; 40ml.g-1 (v/m); stirring for 16 hours; centrifugation 4,000 RPM.
b) reducible phase: 0.1M $NH_2OH.HCl$; 40ml.g-1 (v/m); (pH=2 with HNO_3); stirring for 16 hours; centrifugation 4,000 RPM.
c) oxidizable phase: 8.8M H2O2 (pH=2 with HNO3); 10ml.g-1 (v/m); room temperature for 1 hour; 85°C; volume reduction; new addition of extractor 10ml.g-1; 85°C for 1 hour; volume reduction; 1M NH_4Ac (pH=2 with HNO_3); 50ml g-1 (v/m); agitation for 16 hours, centrifugation (4,000 RPM).
d) residual phase: Methodology like that used for total extraction.

5.5.1- Analyses by sequential extraction in Brazil

Several studies addressing sequential extraction analyses have been done in Brazil. Most likely, studies on sediments from Sepetiba bay, in Rio de Janeiro, developed by FISZMAN et al. (1984) apud LACERDA (1994) registered the first essays on the subject. These authors, studying sediments from Sepetiba Bay contaminated with metals Fe, Zn, Pb, Cr, Cu and Cd, compared the result of the unstable fractions of the sequential extraction (exchangeable fraction of adsorbed metals and the soluble fraction linked to carbonates) with different concentrations of hydrochloric (HCl) and nitric (HNO_3) acids.

JORDAO et al. (1990), using the sequential extraction methodology of TESSIER et al. (1979), analyzed aquatic sediments collected near the Companhia Paraibuna de Metais, in Minas Gerais. The levels of Cd, Pb, Cu and Zn associated with the exchangeable, carbonate, reducible, organic, and residual fractions were evaluated.

GATTI (1977) evaluated the sediments of two oxbow lakes of the Moji-Guaçu River, in São Paulo. The study used a method developed by KHEBOIAN et al. (1987) apud GATTI (op. cit.) and was characterized by presenting simplified procedures, and performing analyses of potentially bioavailable metals using extraction with HCl 0.1 M.

NASCIMENTO and FENZL (1997), evaluated the sediments of the Guamá River and the main drainage channels of Belém do Pará, using the modified method of TESSIER et al. (1979), for the metals Cr, Mn, Co, Ni, Cu, Zn and Pb.

LINHARES et al. (1996) and MESTRINHO (1998) analyzed Cu, Pb, Zn, Cr, Cd, Fe and Mn in bottom sediments of the Paraguaçu River, north of the Todos os Santos Bay, in the State of Bahia. The sequential extraction procedure for the analyses of heavy metals was conceived by NAIR and BALCHAND (1993) apud OLIVEIRA (2000).

Studies on the biogeochemistry of heavy metals in the mangrove ecosystem was carried out by LACERDA (1994) and OLIVEIRA (op. cit.). They presented the geochemical distribution of metals Fe, Mn, Zn, Cu, Pb and Cr in the upper sediments of Sepetiba bay (predominantly the reducible phase) and in the mangrove forest of the Itacuruçá Experimental Forest (predominantly oxidizable phase) in Rio de Janeiro. While OLIVEIRA's research (op. cit.) evaluates the availability of metals Pb, Zn, Cr, Cu, Cd, Ba Mn, Fe and Al, in Camamu Bay, located on the south coast of the State of Bahia.

MOZETO (1997) carried out a study on the “Characterization of the stock of heavy metals, volatile and semi-volatile organic compounds and nutrients in the sediment and particulates of the Guarapirange and Billings dams in the Metropolitan Region of São Paulo”. A study based on the method by CAMPBELL et al. (1988) apud MOZETO (op. cit.) characterized the metals Cd, Cr, Cu, Ni, Pb and Zn in the potentially available form.

AMARAL SOBRINHO et al. (1977) and GOMES et al. (1997) conducted a study on soils incubated in laboratories. AMARAL SOBRINHO et al. (op. cit.) used alkaline waste from Companhia Siderúrgica Nacional to dispose of it in the soil and, after 18 months, evaluate the metals Ni, Zn, Pb, Cd, Cu and Mn, following the modified method of TESSIER et al. (1979). A study by GOMES et al. (1997) applied Cd, Cr, Cu, Ni, Pb and Zn salt solutions in oxisol soil, with purpose of adapting the metal fractional extraction method and evaluating its components in the soluble, exchangeable, linked to organic matter, and to Al and Fe oxides and residual.

GARDOLINSKI (1998) developed a study on sediments, using the BCR methodology. It analyzes extractors by plasma source mass spectrometry and uses the Isotopic Dilution method for quantitative determinations as an alternative to external calibration. To change the natural isotopic ratios, solutions of material enriched in the isotopes ^{63}Cu, ^{66}Zn, ^{112}Cd and ^{208}Pb were added.

The application of the method allowed to determine with precision and accuracy, concentrations in the extracts that vary from 8.1 to 632.6 μg/l for Cu, from 57.6 to 5785.0 μg/L for Zn, from 2.3 to 1086.0 μg/L for Pb and 2.3 to 74.2 μg/L for Cd.

A study for the establishment of an Analytical Protocol for soil sample preparation for metal determination was carried out by QUINAGLIA (2001). The procedures for preparing soil samples for the determination of metals were done within the procedures standardized by the USEPA through the document Test Methods for Evaluating Solid Waste - SW - 846, USEPA - 3051.

The protocol verified the concentrations of metals in different land use and occupation scenarios (permanent preservation, agricultural, residential and industrial areas) in the city of Paulínia, São Paulo. The metals evaluated were As, Ag, Ba. Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Hg, V and Zn e, the methodology proposed by USEPA - 3051 uses only 9 ml of nitric acid (HNO_3) + 3 ml of HCl in a closed microwave system.

5.6. Remediation of contaminated areas

In 1986, the Environmental Protection Agency (EPA) formulated the first sequence of correction procedures for a contaminated area[31] with the objective of cleaning the soil and groundwater of toxic substances19. These corrective actions were developed in five phases, the initial one being an inspection and preliminary assessment of the site, going through the proposition of remediation techniques until the implementation of corrective and stabilizing measures (BERTENFELDER 1992).

In this period, we had in Brazil the second largest radioactive disaster in the world, namely the accident with cesium-137 in Goiânia and, according to TERRA and LADISLAU (1991), “the non-definition of those responsible for the accident delays the due care for the victims, either medically or financially” which characterized a disjointed action by institutions, due to the lack of specific laws on industrial contamination and its consequences on human health.

Meanwhile, in the Netherlands, in response to the Lekkerkirk case[32], laws called the “Soil Protection Act, 1987” and the “Interim Soil Cleaning Act, 1993” regulate contamination prevention and remediation measures. of the soil (GLOEDEN 1999).

In this context, since the last decade, in São Paulo, an expressive number of works involving the management of areas contaminated with industrial waste and propositions for remediation of sites have abounded, such as MARKER et al. (1994), POMPEIA (1994), SANCHEZ (1995), CUNHA (1997), GLOEDEN et al. (1997), HASSUDA (1997), LEITE et al. (1997), SÍGOLO (1997), ANJOS (1988), GLOEDEN (1999), CETESB (1999), CROZERA (2001), SILVA, A.L.B. (2001), SILVA, F. A. N. (2001), TOSO JÚNIOR (2001) and BORBA (2002).

The term remediation refers to the approach of an educational nature, an “action or process of correction or domain of knowledge or problem”

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[31] According to CETESB (op. cit.), contaminated area can be understood as “areas where there is demonstrably pollution caused by any substance or waste that has been deposited, accumulated, stored, buried or infiltrated in it, and which determine negative impacts on the goods to be protect".

[32] According to SANCHEZ (2001), 268 houses were built in landfill areas in Lekkerkirk, near Rotterdam, Holland. In this industrial waste landfill, 1651 buried barrels of chemical substances were found, mostly organic compounds, such as xylene and toluene, which penetrated slowly into the water and sewer pipes. The area's remediation process cost the equivalent of US$65 million at the time.

(WEBSTERS 1995). However, this term was introduced in the United States and Europe by opinion makers, as a “set of measures aimed at cleaning sites degraded by industrial activities”, notably the disposal of toxic waste, which has caused soil or soil contamination. aquifer (SÁNCHEZ 1994).

The USEPA defines remediation as a set of corrective actions applicable to a given site contaminated with hazardous waste. In practice, these actions minimize the effects of contamination, which means that it is difficult to recover the site (BERTENFELDER 1992). While BITAR (1997) defines remediation as treatment techniques that are intended to “eliminate, neutralize, immobilize, confine or transform elements or substances present in the environment and, thus, achieve the chemical stability of the environment”.

The term remediation is sometimes confused with recovery. GLOEDEN (1999) and SANCHEZ (2001) discussed the differences and application of these terminologies, which according to (GLOEDEN op. cit.) can be used when determining measures to reconcile the current and future use of the contaminated area. Within this context, the recovery of contaminated areas would be the entire process of applying corrective measures necessary to minimize or eliminate contamination, with the purpose of using the area for a specific purpose, while remediation is related to containment measures or isolation of contamination. While SANCHEZ (op. cit.) emphasizes recovery as measures to eliminate or reduce the amount of harmful substances present in the soil or groundwater, while remediation would be related to measures to isolate the most contaminated sectors and removal of contaminants to safe levels for human health and the ecosystem.

However, the application of the term remediation sometimes becomes unfounded when dependent on legal support, since, so far, there is no specific law in Brazil for remediation of contaminated sites. However, the same does not occur with the specification of the term recovery in the Federal Constitution of 1988, regulated by Federal Decree 97.632/89 for mining projects and called Plan for the Recovery of Degraded Areas. Under these conditions, recovery must be understood as the result of the application of management techniques aimed at making the area suitable for a new use (SANCHEZ 2001).

SCHIANETZ (1999) did not use the term remediation and correlates the environmental liabilities[33] of areas contaminated with industrial waste with actions for their recovery, such as: need for immediate actions; recovery goals; duration of recovery action; types of contaminants and their relationships with the subsoil; available financial resources and; legal aspects related to the safety of the operation.

The management manual for contaminated areas (CETESB 1999), the first Brazilian protocol on contaminated areas, defines remediation as the "application of a technique or set of techniques in a contaminated area, with the purpose of removing or restricting the contaminants, in order to ensure a use for the area, with acceptable limits of risks to the goods to be protected".

Thus, CETESB's management system for contaminated areas includes a step for investigation and possible remediation (selecting, among the various options of existing techniques, those most appropriate for the case under consideration) and then a remediation project (technical basis for the agency manager or environmental control body to assess the possibility of authorizing or not the implementation and operation of the proposed remediation systems).

However, two decades after the first regulations made by the United States[34] for cleaning contaminated soils, and after the intense technological research sponsored by industrialized countries, in particular the United States, Canada, England, the Netherlands and Germany, it appears that the difficulties for recovering these contaminated areas continue. This conclusion stems from the complexity involved in the contamination of the sites, the applied techniques that do not fully reach their objectives and, notably, the high costs for implementing the remediation.

These conditions have favored the specificity of remediation techniques with lower costs, such as those presented at the "Sixth and seventh International Conference on Contaminated Soil", held sequentially,

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[33] 30 According to SCHIANETZ (op. cit.), environmental liabilities are old depositions and contaminated sites that pose risks to the well-being of the community, according to the technically supported assessment of the competent authorities. However, for SÁNCHEZ (op. cit.), the environmental liability is the accumulation of environmental damage (impacts) that must be repaired to maintain the environmental quality of a given location.

[34] *Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)*, passed in 1980, was the first law dealing with soil and groundwater contamination, also known as "Superfund". This law was preceded by specific regulations for water, air and solid waste, respectively, the Water Pollution Control Act (1948), the Clean Air Act (1955) and the Solid Waste Control Act (1965) (SÁNCHEZ 2001).

in 1988, in Edinburgh, UK, and 2000, in Leipzig, Germany. In these conferences, the difficulties of achieving more restrictive standards with current technologies were emphasized, the need to live with contaminated areas and the urgency in using common sense to determine sites with immediate risks, in addition to emphasizing research on mitigation techniques of the contaminants, characterized by its low cost in the execution of the remediation.

In these circumstances, several world organizations, especially institutions linked to the European Union[35], Eastern Europe and North America, have been presenting cooperation proposals, for the exchange of scientific knowledge and propositions of methodologies and tests of new remediation technologies for soils and the groundwater.

In Brazil, since 1992, some soil decontamination techniques have been carried out by the private sector, among them the Bergmann process and conventional technologies such as incineration, chemical extraction, discoloration, biodegradation, stabilization and vitrification. However, one of the major obstacles to the implementation of remediation in contaminated soils was related to the operational cost of the technologies, which ranged from US$ 122/m3 when the Bergmann process was used, to US$ 1,282/m3 for the cost of incineration with removal of the contaminant (ROHRIG and SINGER 1996).

However, in 1997, the *Química e Derivados* journal presented a great discussion called “Environmental control reaches the subsoil”. The article presents CETESB's action plan proposals for contaminated sites in conjunction with the German Government Environmental Agency (GTZ) and emphasizes the procedures for developing the Contaminated Areas Manual, in addition to establishing reference and intervention values. for soil and groundwater in the State of São Paulo (FURTADO 1997).

The publication presents the main remediation technologies used by large consulting companies in Brazil, in addition to a schedule of activities with the main stages of the recovery process of soils contaminated with industrial waste (Table 5.7) carried out by the private sector.

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[35] The Concerted Action on Risk Assessment for Contaminated Sites in the European Union (CARACAS); Contaminated Land Rehabilitation Network for Environmental Technologies in Europe (CLARINET); Network for Contaminated Industry In Europe (NICOLE) and Risk Abatement Center for Central and Eastern Europe (RACE).

During this period, the methodology adopted for the diagnosis and evaluation of contaminated areas followed the procedures applied by USEPA, and sequenced in three phases:

Phase 1 – Compliance audit, when the pertinent environmental legislation will be surveyed; Municipal, State, Federal and Environmental licenses; maps and reports of environmental risks, occupational health, ergonomics and accident notifications, in addition to inspection and knowledge of equipment installed in the open air and underground;

Table 5.7 - SCHEDULE OF ACTIVITIES FOR SOIL RECOVERY

ETAPA	MESES											ANOS				
	2	4	6	8	10	12	14	16	18	20		4	6	8	10	
INVESTIGATION	■	■	■													
MODELS				■												
DIAGNOSTIC					■											
RISK ANALYSES						■										
RECOVERY ALTERNATIVES							■									
DEFINITION OF GOALS									■							
APPROVAL OF AUTHORITIES											■					
IMPLANTATION												■				
OPERATION / MONITORING													→	→	→	

Source: CSD - GEOKLOCK

Phase 2 - Outline of contamination, when information will be collected to quantify the existing level of contamination in the soil and groundwater, through geological and hydrological knowledge of the area, use of standardized procedures for sampling and characterization of the source/s contamination and qualification and quantification of toxic substances through chemical analyses. At this stage, priorities for remediation should also be established, the immediate risk to public health, in addition to costs and details for remediation, and

Phase 3 – Detailed program of monitoring and corrective actions, through health and ecosystem risk programs, application of remediation techniques and systematic evaluation of the persistence of toxic substances in the contaminated site.

However, the number of contaminated sites that have been identified in Brazil is increasing, due mostly to the inadequate or clandestine disposal of industrial waste[36] that existed in the past. Although there is no register of contaminated areas in Brazil, only the state of São Paulo contemplates a program for the metropolitan region, which according to ALVES (1996) already has 2300 potentially identified areas. Data presented by GLOEDEN (1999) present only for the Guarapiranga basin, in the State of São Paulo, 1267 potentially contaminated areas.

With the implementation of specific protocols for contaminated sites in the State of São Paulo, in particular the Manual for the Management of Contaminated Areas (Figure 5.11), the Reference Values for soil and groundwater quality and the new legislation implemented by the city hall of São Paulo for the occupation of urban lots that have guidelines and procedures related to the management of contaminated areas in the Municipality[37] , the state of São Paulo has become a pioneer in South America for having specific and legal mechanisms for the evaluation of contaminated sites.

From the implementation of state protocols, CETESB presented in May 2002 the first dataset of contaminated areas, comprising 255 sites already in the remediation phase. This register, available on the internet (www.cetesb.sp.gov.br/Solo/areas_contaminadas/relacao_areas.htm), comprises a form with data on the contaminated area.

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[36] According to the National Health Foundation (FUNASA), a federal government agency, the areas with the greatest potential risk to human health are: Santana, in the State of Amapá, presence of arsenic; Santo Amaro da Purificação, in the State of Bahia, contamination with lead and cadmium; Duque de Caxias, in Rio de Janeiro, pesticide contamination; Goiânia, Goiás, contamination with radioactive material and, in São Paulo, among others, Condomínio Barão de Mauá, presence of benzene, Recanto dos Pássaros in Paulínea, presence of organochlorines, and Ajax Battery Manufacturing Co., contamination with lead.

[37] Decree No. 42.319, of August 21, 2002.

5.6.1. Remediation technologies

After the industrial revolution, responsible for the concentration and inadequate disposal of toxic waste, and the problems caused to human health by the migration of heavy metals in the soil and groundwater in potentially available forms, such as the world-renowned examples of the "Love Canal", in the United States and "Lekkerkerk" in the Netherlands, adequate forms of waste disposal have been intensively studies.

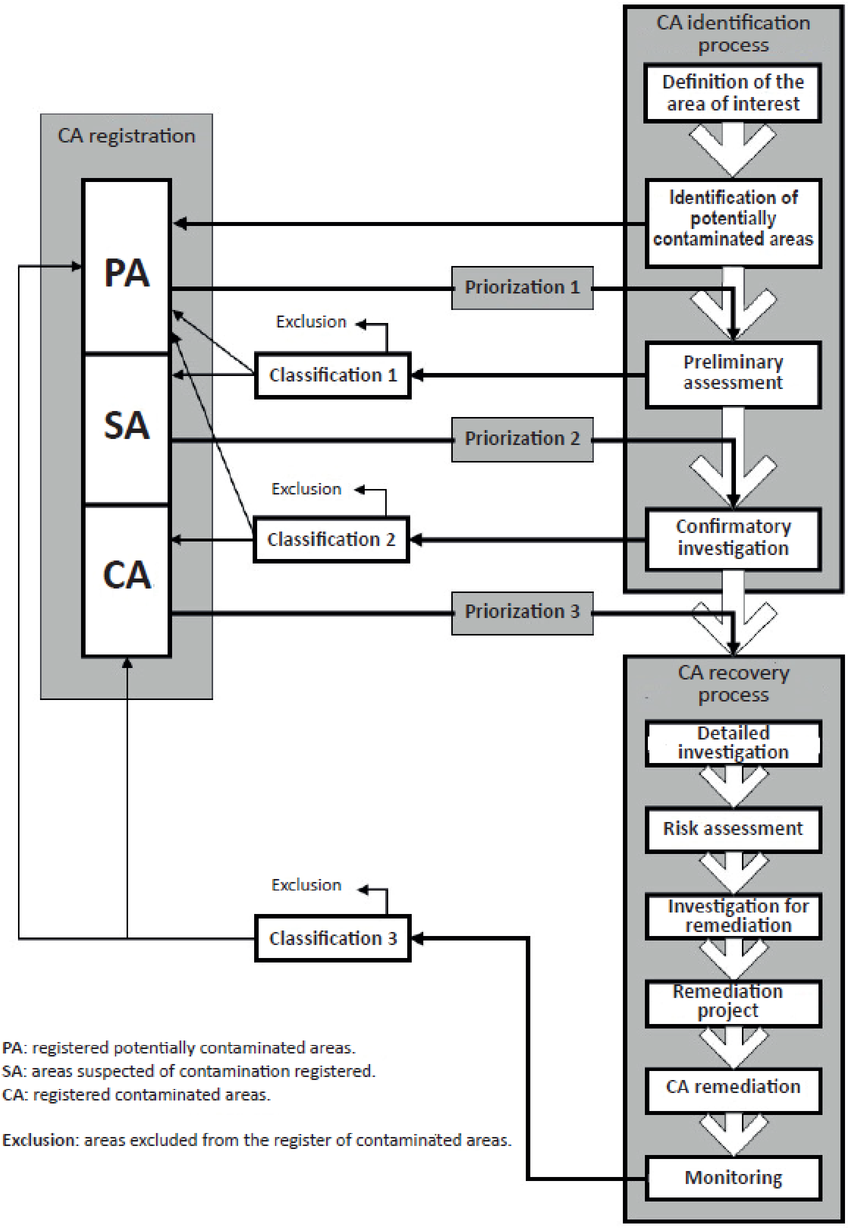

Figure 5.11 – Flowchart of procedures for evaluating contaminated sites. Source: CETESB (1999).

Remediation techniques have evolved rapidly, especially those arising from processes largely applied in metallurgy. However, research on contaminated sites coexisted for a long time, divided into two large groups of remediation technologies (USEPA 1990, 1997 and 1997a, ANDERSON 1994a, 1994b, 1994c, 1994d, 1994d and 1994f). One carried out ex situ, characterized by techniques that promote the removal of the soil for decontamination and subsequent replacement in the place of origin or disposal in an appropriate landfill. And the in-situ technique, performed at the site of contamination, widely used to remove contamination from soil and groundwater.

According to SCHIANETZ (1999), remediation techniques can be differentiated between in-site processes (without material removal), on-site (removal and on-site treatment) and off-site (off-site treatment). There are strengths and weaknesses that must be evaluated, according to Table 5.8.

The main remediation techniques tested by USEPA, during the 1990s, in industrialized countries, and applied on a pilot and real scale (ROEHRING and SINGER 1996), were prompted by the significant number of potentially contaminated areas in the European Community, estimated in about 1,500,000 (CROZERA 2001), and the 500,000 areas in North America (SANCHEZ op. cit.).

This was possible thanks to specific policies for these sites and the availability of financial resources by the Governments involved. According to CUNHA (1997), between 1980 and 1986, the Superfund allocated US$ 1.6 billion and US$ 9.0 billion, respectively, and according to SANCHEZ (2001), the average cost of Superfund remediation per site was US$ 29 million.

However, in 1993, USEPA carried out the first selection of remediation technologies most frequently used in contaminated sites and controlled by Superfund, including steam extraction in the soil, various bioremediation processes and thermal desorption to soil and groundwater.

Table 5.8 – STRENGTHS AND WEAKNESSES OF THE DIFFERENT REMEDIATION PROCESSES

In-site process	
Strengths	○ relatively cheap
Weaknesses	○ difficulty in decontaminating uniformly; ○ the resulting problems are difficult to assess; ○ consumes a lot of time; and ○ successful recovery cannot be reliably verified
On-site process	
Strengths	○ successful recovery is easy to repeat
Weaknesses	○ after treatment the soil is biologically dead and mineralogically altered; ○ the use of solvents for extraction compromises their separation at the end of the process; ○ in excavation there are risks to the environment and health; and ○ 2 to 3 times more expensive than in-site processes.
Off-site process	
Strengths	○ generally profitable; ○ the area has an immediate destination for use
Weaknesses	○ the problem is transferred; ○ treatment centers are needed for decontamination; and ○ the great expense in transport and protection at work

Source: SCHIANETZ (1999)

The application and development of these techniques on Superfund sites led to the creation of a collection called Innovative Site Remediation Technology, organized by the American Academy of Environmental Engineers with the assistance of the USEPA, consisting of eight volumes. The work was carried out by more than 100 specialists, who classified as main remediation technologies, bioremediation, chemical treatment, treatment by extraction, solidification and stabilization processes, soil washing and vaporization, thermal desorption, destruction thermal and vacuum steam extraction.

The publication constituted a major evaluation of the quantitative results of the main techniques employed by USEPA. In the bibliography, the potential application of techniques, their processes and evolution, their limitations and their potential as innovative technology were widely discussed (ANDERSON 1994a, 1994b, 1994c, 1994d, 1994e and 1994f).

USEPA (1997) presented three classes of technologies used specifically for heavy metals, classified as containment, solidification/stabilization and separation/concentration (Table 5.9).

Table 5.9 - REMEDIATION TECHNOLOGIES

Technology classification	Specific technology
Containment	○ Coverage ○ Vertical barriers ○ Horizontal barriers
Solidification / Stabilization	○ Micro-encapsulation of polymers ○ Glazing
Separation/Concentration	○ In situ soil washing ○ Ex situ soil washing ○ Pyrometallurgy ○ Electrokinetics

Source: USEPA (1997)

USEPA (1997a) selected the most promising in situ remediation technologies for sites contaminated with organic and inorganic compounds. The proposition was determined by the significant increase of these technologies in the processes of selection and evaluation of the remedies developed in the Superfund sites. The soil treatment technologies were:

- **Electrokinetics** – **a)** electromigration (transport and exchange of chemical species within the electrical gradient, leading to the capture of contaminants (Figure 5.12) **b)** electro-osmosis (transport of fluid in the electrical gradient); and **c)** electrolysis (chemical reactions associated with the electric field).

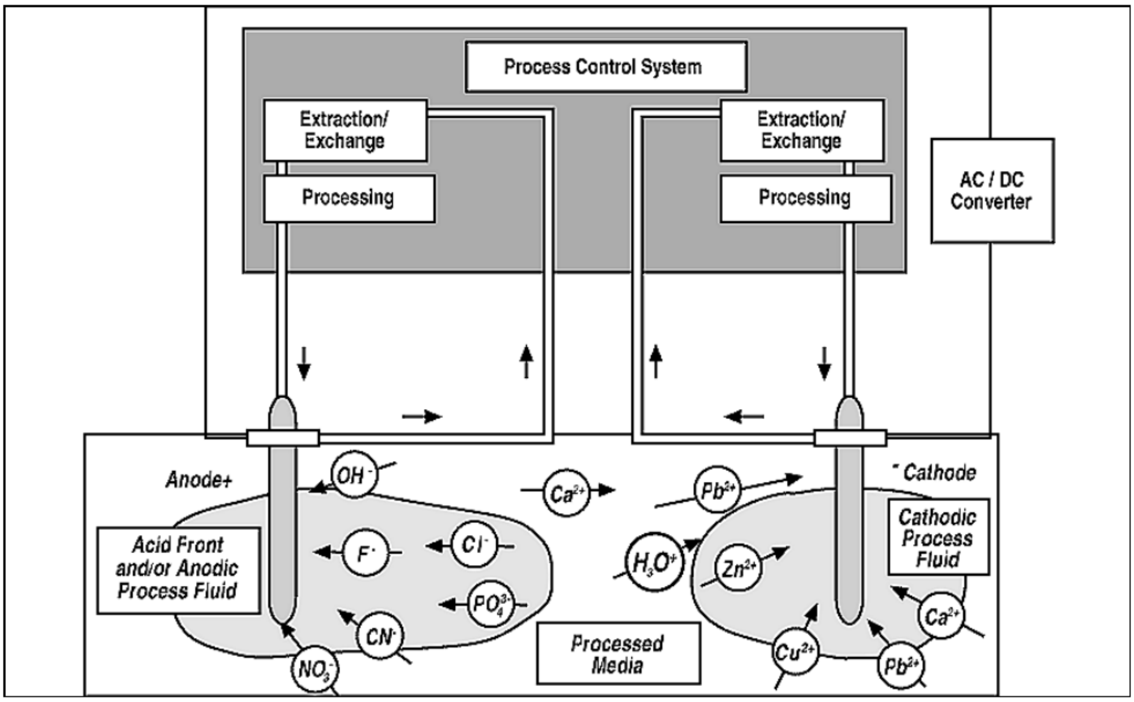

Figure 5.12 - Remediation of soil contaminated with electromigration. Source: USEPA (1997a)

- **Phytoremediation** – **a)** phytoextraction (technology that uses hyperaccumulating plants to transport metals (Ni, Co, Cu, Cr and Zn) from the soil into the root); **b)** phytostabilization (use of plants to limit the mobility and bioavailability of metals (Zn, Pb and Cu) in the soil, and **c)** rhizofiltration (use of aquatic plant roots to absorb, concentrate and precipitate metals from waste).
- **In situ soil flushing** – used in soils with high permeability when water or chemical reagents are used to solubilize and extract contaminants (Figure 5.13).

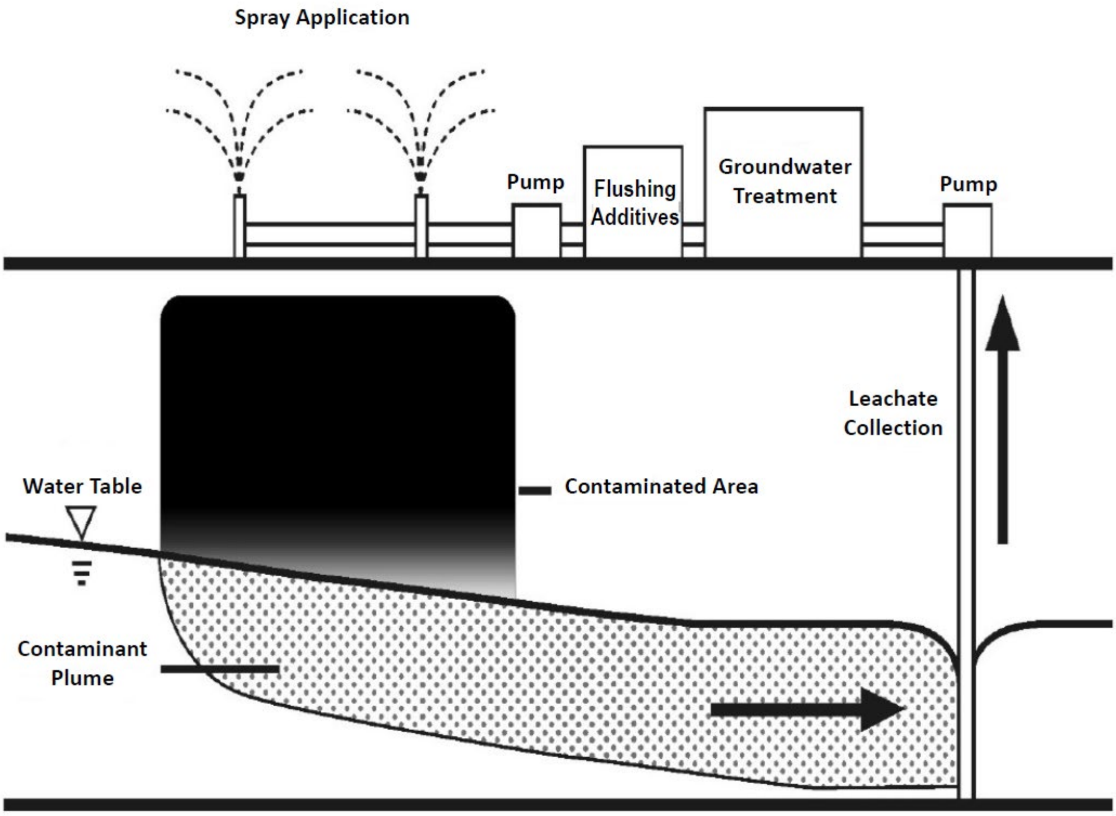

Figure 5.13 - Remediation by soil washing. Source: USEPA (1997a).

- Solidification/stabilization (S/S) – solidification is the process of changing physical characteristics in the waste to control and reduce the mobility of contaminants, creating a physical barrier to leaching. While stabilization is the treatment process that converts the contaminant to low mobility forms through thermal and chemical interactions (immobilization). Examples of S/S are soil vitrification and the use of in-situ stabilization reagents (Table 5.10).

Table 5.10 – OVERVIEW OF SOLIDIFICATION/STABILIZATION TECHNOLOGIES

In-situ stabilization reagents	Vitrification
Addition of pozzolanic reagents with or without additives to physically and chemically convert contaminants to less mobile forms.	Use of energy to melt soils and physically and chemically encapsulate contaminants into less mobile and more stable forms.
Broad applicability to most metals, including arsenic, mercury, and hexavalent chromium.	Usually applied to arsenic, lead, chromium, copper, zinc, asbestos, and radioactive metals.
Performance is highly dependent on low clay percentage.	The presence of volatiles and high concentrations of organic contaminants can reduce its efficiency.

Source: USEPA (1977a)

JAAGUMAGI (2002) presented, in addition to in-situ and ex-situ techniques (removal followed by treatment and disposal), natural attenuation as the third and newest basic category of remediation for cleaning sediments from port channels. According to the author, natural attenuation is an approach based on procedures and monitoring of naturally occurring biological and chemical processes, reducing contamination of soil and groundwater. It requires the detailed knowledge of chemists, physical chemists, hydrologists and biologists. This new form of remediation was established by the European Conference on Natural Attenuation, held in October 2002, in Heidelberg, Germany.

According to OLIVEIRA (2000), Monitored Natural Attenuation (MNA) is characterized as the most economically viable remediation technology for the geochemical monitoring and microbiological activity of organic contaminants in the sub-surface. These data are supported by remediation projects using ANM in underground tanks in the United States (Figure 5.14). However, for the National Research Council (NRC) of the United States, ANM is a remediation technique developed so far for organic contaminants, BTEX, oxygenated hydrocarbons (low molecular weight alcohols, ketones and esters) and methylene chloride.

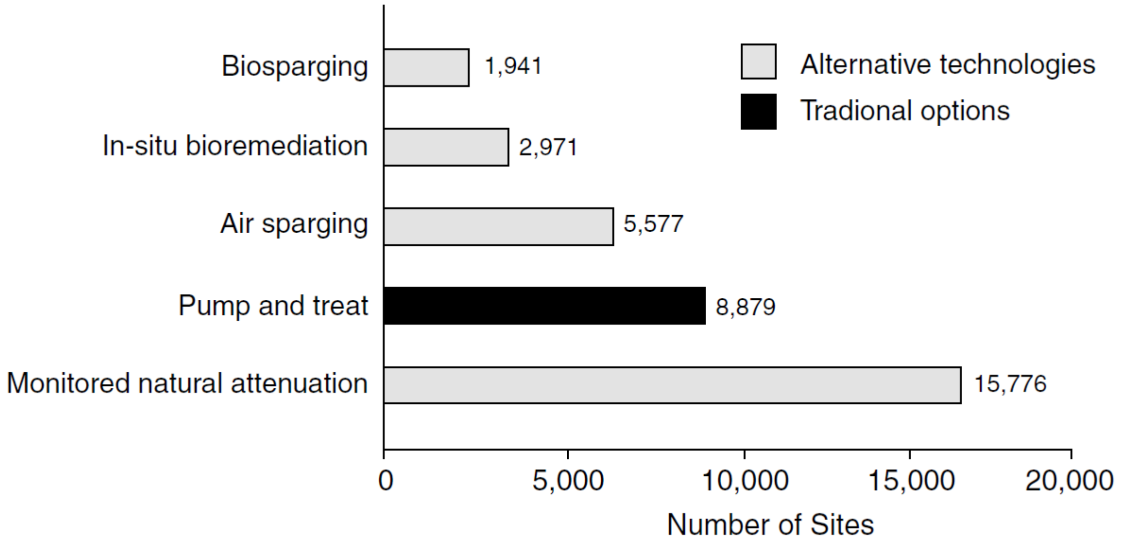

Figure 5.14 – Remediation programs in underground tanks. Source: TULIS et al. (1997) apud OLIVEIRA (2000).

Another way to implement remediation techniques in contaminated sites is defined by characterizing the target to be achieved in the remediation project (SMITH et al. 1995). Through this procedure, criteria and approximate options for the main objectives of remediation should be emphasized, with the reduction of the volume of the contaminant as preponderant; the establishment of a way to prevent the mobility of the contaminated environment and reduce its mobility. These procedures are divided into the following groups:

1. Treatment by immobilization – in-situ techniques characterized by reducing the mobility of contaminants in the soil matrix or the transport of contaminants in water, through mechanisms of reduction of infiltration in the contaminated environment through the use of barriers, reduction of infiltration by modifying the permeability of the contaminated matrix, reduction of the solubility and consequently the mobility of the contaminant in groundwater, and the control of the flow of contaminants in the water to allow collection and treatment (SMITH et al. 1995). The most used techniques include encapsulation system, vertical barriers, horizontal barriers, and solidification/Stabilisation.

2. Toxicity reduction treatment - techniques applied to reduce toxicity by chemical and biological processes. It generally converts metallic contaminants from the solid waste matrix to a less toxic form. The main chemical treatment technologies are:

- **Chemical oxidation** – reactions that change the oxidation state of atoms through the loss of electrons. The predominant reactions are precipitation and solubilization, and processes are basically used for organic compounds;
- **Chemical reduction** – a reduction process in which the oxidation state of an atom tends to decrease. The main reactions are precipitation and solubilization, and are used for both organic and inorganic compounds, and
- **Chemical neutralization** – reactions regulating the concentrations of hydroxide and hydrogen ion solutions. They are used to treat solids that are excessively acidic or basic.

The biological processes used in the remediation of contaminated areas obtained through the decomposition of the organic molecule into simpler molecules, for example: CO2, CH4, inorganic salts and water. The process involves absorption, oxidation, reduction, bioleaching, bioextraction, biosorption and biological reduction or oxidation reactions. The main biological treatment technologies are:

- **Bioaccumulation** – is the process of transferring metal from the contaminated matrix to biomass, with the metal being able to accumulate in selective living organisms or non-living biomass;
- **Biological redox** – is a technique used to select microorganisms through the reduction or oxidation of metals, and
- **Methylation** – is the process by which organisms attack the methyl group (CH3) to form inorganic metals.

Table 5.11 - REMEDIATION TECHNOLOGIES

TECHNOLOGY	OBJECTIVES	IMPLEMENTATION	COSTS	EFFICIENCY
Ex-situ bioremediation	Degradation of organic contaminants in solid and liquid media outside the contaminated area. e.g.: landforming	-Excavation and removal of contaminated soil (CS); -Area for disposal of CS; -Implanting microorganisms; -Periodic chemical analyses; -Periodic cell maintenance	BRL 75,000/Year	Average, depending on the type of contaminant and concentration.
In-situ bioremediation	Degradation of organic contaminants in the contaminated site. e.g.: bioventilation	-Evaluation of the microorganisms used; -Oxygen and nutrients system; -Periodic chemical analyses	BRL 80,000/Year	Low, depending on the type of soil and contaminant, in addition to the adaptation of the microorganism to the environment.
Soil Vapor Extraction SVE	Cleaning of unsaturated soil by means of vacuum (organic contaminants)	-Area to be reached by the vapours; - Periodic maintenance of the system; -Periodic chemical analyses	BRL 45,000/Year	High, depending on the type of contaminant and soil
Reactive permeable barriers	Contamination plume control, flow direction, organic (degrades) and inorganic (precipitates)	-Excavation and removal of contaminated soil; -Disposition of the (CS); - Installation of barrier -Periodic chemical analyses	BRL 135,000/Year	High
Pump and Treat	Extraction of the free phase of hydrocarbons in the saturated zone	-Installation of pumping system; -Deposition and treatment of pumped water; -Periodic monitoring	BRL 55,000/Year	High for the free phase, if the environment conductivity is high
Monitored Natural Attenuation	The system's natural tendency to stabilize altered by the presence of contaminants	- Preliminary assessment of natural attenuation conditions; - Periodic monitoring of contaminant concentrations	BRL 45,000/Year	High depending on type of contaminant and contaminated environment

Source: KOLESNIKOVAS (2000)

3. Treatment by concentration and separation – technologies developed from ore treatment techniques. The main techniques are the physical processes of pyrometallurgical and hydrometallurgical separation. In-situ technologies are soil washing processes and electrokinetic groundwater extraction. The main problem involving the implementation of these technologies is the high cost and obtaining a desirable level of results.

The main ex-situ separation techniques are flotation, magnetic separation, gravimetric separation, classification by settling velocity and sieving. While the main in-situ separation techniques are soil washing and electrokinetic treatment.

According to KOLESNILOVAS (2000), the main technologies currently used for the remediation of soils and aquifers contaminated with industrial waste in Brazil are no more than six (Table 5.11). These technologies have been applied in several contaminated sites, especially in the state of São Paulo.

5.6.2 - Main remediation technologies applied to metals

Some technologies for treating soil and water contaminated with heavy metals, especially lead, cadmium, zinc, and copper, are found in great density in the literature. Hence, its application and efficiency in the remediation process depend on the type of remediation proposed (containment, stabilization, or cleaning), access to technologies available on the market, in addition to the cost of remediation. These factors have led many contaminated sites to use more than one remediation technology (associated technologies) so that the recovery process of the area is successful.

Table 5.12 - CONTENTION TECHNOLOGIES

Site Name	Specific Technology	Key Metal Contaminants	Associated Technology	Status
Ninth Avenue Dump, IN	Containment	Pb	Vertical barrier and cover	Selected
Industrial Waste Control, AK	Containment	As, Cd, Cr, Pb	Coverage and drains	In operation
E. H. Shilling Landfill, OH	Containment	As	Clay Cover and Berm	Selected
Chemtronic, NC	Contention	Cr, Pb	Coverage	Selected
Ordnance Works Disposal, WV	Contention	As, Pb	Coverage	Selected
Industriplex, MA	Contention	As, Pb, Cr	Coverage	Selected

Source: USEPA (1997)

Table 5. 13 - SOLIDIFICATION/STABILIZATION TECHNOLOGIES

Site Name	Specific Technology	Key Metal Contaminants	Associated Technology	Status
DaRewal Chemical, NJ	Solidification	Cr, Cd, Pb	Pumping and treatment	Selected
Marathon Battery Co., NY	Chemical fixation	Cd, Ni	Dredging, off-site disposal	In operation
Nascolite, Millville, NJ	Soil stabilization in wetlands	Pb	On-site disposal	Selected
Roebling Steel, NJ	Solidification/stabilization	As, Cr, Pb	Capping	Selected
Waldick Aerospace, NJ	Solidification/stabilization	Cd, Cr	Off-site disposal	Compelted
Palmerton Zinc, Pa	Stabilization	Cd, Pb	-	In operation
Tonnoli Corp., PA	Solidification/Stabilisation	As, Pb	Chemical Barrier	Selected
Whitmoyer Laboratories, PA	Oxidation/fixation	As	Pump and treatment, capping and revegetation	Selected
Bypass 601, NC	Solidification/stabilization	Cr, Pb	Coating, pump and treatment	Selected
Flowood,MS	Solidification/stabilization	Pb	Coating	Complete
Independent Nail, SC	Solidification/stabilization	Cd, Cr	Coverage	Complete
Pepper's Steel and Alloys, FL	Solidification/stabilization	As, Pb	On-site disposal	Complete
Gurley Pit, AR	Solidification/stabilization	Pb		Complete
Pesses Chemical, TX	Stabilization	Cd	Concrete capping	Complete
E.I. Dupont de Nemours, IA	Solidification/stabilization	Cd, Cr, Pb	Capping and revegetation	Complete
Shaw Avenue Dump, IA	Solidification/stabilization	As, Cd	Capping and groundwater monitoring	Complete
Gould Site, OR	Solidification/stabilization	Pb	Capping and revegetation	In operation

Source: USEPA (1997)

USEPA (1997) presented a list of the main contaminants that underwent in-situ treatment focusing only on contamination in the soil. The identified metals included lead (445 sites), arsenic (388 sites), chromium (352 sites), cadmium (276 sites), nickel (276 sites) and zinc (273 sites), in addition to mercury and copper in smaller proportions in Superfund sites. The main technologies identified in the Superfund were containment, stabilization/solidification, and soil washing. Table 5.12 presents the containment technologies applied at the main Superfund sites. Table 5.13 presents the solidification/stabilization technologies applied in Superfund. Table 5.14 presents ex-situ (soil washing)1 and in-situ (soil flushing)2 soil washing technologies applied in Superfund.

Table 5.14 - SOIL WASHING TECHNOLOGIES

Site Name	Specific Technology	Key Metal Contaminants	Associated Technology	Status
Ewan Property, NJ	Water Treatment	As, Cr, Cu, Pb	Pretreatment with solvent extraction to remove organics	Selected
GE Wiring Divices, PR	Water with KI additive solution	Hg	Waste treatment, onsite disposal and capping with clayey soil	Selected
King of Prussia, NJ	Treated Water with Additives	Ag, Cr, Cu	Soil Disposition in Soil	Complete
Zanesville Well Field, OH	Soil Wash	Hg, Pb	SVE to remove organics	Selected
Twin Cities Army Ammunition Plant, MN	Soil washing	Cd, Cr, Cu, Hg, Pb	Soil leaching	Complete
Sacrament Army Depot CA	Soil washing	Cr, Pb	Off-site liquid waste disposal	Sorted, later withdrawn
Lipari Landfill, NJ	Soil flushing	Cr, Hg, Pb	Containment with horizontal barriers and wetlands	In operation
United Chrome Products, OR	Soil flushing	Cr	Electrokinetics	In operation

Source: USEPA (1997)

From 1987 to 1994, several heavy metal contaminated soils were remediated in Europe using electrochemical technology (USEPA 1997a). This in situ technology has shown good results (Table 5.15) for different types of soils and heavy metals. On the other hand, phytoremediation, used in areas with low to moderate concentrations of metals in the subsurface, has generally been applied in association with other remediation techniques. Examples of phytoremediation in different countries show the following results for metals in dry leaves (Table 5.16).

Table 5.15 - ELECTROCHEMICAL REMEDIATION TECHNOLOGY

Site	Volume (ft^3)	Metals	Initial Concentration (mg/kg)	Final Concentration (mg/kg)
Ink Industries	8,100 clayey soil	Cu	1.220	<200
		Pb	>3,780	<280
Electroplating plants	1,350 clayey soil	Zn	>1,400	600
Sawmill plants	6,750 clayey soil	As	>250	<30
Temporary landfill	194,400 clayey sand	Cd	>180	<40
Air Force Military Base	68,000 clay	Cd	660	47
		Cr	7,300	755
		Cu	770	98
		Ni	860	80
		Pb	730	108
		Zn	2,600	289

Source: USEPA (1997a)

Table 5.16 HEAVY METALS PHYTOREMEDIATION

Metal	Plant species	Percentage of metals in dry leaf (%)	Location
Zn	*Thlaspi calaminare* *Viola species*	<3 1	Germany Europe
Cu	*Aeolanthus biformifolius*	1	Zaire
Ni	*Phyllanthus serpentinus* Alyssum	3.8 >3	New Caledonia Southern Europe and Turkey
Pb	*Brassuca juncae*	<3.5	India
Co	*Haumaniastrum robertii*	1	Zaire

Source: USEPA (1997a)

At ConSoil' 98 several remediation technologies for heavy metals were presented, including hydrometallurgical techniques for the removal of metals by leaching have shown significant results with the use of citric acid (H3C), Na2 EDTA and HCl-CaCl2 (Table 5.17), the washing of fine particles from the soil contaminated with zinc by flotation and the use of technologies using phosphates, sediments of biological origin and ash for the stabilization of highly contaminated soils in mining areas (KONTOPOULOS and THEODORATOS 1998).

Table 5.17 - LEACHING TESTS FOR METAL EXTRACTION

	Pb	Zn	Cd	As	Ca	Mg	Al	Fe	Mn
Initial levels (mg/kg)	34800	2020	100	2800	72800	15200	12900	60000	3500
Citric Acid (H_3C) 3.3 moles H_3C/kg soil % 6.6 moles H_3C/kg soil %	54.6 66.1	61.4 72.8	72.0 92	3.6 10	65.2 70.9	37.5 53.3	9.3 12.1	3.5 5.5	74.3 86
Na_2 EDTA% 2.5 moles Na_2H_2L/kg soil 2.5 moles Na_2H_2L/kg soil	75.6 79.9	55.4 67.8	96.0 100	21.0 26.1	78.7 82.6	6.4 6.7	6.3 7.9	2.8 4.2	82.9 90.0
HCL 5.6 moles HCL/kg soil % 6.7 moles HCL/kg soil %	88.1 91.1	87.8 91.3	87.4 91.8	0.01 6.1	 91.7	88.1 93.9	 47	1.4 7.0	88.1 91.1

Source: PAPASSIOPI et al. (1998)

Table 5.18 – IN-SITU SEDIMENT REMEDIATION

Remediation	Contaminant type	Technology	Implementation
Removal of contaminants and biological concentration	Ni, Zn, Cu, Cd	Phytoextraction (entry of metals in the plant)	Introduction of plant species, cultivation and incineration
Chemical transformation	Metals	Metal precipitation	Salt infiltration and wetland construction
Fixation of contaminants by sorption or immobilization	Metals	Precipitation of metals as hydroxides or insoluble complexes. Encapsulation of metals in inorganic matrix.	pH increase by addition of lime or alternative hydroxides; Precipitation or adsorption near plant roots. Addition of cement; Glazing using electric current; Metal adsorption on aluminosilicate and clay surfaces.
Reduction of advective dispersion near the water surface.	All contaminants	Increased hydrological resistance. Erosion reduction. Hydrogeological isolation.	Layered coating; Sediment denitrification. Introduction of plant species; drainage diversion;
Reduction of advective dispersion near groundwater.	All contaminants	Increased hydrogeological resistance. Hydrogeological isolation.	Clay layer application.
Containment actions	All contaminants	Risk reduction	Changing the role of the navigable channel.

Source: ZEMAN and PATTERSON (2000)

In PRAGUE (2000)[38], considerable emphasis was given to the in-situ remediation of sediments, especially in port channels with large movement of industrialized products. These sediments usually need to be dredged, remediated and disposed of properly. Thus, the main in-situ remediation techniques for heavy metals in sediments are presented in Table 5.18.

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[38] *Fifth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe*, September 12-14, 2000, Prague/Czech Republic.

Studies developed by MARSEILLE et al. (2000) focused on the mobility of heavy metals in plant species (Table 5.19.) and contaminated sediments dredged from the Scarpe River in northern France. The contamination, originating from zinc metallurgy, presented the following concentrations (mg/kg) in the sediments: Zn (6000); bp (600); Mn (230); Fe (17000) and Ti (1400).

Table 5.19 - CONCENTRATIONS OF Zn, Pb, Cd and Cu IN ROOTS

Species	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Cu (mg/kg)
Urica diosca	1040±10	29.4±0.4	30±0.7	33.6±0.4
Epilobium Parviflorum	430±7	8.7±0.2	5.3±0.2	9.5±0.1
Epilobium hirsutum	330±10	7.1±0.7	5.2±0.2	8.0±0.2
Polygonum hydropiper	2400±90	88±4	210±20	63±3
Rononculus Sceleratus	1000±1600	50±60	100±140	30±43
Ellytdrigia repens	1700±50	44±4	184±6	60±3

Source: MARSEILLE et al. (2000)

As for the sites contaminated with heavy metals in the state of São Paulo and which are in the process of remediation and available on the CETESB website, it appears that in many contaminated sites, control techniques have already been applied (Table 5.20).

One of the sites assessed by CETESB is Plumbum Mining and Metallurgy Company’s, on the banks of the Furnas Iporanga/SP river. According to Pompeia (2002), the environmental recovery plan for this contaminated site includes removal and isolation of active sources of contamination, minimization of the secondary transport of heavy metals, reduction of the risk of human exposure to pollutants, making the remaining levels of surface contamination compatible with conservation and tourism uses, and establishment of mechanisms for monitoring the remaining contamination.

Table 5.20 - SITES CONTAMINATED WITH LEAD AND ASSOCIATED METALS

SITE	CONTAMINANT	IMMEDIATE ACTION	REMEDIATION
Tonolli do Brasil, Jacareí/SP	Lead	- Waste coverage; -Removal of residue/soil; -Treatment of contaminated liquids; -Environmental monitoring	To be defined
Saturnia Sistemas de Energia Ltda, Sorocaba/SP	Lead	-Waste coverage; -Prevention / water consumption; -Treatment of contaminated liquids; -Environmental monitoring	Pumping and treatment of groundwater
Ajax Accumulators Co, Bauru/SP	Lead	-Prevention of food consumption; -Environmental monitoring	To be defined
CAF Argentifera Furnas Mining Co., Iporanga/SP	Lead	- Waste/soil removal	Project - Waste removal
Emplas Metal Trade and Processing Co., Elias Fausto/SP	Lead	-Environmental monitoring	To be defined
Gerdau Co., Cotia/SP	Lead, Hydrochloric acid	-Prevention of water consumption; -Treatment of contaminated liquids; -Environmental monitoring	To be defined
Mangels Industries, São Bernardo do Campo/SP	Lead, zinc, barium	-Treatment of contaminated liquids	Pumping and treatment of groundwater
Panasonic Co., São Jose dos Campos/SP	Lead, cadmium, zinc	-Physical and hydraulic barrier; -Removal of waste/soil; -Treatment of contaminated liquids; -Environmental monitoring	Pumping and treatment of groundwater
Prolub Refinery, Presidente Prudente/SP	Lead, cádmium, chromium	- Environmental Monitoring	To be defined
Santa Gertrudes Lakes Region, Santa Gertrudes/SP	Lead, cadmium, zinc, boron	-Waste coverage; - Landfill stability; -Isolation of the area; -Prevention of water and food consumption; -Environmental monitoring	Removal of contaminant and sediment cover from the bottom of lakes
Polibrasil Resin Co. Mauá/SP	Lead, cadmium, mercury	- Environmental monitoring	To be defined

Source: www.cetesb.sp.gov.br/Solos/areas_contaminadas/relacao_areas.htm

CHAPTER 6: AREA CONTAMINATION HISTORY

Two mining-metallurgical complexes for the production of lead alloys were installed in Brazil in the 1950s, one in the Ribeira valley, on the border between the states of São Paulo and Paraná, and another in the state of Bahia, comprising the lead mines southwest of the state, and a metallurgy plant, in the Recôncavo Bay area.

The mines and processing of lead were called Mineração Boquira, while the metallurgy was called Companhia Brasileira de Chumbo (COBRAC), both with French and national capital, which originally belonged to the French group Penarroya. The mining operations began in 1959, with 26,790 t of lead concentrate and its production increased continuously, reaching, in 1979, the amount of 263,210 t of lead concentrate (ESPOURTEILLE and FLEISCHER 1980).

Mining of lead ore was carried out on the crests of the Sobrado, Pelado and Cruzeiro hills, in amphibolites from the metasedimentary sequence of the Boquira Formation, in addition to underground galleries. Lead occurs in sphalerite and galena minerals, with levels ranging from 0.10 to 39.8% of Pb.

From 1959 to 1979, the Sobrado, Pelado, and Cruzeiro mines produced a total of 4,113,533 t, with contents ranging from 8.28 to 11.90% of lead, and 1.5 to 25% of zinc. This ore was benefited by the flotation process until the beginning of 1992, when mining activities and ore processing of this element were paralyzed (ESPOURTEILLE and FLEISCHER op. cit.).

As the main environmental liability, the beneficiation process produced a large reject basin of lead concentrate, resulting from the flotation process. The basin, without waterproofing, is located 1,000m from the urban area of Boquira and contains a total of 6,000,000 t of contaminated waste, mostly lead, zinc and cadmium (NASCIMENTO 1989). Until 2002, the tailings basin was abandoned and the heavy metals contained therein were leached by rainwater into the São Francisco River.

The processed concentrate of lead ore was transported by train, over a 700 km route, from Boquira to Santo Amaro da Purificação. In 1960, COBRAC started operating at the site and produced 5,870 tons of refined Pb and 8,450 tons of slag per year. In all, the metallurgy produced until 1993, when it was abandoned, a total of 491,000 t of slag (SANTOS 1995).

6.1 Regional characterization of the study area

6.1.1 Location

The Plumbum Plant is located northwest of the urban area of the municipality of Santo Amaro da Purificação, 300m from the right bank of the Subaé River, in the Recôncavo Bay area, State of Bahia (Figure 6.1).

6.1.2. Hydrographic basin

The hydrographic basin of the Subaé river has a drainage area of 580 km2 and 46 km in length. Its main tributary is the Sergi River, with its mouth north of the Todos os Santos Bay (TSB) area, forming the island of Caraíba in its estuary.

The Subaé River has a flow of around 1.273 m3/s, at a collection point right after the contribution of its effluent, the Sergi River, north of Santo Amaro (BAHIA 1996).

The framework for the waters of the Subaé River and its tributaries was established in 1995, with the stretch between its source, in the municipality of Feira de Santana, and the estuarine zone (south of the city of Santo Amaro) classified as class 2[39] and the estuarine to its mouth, in the TSB, as class 7 (BAHIA 1995).

The water quality of the Subaé River is mainly compromised downstream, where it receives a large contribution of organic loads from the paper industries and all domestic waste and sanitary sewage from the town of Santo Amaro, making its condition critical up to its mouth.

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[39] Class 2 and 7 waters are, respectively, classified as fresh and brackish water, the former intended for domestic supply, after conventional treatment; the protection of aquatic communities; and primary contact recreation (water skiing, swimming and diving), the second is intended for primary contact recreation; the protection of aquatic communities; and the natural and/or intensive breeding (aquaculture) of species intended for human consumption (CONAMA 1986).

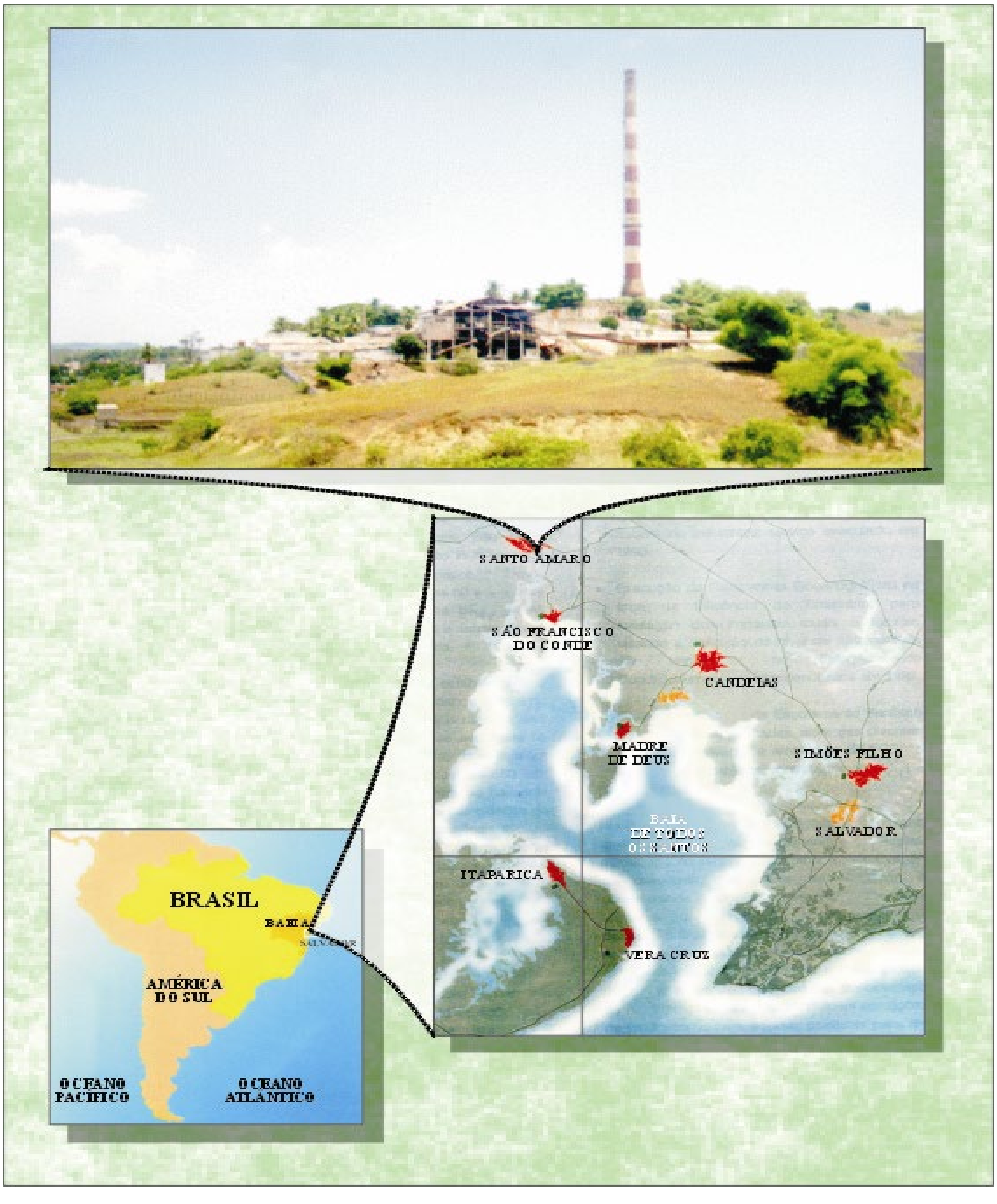

Figure 6.1 – The Plumbum Co. site location map. Source: ANJOS (1998)

6.1.3 Weather

The climate in the area is humid to subhumid and dry to subhumid, presenting, in the dry months, precipitation below 100mm, but above 60mm, average annual temperature of 25.4 °C, with average maximums of 31 °C and average minimums of 21.9 °C, with the rainy season lasting from April to June. Annual rainfall ranges from 1,000 to 1,700mm and the rivers are perennial (BAHIA 1996).

Studies on average precipitation during the months of the year, carried out based on data collected from 1961 to 1963, present, respectively, the months of May and December as responsible for the highest and lowest precipitation (BAHIA op. cit.).

6.1.4 Geology and geomorphology

Geologically, the area is inserted in the NE feature of the São Francisco craton, in the sedimentary Basin of the Recôncavo Bay, of Mesocenozoic age, delimited by a subparallel system of normal faults (rift) and presenting predominantly siltic shales, dark gray, greenish, sandstones fine and clayey from the Santo Amaro Group.

The geomorphology of the area is characterized by the Coastal Lowlands, and represented by lowered hills and tablelands with altitudes below 100 m and interfluves presenting slopes with concave aspects, carved in shales of the Santo Amaro Group of rocks (BAHIA op. cit.).

6.1.5 Soils

Most of the soils in the region are characterized as vertisols and cambisols, originating from greenish shales interspersed with limestone from the Santo Amaro Group, which occur in an elongated form, predominantly in the north/south direction, approximately 70 km long and around 10 km wide. They are characterized as clayey to very clayey soils, with clay content from the montmorillonite group, which exhibit contraction and expansion characteristics depending on their moisture content, moderately drained to poorly drained and with low permeability (BAHIA 1996).

6.1.6 Anthropogenic Actions

The main anthropic actions that occur in the watershed of the Subaé River are:

a) Deforestation of areas close to springs and river courses, inducing silting process and affecting its water regime;
b) the bad use of the soil in agricultural activities, removing the vegetation cover, what may cause the erosion of the margins and the silting of the riverbeds;
c) the use of vinasse for fertilization and irrigation of sugarcane;
d) mining of sand on the banks and bed of the Subaé river, close to the Plumbum Co., facilitating the erosive process and, consequently, the silting up of the urban area of Santo Amaro da Purificação;
e) inadequate deposition of slag in urban areas and on the banks of the Subaé River, compromising the soil quality and possibly polluting surface and groundwater;
f) disorderly occupation of the river estuary by low-income families and impactful enterprises, causing the destruction of mangroves on the outskirts of the towns of Santo Amaro and São Francisco do Conde, and
g) the occurrence of landfills and the deposition of garbage near the drainage network (ANJOS 1998).

6.2. The PLUMBUM Co. environmental liabilities

The installation of COBRAC did not comply with any project that considered aspects inherent to the vulnerability of the Subaé river basin, the area's climate, its proximity to the urban area of Santo Amaro, nor did it include measures to control emissions and toxic waste produced by the metallurgical process[40] (ANJOS 1998).

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[40] Studies carried out in the Subaé River Basin identified that the pollution from the Plumbum Co. is due to the installation of metallurgy in the area where low-speed winds and constant temperature inversions predominate, making dispersion difficult and favoring the precipitation of particulates in the urban area; the proximity of the metallurgy to the bed and flood areas of the Subaé River; the overflow of the tailings basin, in periods of high rainfall; the low flow of the Subaé River, making it difficult to dilute and disperse the liquid effluents released without treatment; the inadequate deposition of slag in landfills, and its reuse for the construction of roads and residential areas, significantly increasing the contamination of the soil, surface water and the populations residing in the vicinity; of particulates expelled by the metallurgy

Thus, in 1961, a year after the beginning of the production of lead alloys, the headlines in the area's largest newspaper "O Archote" read, "COBRAC: Lead and Death Manufacturing Co."[41] . The report included a study by Dr. Hans Dittmar, hired by the local community alarmed by the high death toll of cattle and pigs. The research carried out at that time showed the environmental incompatibility of the undertaking.

According to Oliveira (1977), the study by Dr. Dittmar concluded for the shutdown of the metallurgy operations, based on the violation of Decree No. 50,877 of June 29, 1961, regarding the pollution of watercourses. The problem was solved with the acquisition by COBRAC of all the land belonging to the cattle ranchers affected and compensation for the dead animals.

Measures to control atmospheric contamination were developed by the metallurgy, in addition to the acquisition of land and animals, so that it could continue its production without so aggressively affecting the environment (especially the death of animals, the main reason for requesting the study) of its surroundings. Hence, it was only at the beginning of the 1970s that the first research on contamination in the area was carried out by the Federal University of Bahia[42].

As a result of the study on the contamination of the Subaé River, the Special Secretariat for the Environment of the Federal Government (SEMA) signed an agreement with the Center for Research and Development (CEPED), currently the executing agency of the environmental policy of the

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chimney, contaminating edible vegetables, surface water, soil and the populations surrounding the metallurgy (ANJOS op. cit.)

[41] "Claiming that the processes used by COBRAC in the industrialization of lead were among the most primitive, the chemical engineer Hans K. Ditmar states, after lengthy and meticulous studies, that the population of Santo Amaro was in great danger, in view of the emanations of highly poisonous gases from that factory. He was hired by a group of disadvantaged people, led by Mr. José Andrade and, according to the studies, the poison contained in the gases emanated from the lead factory was responsible for the death of about 250 donkeys, 200 head of cattle, in addition to many other animals. It is also known that people have also been victimized. The fact was denounced by the President of the Chamber, Mr. Viraldo de Senna, who presented the engineer's report in plenary and, in view of the danger to life to which the population is subjected, requested immediate action by the responsible authorities. In his report, Dr. Hans Dittmar demonstrates deep conviction in his statements, having even pointed out that he agreed to debate the subject anywhere in the country. According to the aforementioned technician, the danger of emanations increased considerably with the rains." "O Archote" newspaper of December 16, 1961.

[42] A study titled "Polarographic determination of Pb^{+2} and Cd^{+2} in waters of the Subaé River – Santo Amaro-Ba", carried out by Prof. José Oscar N. Reis, investigated the contamination of the Subaé River by effluents from the metallurgical plant, which at that time released the effluents directly into the river, found values for the studied metals that exceeded the maximum limits allowed for the waters and established by the World Health Organization (WHO) (OLIVEIRA op. cit.).

State of Bahia, and the interdisciplinary team of the Recôncavo Bay Ecological Studies Project (PEER) at UFBA, with the objective of investigating the levels of contamination with heavy metals in the waters, sediments and fauna in the Todos os Santos Bay area (OLIVEIRA 1977, TAVARES 1990).

The first stage of the study demonstrated that zone III, comprising the estuary of the Subaé River, represented the most critical zone, where the concentrations of Pb and Cd found in molluscs were, on average, dozens of times higher than the limits for consumption established by the WHO. In addition, according to the company itself, the amount of cadmium discarded into the environment during this period was approximately 395 t, of which, about ⅔, was released directly into the Subaé River (OLIVEIRA op. cit.).

In compliance with Law No. 3,163 of 10.04.73, which requires preventive control of pollution, COBRAC requested CEPED in 1975 for a license for the expansion and modernization of the metallurgy. The project proposed by COBRAC presented new control technologies for liquid and atmospheric effluents, and provided for an increase in the production of lead alloys from 30,000 tons/year to 45,000 tons/year.

CEPED's technical propositions on the expansion license[43] (although the company did not have an operating license due to the lack of specific regulation) was based on studies carried out in partnership with SEMA on the contamination of the Subaé River, and its implication in the implementation of important fish farming projects in Todos os Santos Bay, which would make it self-sufficient in fishing. The CEPED team responsible for the analyses presented an unfavorable report on the project presented by COBRAC.

Based on the enrichment of Pb and Cd in the sediments of the Subaé estuary (SOUZA et al. 1978 apud TAVARES 1990), new studies found high concentrations of cadmium in oysters, crabs and mussels in the region studied (TAVARES 1978 and TAVARES et al. 1983 apud TAVARES op. cit.).

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[43] According to the team responsible for the analyses, even COBRAC presenting the best viable technology, it would not obtain “zero” content of cadmium and other metals in its effluents, and if the expansion or maintenance of the current situation were authorized, there would be a risk of an uncontrollable and irreversible worsening (OLIVEIRA 1977).

Once contamination in shellfish was confirmed, investigation was carried out to include consumer populations (CARVALHO et al. and CARVALHO 1980 apud TAVARES op. cit.). The studies were carried out in three villages in the Subaé estuary in an unexposed population of fishermen in the south of the State, as a reference. The studies showed significant levels of Pb and Cd metals in Subaé fishermen in relation to the reference population.

As for the pollution caused by atmospheric emissions and the slag produced by COBRAC and distributed to the population for paving backyards, schoolyards and roads, in addition to chimney filters used as carpets and bed mattresses, studies were initiated in 1980 to evaluate the effects of the presence of metals on fruits, vegetables and population aged 1 to 9 years, within a radius of 900 m from the factory chimney.

PETERSEN (1982) apud TAVARES (op.cit.) studied the contamination in fruits and vegetables and found the highest concentrations of metals in leafy vegetables and the lowest in local fruits. Regarding the child population, blood and hair were established as bioindicators in a population of 592 elements mostly contaminated with the studied metals (CARVALHO 1982, CARVALHO et al. 1984, CARVALHO et al. 1985, CARVALHO et al. 1986 and SILVANY- NETO 1982 apud TAVARES 1990)

The findings were presented to state authorities and served as a basis for the State Council for Environmental Protection (CEPRAM) to demand the following mitigating measures from COBRAC:

- remove the resident population within a radius of 500 m, to other locations;
- take charge of the treatment of affected children;
- build a 90 m high chimney, where the air emissions should converge;
- install an efficient filtration system at all sources of particulate matter, and
- suspend the donation of slag and used chimney filters and provide clothes for factory employees, for exclusive use at work.

According to the State Environmental agency, the Center for Environmental Resources (CRA), all measures were complied with by

COBRAC, except the first, on the grounds of economic unfeasibility for the 500 m radius (TAVARES op. cit.).

Five years later, in 1985, a second investigation was carried out in the area for populations in the same age range as in the previous study, and residents between 300 and 900 m from the factory chimney, to assess the effects of the measures established by CEPRAM, in 1980. The results indicated a decrease in the degree of intoxication in children, but the values of Pb and Cd in the child population remained high, with the occurrence of new cases (TAVARES op. cit.)

In 1987, investigation was carried out with the aim of evaluating the effect of waste on the health of the child population caused by the presence of slag in the peridomestic soils around COBRAC. Soil samples were collected during the 1980 and 1985 campaigns and a decrease in Pb and Cd contents was observed in the soils during the five years between the two studies.

In 1989, a new study on atmospheric emissions at two urban occupation points, 526 to 955 m from the chimney, was carried out by PEER. The results, together with the studies carried out in the field campaigns of 1980 and 1985, in addition to studies on contamination in peridomestic soils, were analyzed by TAVARES (1990) and who concluded:

- the aerial emissions produced by metallurgy violently hit the child population residing within a 900m radius of the COBRAC main chimney;
- lead concentrations in children's blood were very high in 1980, and only surpassed by those identified in similar studies in Idaho, USA;
- Cadmium concentrations in the children's blood were the highest known in the world, due to environmental exposure, while clinical and subclinical effects were not observed. Kidney damage, which is a long-term clinical effect (~10 years), may still begin to appear in the studied children;
- the distribution of slag throughout the region constitutes an additional factor for the increase in cadmium levels, but not lead, in the children's blood;
- the profile of the child most at risk of poisoning in Santo Amaro da Purificação is: black child, malnourished, young, living for at least 6

months in an area close to the metallurgy (<500m), probably on the side of the road and child of metallurgy worker;

- the profile of the child most at risk of absorbing Cd in Santo Amaro da Purificação is: white child, with worms and living close to the metalworks, with a house containing slag;
- the metal content in the soil contributed to the high cadmium and lead values in children;
- restorative/mitigating measures taken by the factory significantly reduced cadmium levels and, to a lesser extent, lead levels, as well as the levels of these metals in infant blood. However, new cases of risk of intoxication continued to emerge, indicating that such measures were insufficient;
- cadmium levels in the child population were reduced by 67.8% in the period from 1980 to 1985. Even so, 89% of this population had cadmium levels above the normal reference value, and
- lead levels were reduced by 37.7%, yet 26% of the child population had concentrations above the US tolerance limit and 4% above the critical limit; and the high leaching of cadmium contained in the soil seems to have been the main responsible for the reduction of cadmium levels in the children's blood during the period.

In 1988, COBRAC became part of the Trevo Group and was renamed Plumbum Mining and Metallurgy Company. In 1991, it applied for an operating license for its lead alloy production facilities in Santo Amaro.

In early 1993, the Development Bank (DESENBANCO) approved the first financing for the POC/Automatic line for the environment for Plumbum, with a view to installing anti-polluting equipment in its factory located in Santo Amaro. However, the company did not conclude the negotiations.

In the same year, through Resolution No. 812/93, the issuance of the operating license granted by CEPRAM was authorized. During licensing, it was found that the slag was not properly classified, one of the reasons being that the toxicity characterization test, carried out in 1986, used the CETESB standard No. 15.510, outdated at the time, therefore making it inadequate (SANTOS 1995).

The resolution that established the Operating License[44] included an extensive list of control measures and, possibly, was one of the factors that induced the deactivation of the enterprise.

Within this framework, the publication "Environmental Epidemiology: A project for Latin America and the Caribbean", edited by the Pan American Center for Human Ecology and Health (PACHEH), included the case of Plumbum as a reference for lead and cadmium contamination in Brazil, in Santo Amaro da Purificação (PACHEH 1993).

Also at that time, Public Civil Action No. 264/93, filed by the Public Prosecutor's Office in Santo Amaro, asked the State Environmental agency for expertise regarding the contamination from the Plumbum Co. The thirteen issues required in the Public Civil Action clearly demonstrated the extent of contamination and the environmental damage caused by the company. It is important to emphasize, among the measures required to control contamination, the implementation of a free epidemiological surveillance system for intoxication by heavy metals (Pb and Cd) in the city of Santo Amaro.

Although the Operation License issued in June 1993 required in its first article - paragraph XI, the performance, within 90 days of a new leaching and solubilization test for the characterization of the slag, contemplating the parameters: Pb, Cd, Zn , As, S and Cu, it was the CRA that presented, in December 1993, the result of analyses of slag samples, characterized as hazardous waste for lead and cadmium (SANTOS 1995).

However, in early January 1994, alerted by the newspapers about the shutdown of Plumbum's operational activities, the CRA agency verified, through inspection, the closing of all productive activities and the dismissal of all employees in the operational area.

From that moment on, CRA sought together with the Plumbum Co. to carry out a final disposal plan for the slag and monitoring of surface and

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[44] Resolution No. 812 of June 20, 1993, which established the operating license, required an expressive number of measures, including: carrying out new slag characterization tests, contemplating the parameters Pb, Cd, Zn, As, S and Cu ; submit an environmental monitoring plan for the water table in the slag disposal area of influence, based on the use of piezometric wells, carry out self-monitoring of the Subaé River, upstream and downstream of the overflow point of the effluent containment system, for the Pb and Cd parameters, carry out epidemiological studies to assess the industrial impact on the health of workers and the population, in addition to requesting a solution from technology centers for remediation of slag.

underground water possibly contaminated with the slag leachate. However, in view of Plumbum's denial regarding its toxicity, it took two years (Table 6.1) for the company to accept slag as hazardous waste (SANTOS 1995).

However, before the CETESB result, which characterized slag as hazardous waste, Plumbum rented its facilities to a napkin manufacturer called Boka Loka Industries. In view of the incident, CRA notified the said company to apply for environmental licensing.

CRA’s Technical Propositions no. 055/95-SFA/CRA determined that the Boka Loka factory could not start operating before the environmental requirements provided for in the Environmental Legislation of the State of Bahia were adopted and the implementation of the Plan for the final disposal of the slag produced by the Plumbum Co.

During the years 1996 and 1997, the reuse of this area was questioned by various segments of society, including newspapers with wide circulation in the state[45], the Santo Amaro City Council and researchers from UFBA and USP, due to the great potential for contamination. existing in the area and the contradictions observed in Boka Loka's environmental licensing process, with the factory operating without licensing until September 1998.

In the meantime, three new studies were carried out by the PEER Group: the first published in 1995, with cattle grazing on Plumbum's premises, revealed that the rates of chromosomal alterations were higher among animals from Santo Amaro (5.6%) than among control animals (0.3%), while the mean lead level in Santo Amaro cattle was 24.4 µg/dl and 1.7 µg/dl among control animals; the second study showed high concentrations of lead, cadmium and organochlorides in sediments and molluscs from the entire ecosystem north of Todos os Santos Bay (TAVARES 1996); and the third in 1998, in children exposed to slag stirred up from the sub-base of the paving the Ruy Barbosa Street, in Santo Amaro, when they were opened for the implementation of the Bahia Azul Project, an environmental sanitation program for Salvador and the cities surrounding the

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[45] “Factory accused of polluting Subaé will be inspected today”. The company's industrial manager, Odair Gonçalves, denies that his factory is polluting the municipality and questions the report by geologist José Ângelo. He says he had requested analyses through three different laboratories and hopes that the tests confirm that the factory does not cause any damage to the environment. He guarantees that he has an operating license from the city hall and that since 1994 he has asked the CRA for an authorization license, while all the other bureaucratic steps have been completed (Jornal A Tarde, 11/11/97). Subsequently, the results of the reports prepared by Boka Loka were publicly presented.

TSB found that the mean level and the respective standard deviation of the children's PbS was 17.1±7.34 µg/dl (CARVALHO et al. 2001)

In December 1998, the Department of Mining Engineering at the Polytechnic School of the University of São Paulo (PMI) concluded the first investigation on the toxicity and contamination routes resulting from the leaching of slag on the Plumbum's premises (soil, surface, and groundwater), the main geochemical processes and physical-chemical parameters responsible for the retention or availability of metals, as well as a proposal for a remediation and monitoring technique for the area.

The investigation concluded for new research being carried out in the area, and was called “Strategies for remediation of a site contaminated with heavy metals – the case of the Plumbum Co.”.

The studies carried out by USP served as the basis for the Urban Master Plan for the Development[46] of Santo Amaro, approved by the City Council in December 2000, with one of the main propositions being the definition of the Plumbum region and its surroundings as an area unsuitable for human activity. In addition to the master plan, this research resulted in the PURIFICA Project financed by FINEP and developed from 2000 by UFBA, USP, CEPED and CRA.

Concurrently with the Purifica project and with funding from the State of São Paulo Research Foundation (FAPESP), USP continued investigations at the Plumbum site, evaluating the wetland technique as an alternative control measure to contain heavy metals from of the slag leaching process.

In January 2001, another research project developed by the University of São Paulo began, the project called “The impact of supplementation with iron and vitamin C on blood levels of lead, in children exposed to different levels of lead”, carried out by the Department of Nutrition at the Faculty of Public Health at USP, with funding from FAPESP.

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[46] Santo Amaro's Urban Development Master Plan was the first attempt to assess contaminated soil throughout the city. Through 10 soil samples collected in different streets, the total lead concentrations were analyzed and their results compared with the concentrations used in Europe for soil multifunctionality. These results were taken from the the City Council Master Plan.

Table 6.1 – EVOLUTION OF UNDERSTANDINGS HELD BETWEEN CRA AND PLUMBUM, DURING THE PERIOD OF 1994 AND 1995.

12/14/93	At CRA's request, CEPED carried out new tests to characterize the slag, resulting in hazardous waste.
01/12/94	First agreement signed between CRA and Plumbum, when the company undertakes to carry out four corrective measures.
02/24/94	Inspection carried out at Plumbum and found that no measurements were taken
03/15/94	Plumbum requests new deadline for delivery of the Decommissioning Plan
04/13/94	CRA extends deadline for delivery of the Deactivation Plan.
05/25/94	Plumbum presents a Plan and result of the toxicity of slag as inert waste. Meanwhile, the result of the same sample carried out by CEPED at the request of CRA characterized slag as hazardous waste.
07/0794	The CRA does not accept the Deactivation Plan proposal.
09/27/94	Plumbum presents a Plan and requests joint sampling with CRA and sending it to specialized laboratories.
08/11/94	Plumbum sends results of analyzes carried out by SGS do Brasil (inert waste), while the CRA result carried out by CEPED characterized the same samples as hazardous waste.
08/03/95	Re-analyses of samples by CETESB.
09/27/95	Inspection and finding that no required measures were taken.
10/26/95	CETESB communicates to CRA that it has sent analyses results to Plumbum.
06/11/95	Plumbum was notified to send results to CRA.
11/16/95	CRA receives result of re-analyses of slag characterized as hazardous waste.
11/10/95	CRA requests a hydraulic encapsulation project for the slag valley or Plumbum presents a control proposal that suits it, as long as it meets the environmental control requirements. Plumbum alleges a lack of resources to execute the propositions.

Source: SANTOS (1995)

The work had an immediate social application, as it looked for supplementing 520 preschool children with iron and vitamin C exposed to different levels of lead. The study separated children, according to their blood iron levels, into 3 groups: anemic; iron deficient; and adequate, identifying the respective levels of lead (RONDÓ et al. 2000).

The study was conceived, initially, as a result of a report at national level, by the Globo News Network, in August 2000, on the contamination of the Plumbum site in Santo Amaro da Purificação, and was carried out by the Polytechnic School of the University of São Paulo for evaluation of the area.

In April 2001, the local Court confirmed the receipt of funds for the project to remediate the area contaminated with slag[47], following the recommendations of the Technical |Report No. 055/95-SFA/CRA, which proposed encapsulation as a possible alternative technology,.

In the same year, an investigation was presented by the PEER team on the evaluation of some aspects of Plumbum's environmental liabilities. The work evaluated the concentrations of lead and cadmium in different matrices of bovine and human blood, human urine, soil and grasses around Plumbum's premises. The most significant results were those that assessed that women residing in the vicinity of Plumbum who have chromosomal alterations of 6.5% against 1.5% of the research control area, with recommended values ranging from 1 to 4% (COSTA 2001).

On October 25, 2001, a Public Hearing was held at the National Chamber of Representatives in Brasília, at the request of the Commission for the Defense of the Consumer, Environment and Minorities, to discuss the environmental pollution caused by lead and cadmium slag in the municipality of Santo Amaro in the State of Bahia. In this event, the result of the studies developed by USP, UFBA and the actions developed by the Public Ministry and representatives of civil entities were presented.

Subsequently, the commission evaluated “in loco” the complaints presented in Brasília, concluding with the constitution of a multi-party commission, to evaluate and propose actions for the problem of environmental contamination of Plumbum.

On December 4, 2002, a second public hearing was held with the objective of “gathering subsidies for the preparation of remediation plans for sites and people contaminated with heavy metals in Santo Amaro da

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[47] The resources came from the environmental public civil action against Plumbum Mining and Metallurgy Co., listed under n. 302/97.

Purificação and for the closure of the lead mine in Boquira/BA". The hearing reached the following conclusions:

- after 1 year of activity, the Committee was unable to locate the address of Plumbum, belonging to the Trevo Group, originally from Rio Grande do Sul;
- the French group PENNAROYA exonerated itself from the blame, attributing that the majority owner of the enterprise was the Brazilian group;
- no investigation was carried out on contamination in Boquira;
- the environmentalist group GREENPEACE offered to help with the remediation of Plumbum due to its experience in recovering contaminated areas, but was unaware of the problem in Santo Amaro, so much so that in its report on "Corporate Environmental Crimes in Brazil" presented in Johannesburg, South Africa South during the Summit for Sustainable Development, in 2002, there is no record of Plumbum contamination in Santo Amaro;
- two alternatives evaluated in the field and laboratory for remediation of the area were presented to the Committee, one by UFBA proposing the leaching of metals from the slag and its reuse as a mineral aggregate, the second by USP with investigation that verified the efficiency of the wetland area Plumbum in controlling the migration of metals to the Subaé River, and
- a third alternative, phytoremediation, was presented by a French specialist who presented plant species used in France to remove metals from the soil and subsequently incinerate the metals.

The Commission decided to continue the activities, initially scheduling an audience with the Governor of the state of Bahia. Also present were representatives of ANA (National Water Agency), FUNASA (National Health Foundation), and IBAMA (Brazilian Institute for the Environment).

It is important to emphasize that no representative of the communities of Santo Amaro da Purificação and Boquira was invited to the public hearing, as they were the main and true stakeholders in the solution of the problem. Another important and unexplained fact is what motivated the Trevo Group to develop a large environmental recovery project in its mines and lead metallurgy installed in Vale do Ribeira in the states of São Paulo and Paraná, while its undertakings in the state of Bahia find themselves abandoned.

6.3 The legal process involving the coating of the slag

In the case of the Plumbum Co., the Center for Environmental Resources never required a project to remediate or recover the site, nor a survey of its environmental liabilities. From 1994 to 1995, they requested incomplete procedures, which Plumbum never fulfilled, such as self-monitoring of groundwater, slag final disposal plan, plan to deactivate the decantation basins, and transferring all the slag scattered on the industry's land to the valley that was already being used for slag disposal. In addition, it encouraged the installation of a napkin[48] manufacturer on the metallurgy premises.

Plumbum, even without complying with any measure required by the CRA, according to CUNHA and ARAUJO (2001) pg. 83, in 1995, "through a contract, Plumbum leased part of its facilities for the implementation of a napkin manufacturing industry that, among other obligations, should take care of the environmental liabilities. None of the contracted measures was effectively adopted". These facts reflect Plumbum's lack of commitment to carrying out recovery measures for the abandoned site, transferring the responsibility to another undertaking.

Among the measures required by the CRA, in 1995 the "surface encapsulation of the slag valley or hydraulic encapsulation within the procedures established in the NB-1183 and NB-1264 Standards" (SANTOS 1995) was requested.

However, at no time did the company offer to comply with such determinations, abandoning the project. Subsequently, with the continued use of slag through the City Hall and the State Department of Roads and Highways (DERBA), Public Civil Action 302/97 was instituted by the Public

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[48] "With regard to the request made by the Boka Loka Co., to use Plumbum's facilities to implement a paper manufacturing plant, it is understood as a positive point, as it eliminates the possibility of Plumbum returning to its activities, as well as the possibility of generating employment for the Municipality of Santo Amaro, provided that the environmental requirements provided for in the State Legislation are adopted" (SANTOS op. cit.).

Ministry, requesting compliance with the recommendations of the CRA to "encapsulate" the scum.

The surface "encapsulation" of the slag valley or "hydraulic encapsulation" should be done in compliance with Technical Standards NB-1264 for the storage of non-inert waste or Technical Standard NB-1183 Storage of hazardous solid waste, current NBR-12235 Storage of waste hazardous (1992), and having as a minimum prerequisite (SANTOS op. cit.): control of soil and water pollution, such as: providing a waterproofing system at the base of the storage location; and provide a solids retention system.

In 1995, even indicating "encapsulation", Plumbum was required to present a control proposal that best suited it, as long as it met the relevant environmental control requirements. For failing to meet these requirements, Plumbum was obliged by the court to "encapsulate" the slag, in addition to technical monitoring and inspection by the court expert, the Center for Environmental Resources and the court expert in Process 264/93.

However, through a complaint to CRA, the "encapsulation" project and the ban on UFBA technicians and professors from Plumbum facilities spread in the newspapers. The fact was reported in an article in the newspaper A Tarde on 04/24/2001 "CRA will charge the person responsible for grounding the lead[49]" , and on 04/25/2001 "CRA notifies company in Santo Amaro[50]" .

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[49] "The Center for Environmental Resources (CRA) communicated this Tuesday that it will warn and fine the company responsible for grounding works for lead slag from the former facilities of the extinct Companhia Brasileira de Chumbo (Cobrac), in the municipality of Santo Amaro da Purification. The works were started without licensing or authorization from the state environmental agency." "Part of the 400,000 tons of lead and cadmium slag, heavy materials highly harmful to humans, that Plumbum Mining and Metallurfy Co. left in Santo Amaro da Purificação after 44 years of activity, have been buried since last Friday by Grupo Trevo , using a technique called encapsulation. Authorization would have been given by Judge Maria do Carmo Caribé, despite the fact that the area is the subject of studies trying to find an adequate solution to the problem." "The complaint was made yesterday by teacher Virginia Monteiro, environmentalist and former city councilwoman. According to her, the works have been carried out without any authorization from the Center for Environmental Resources (CRA), which in 1998 signed an agreement with the University of São Paulo (USP) and the Federal University of Bahia (UFBA)."

[50] "For the CRA, the adoption of any measures, even those determined by the Courts, that prevent the risks of contamination, must be adequate to the environmental norms and, therefore, lack the due environmental licensing, explains the biologist Epaminondas Daltro, inspection coordinator CRA Environment. "That is why the company had to present the technical project of the work and a copy of the court order attached to the application to obtain the environmental license", explained Daltro".

The slag "encapsulation" works carried out by Plumbum were not interrupted and there was no further information about the request for the environmental license that the company had to present.

In this way, the project was carried out without the supervision and authorization from the CRA agency. It is important to emphasize that there was no representation of the Environmental Agency at the meeting scheduled by the town's Court[51], to discuss the problems inherent in the area. The Mayor of the Municipality, professors from UFBA and USP, the Public Prosecutor, and Technicians from the City Hall, all attended.

Furthermore, the "encapsulation" project was carried out without the presence of experts in case 264/93. This procedure, among others, is questioned by the Public Ministry through the town's Public Prosecutor. In an official letter dated October 26, 2001, the Public Prosecutor asked for the opinion of an expert, as there was no follow-up by the plaintiff's assistant experts. "First, because it is impertinent, as the follow-up is a matter of liberality and, second, because it is partially untrue, since the collection of field material was accompanied by the subscriber, it is emphasized, even without the advertised integral monitoring of the assistance of the defendant", in addition to the "judicial report presents partiality that nullifies it, besides methodological inaccuracies and flagrant contradictions that, with due respect, need to be commented and repaired: It is imperative, therefore, to challenge the judicial report in the face of the absence and confirmed lack of technical capacity in disciplines outside the medical field" (NETO 2001).

6.4. Characterization of contamination at the Plumbum site

Plumbum, deactivated in 1993, produced and indiscriminately deposited approximately 490,000 t of slag contaminated with heavy metals (Photo 6.1) - mostly Lead (Pb) and Cadmium (Cd). Part of the slag was used by the population of the municipality of Santo Amaro in gardens, patios, squares and school areas and, until 1998, was used by the local

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[51] "The magistrate Maria do Carmo Tamazzi Caribé assured that all encapsulation actions have been supervised by experts from the local Court, and that this measure was a request from the former prosecutor of the city, dated 1997, when she assumed the position in the county. "I accepted the request of the Public Prosecutor's Office in full because I believe that it is the most correct thing to do and I will do even more, stressed the judge, without however advancing the "something more", which she hopes to reveal only today, at the hearing that will be held for the press."

administration to pave streets and landfills and by state agencies for road construction (CRA 1992).

Photo 6.1 – In the center of the photo, in a dark color, you can see the slag slurry contaminated with lead and cadmium.

The waste was deposited in the open, mostly in the valley between the buildings of the metallurgical plant and the Subaé River, without any measure to prevent contamination of the soil, groundwater and surface water.

The main sources of contamination identified at COBRAC, during the investigation of the Center for Environmental Resources, in 1992, at the request of the Public Ministry, were: **i)** particulate matter expelled through the chimney; **ii)** liquid effluents dumped directly into the Subaé River or by overflow from the tailings basin, and **iii)** slag, considered innocuous by the entrepreneur and used for the most diverse purposes.

However, after the abandonment of Plumbum's metallurgy facilities, the slag became the main source of contamination on the site. For preliminary characterization of contamination in the area, procedures established by MARKER et al. (1994), POMPEIA (1994) and GLOEDEN et al. (1997) using sequential procedures for managing contaminated sites.

The investigations were carried out in a pilot area of Plumbum where, for the most part, slag enriched with heavy metals was deposited and a drainage from the slag leachate that flows into the Subaé River.

6.4.1 Composition of concentrated lead ore and other inputs

The concentrated lead ore used by Plumbum originated in Brazil, from the Boquira mines, and was imported. According to OLIVEIRA (1977) is the following (Table 6.2):

Table 6.2 - COMPOSITION OF CONCENTRATED LEAD ORE

Components	Boquira Ore	Imported Ore
Pb	69.30%	75.60%
Fe	2.61%	2.54%
Zn	3.14%	2.39%
CaO	Traces	0.81%
MgO	2.20%	0.57%
Al_2O_3	0.69%	Traces
S	12.94%	14.75%
SiO_2	7.27%	1.00%
Ag	0.0251%	0.0019%
Cu	0.050%	0.432%
Cd	0.037 to 0.140%	Traces

Source: OLIVEIRA (1977)

Other inputs used in the metallurgical process (OLIVERA 1977) included coke (Fixed carbon 89.35%, Sulfur 0.98%, 9.43% and volatile materials 1.22%), oyster gravel (CaO 43.40%, SiO_2 5.74%, MgO 1.05%, Al_2O_3 0.65% and Fe 0.55%), iron ore (Fe 64.74%, SiO_2 3.53% and Al_2O_3 2.16%) and miscellaneous (zinc, caustic soda, coarse salt, saltpeter, sulfur in flakes and calcium chloride).

6.4.2 Preliminary characterization of area contamination

The first stage of the study consisted of the characterization of the source of pollution, through the evaluation of the degree of contamination of the slag, through quantitative chemical analyses for leaching and solubilization of the residue. After checking for the environmental danger, an attempt was made to characterize the concentrations of contaminants around the source (soil and surface and groundwater), carried out in a pilot area on the premises of the enterprise, using techniques (installation of wells to collect water) and standardized procedures (soil and water sampling and chemical and physical analyses of pre-established parameters).

6.4.3 Characterization of the source of pollution

During the entire production phase of the Plumbum Co., the slag contaminated with heavy metals was randomly deposited on the industrial land. Subsequently, at the request of CRA, the slag found scattered on the premises of the enterprise was gathered and deposited in a valley, between the buildings of the metallurgical plant and the Subaé River, again without any measure to prevent soil and groundwater contamination. and superficial (SANTOS 1995).

For the characterization of the source of pollution, ten samples were collected (ESC/01 to 10), using the procedures of NBR 10.007, distributed equidistantly in the longitudinal feature of the body of the dam. The samples were prepared and analyzed according to the procedures recommended in NBRs 10005 and 10006. The parameters established for analyses were Pb, Cd and pH, using the analytical method of Atomic Emission Spectrometry with Flame, Hydride Generation and Cold Vapor (ANJOS 1998).

The results of the chemical analyses, presented in Table 6.3, unequivocally demonstrate that the slag is a hazardous waste, according to NBR 10.004. This conclusion is due to the Pb concentrations in the leaching and slag solubilization extracts.

Table 6.3 - RESULTS OF SLAG ANALYSES

Sample Id.	Leaching (1)		Solubilization (2)		pH	
	Pb (mg/l)	Cd (mg/l)	Pb (mg/l)	Cd (mg/l)	Initial	Final
SLAG/01	115.8	0.22	2.98	0.16	6.3	5.1
SLAG/02	159.0 (3)	0.30	0.96	0.26	6.3	5.1
SLAG/03	73.2	0.13	0.38	0.07	6.5	5.1
SLAG/04	72.5	0.12	4.95	0.10	6.3	5.1
SLAG/05	14.6	0.05	0.52	0.28	6.3	5.0
SLAG/06	119.1	0.04	0.50	0.28	6.3	5.2
SLAG/07	138.2	0.19	0.12	0.01	7.0	5.2
SLAG/08	30.6	0.12	0.29	0.03	6.4	5.2
SLAG/09	1.8	0.05	0.09	0.005	6.4	5.2
SLAG/10	47.2	0.05	0.73	0.03	6.0	5.1

Source: ANJOS (1998)

(1) leaching limit: Cd=0.5 mg/L, Pb=5.0 mg/L. Source: NBR 10.005
(2) limit for solubilization: Cd=0.005 mg/l, Pb=0.05 mg/l. Source: NBR 10.006
(3) Pb and Cd values in bold represent levels above ABNT limits

6.4.4 Characterization of surface water

The characterization of surface waters was based on preliminary results carried out by CRA (SANTOS 1995) in spring waters, immediately downstream of the slag dam, having as environmental indicators the concentrations of metals Pb and Cd, and that presented in some samples concentrations of these metals above the limits established by current legislation.

Based on these results, surface water sampling was collected at the Plumbum site. The place chosen was in a valley where most of the slag was deposited, so to confirm the contamination of these waters. This drainage is of an intermittent nature and its water flow occurs frequently during the months of March to December, as the water comes from the rainfall.

Sampling was carried out in accordance with the procedures of the Water Sample Collection and Preservation Guide (CETESB 1988), and the analytical method for determining metal concentrations was Atomic Absorption Spectrophotometry (Table 6.4).

Table 6.4 - CONCENTRATIONS OF Pb AND Cd, AND PH IN SAMPLES OF SURFACE WATER FROM THE PILOT AREA

SAMPLE ID	Pb (mg/L) (1)	Cd (mg/L) (2)	pH
SWAP-01	<0.05	<0.005	9.6
SWAP-02	**3.13 (104.3)**	**0.013 (13)**	8.3
SWAP-03	**4.67 (155.6)**	**0.069 (69)**	8.0
SWAP-04	**7.81 (260.3)**	**0.084 (84)**	6.8
SWAP-05	**0.13(4.3)(3)**	**0.070 (70)**	**6.8**
SWAP-06	<0.05	<0.005	6.7
SWAP-07	<0.05	<0.005	6.5
SWAP-08	<0.05	<0.005	6.5
SWAP-09	<0.05	<0.005	7.5
SWAP-10	<0.05	<0.005	7.5

Source: ANJOS (1998)

(1 and 2) maximum levels for potentially harmful substances: Pb = 0.03 mg/LPb and Cd = 0.001 mg/LCd. CONAMA Resolution 20/86 for class 2 water bodies.
(3) number of times the concentration obtained is greater than the maximum allowable concentrations.

The sampling of surface waters in the valley of the slag dam was done with the collection of ten samples distributed at selected points throughout the drainage of the valley to the Subaé River. The purpose of this procedure was to identify trends in lead and cadmium contamination and to verify pH values.

The concentrations for Pb and Cd detected at the surveyed points demonstrate that: upstream of the dam, the levels of metals are close to the established maximum limits; immediately downstream of the dam, in the marshy zone, values for Pb and Cd of up to, respectively, 260 and 84 times the maximum values were found at the 4 selected points, while all the other 5 points downstream revealed concentrations close to the maximum values. Given these facts, the results suggest that the vast majority of Pb and Cd leached and/or solubilized from the slag are retained in the wetland, due to the basic pH found in the drainage and the processes of precipitation, sorption and complexation operating in this system (ANJOS 1998).

6.4.5 Groundwater Characterization

Groundwater sampling was carried out in the saturated zone from 4 wells (GWSP-01 to 04), to evaluate the contamination of Pb and Cd metals. (Figure 6.2) (Table 6.5).

The instructions for installing the wells and sampling the water were obtained from the NBR 13895 standard. For the characterization of the metals, chemical analyses were carried out for the total metal of Pb and Cd. The analytical method employed was Atomic Absorption and Atomic Emission Spectrophotometry, complying with the procedures of the Standard Methods for the Examination of Water and Wastewater, 17th Edition.

The pH was determined using a manual electrode potentiometer, and the values found varied between 7.8 and 8.1. The evaluation of the four points showed that upstream of the dam, point GWSP-01, the concentrations of Pb and Cd were below the limits already mentioned. Points GWSP-02 and 03, downstream from the dam, and inserted respectively in the wetland and landfill zone, showed concentrations above the standards, while point GWSP-04, downstream, presents values below the limits established for Pb and CD.

The analyses of these data makes it clear that there is contamination with Pb and Cd in groundwater in the wetland area and at the beginning of the landfill zone.

Table 6.5 - Pb, Cd and pH CONCENTRATIONS IN GROUNDWATER

SAMPLE ID	Pb (mg/l)	Cd (mg/l)	pH
GWSP-01	<0.05	<0.005	8.1
GWSP-02	0.18	0.007	7.9
GWSP-03	0.72	0.008	8.0
GWSP-04	<0.05	<0.005	8.0

Source: ANJOS (1998)

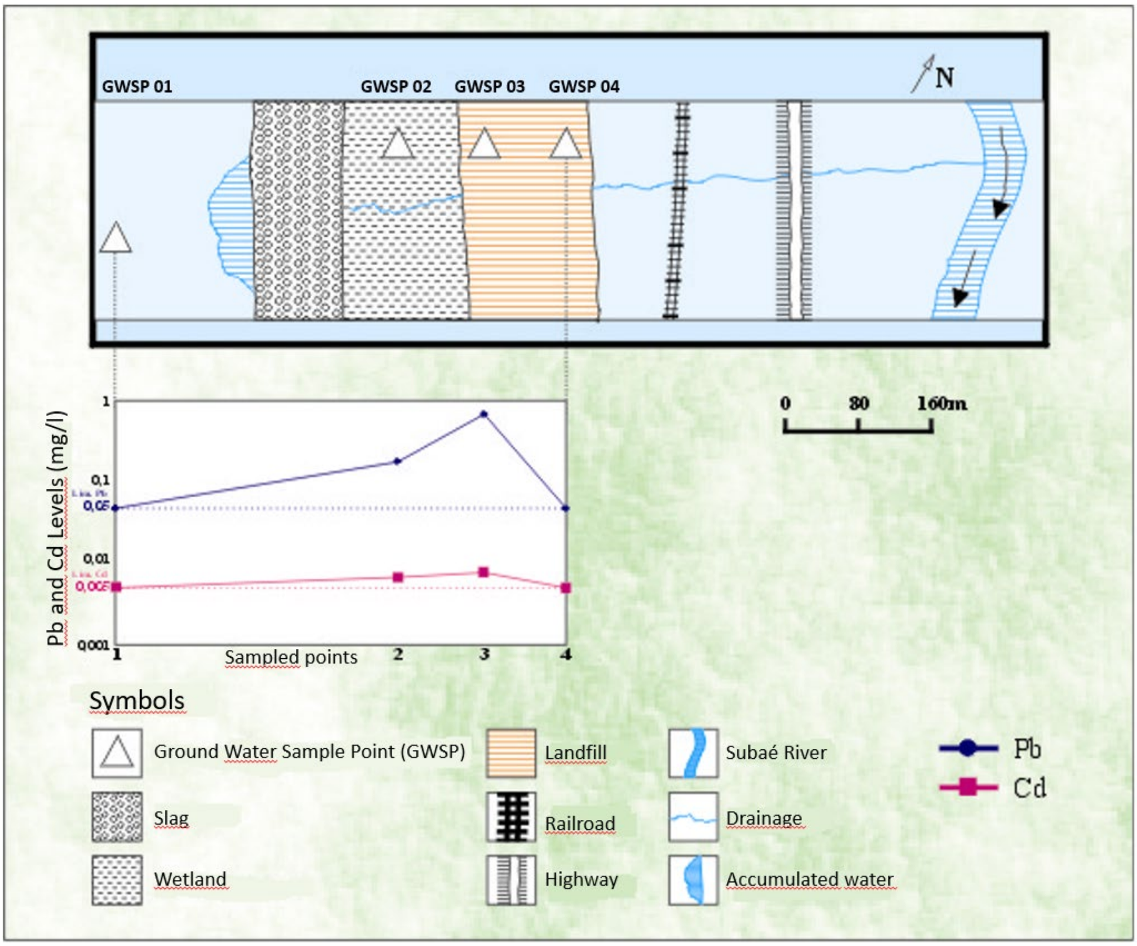

Figure 6.3 - Sampling points and concentration of metals in groundwater. Source: ANJOS (1998).

6.4.6 Soil characterization

The soils found at the site where the Plumbum Co. is located are classified as vertisols, rich in montmorillonite clay (BOYER 1971 and BAHIA 1996).

Soil sampling in the pilot area was based on the collection of surface points and soil profiles. Soil profiles were carried out in the landfill and swamp areas, and aimed to evaluate the spatial distribution and behavior of parameters - heavy metals, pH, CEC, OM and texture -, complemented by surface points.

The instructions for soil sampling were obtained through NBR 10.007. Although this standard deals with sampling of residues, it was considered adequate, because thE study recognizes contaminated soils in a way similar to residues. Quantitative chemical analyses for Pb and Cd were performed by Flame Atomic Absorption Spectrometry, while analyses for determination of CEC, pH and MO were carried out according to the guidelines of the Soil Analyses Method Manual of the Brazilian Agricultural Research Corporation (EMBRAPA). As for the method for determining the texture and classification of the soil, it was obtained following Standard NBR 7181.

The results of the chemical analyses with the levels of Pb and Cd metals, the Cation Exchange Capacity, and percentage of Organic Matter are presented in Table 6.6.

Soil Profile Points (SPP) - 02-01, 03-01 and 04-01 – presented, respectively, high levels of metals (1,800; 2,000 and 8,200 µg/g for Pb and 38; 27 ,9 and 117 µg/g for Cd). These levels are, respectively, related to high CEC (44.3; 32.2 and 47.1 meq/100g), high MO percentages (2.9; 4.5 and 10.9%) and alkaline pH, varying from 7.9 to 8.6. These results confirm that there is no clear relationship that establishes an intrinsic relationship between metal retention, with high values for CEC and MO.

Some conclusions can be established through the results obtained in the pilot area, highlighting:

a) the existence of a source of pollution was found at the Plumbum site, related to the inadequate disposal of the contaminated slag;
b) surface waters located in the marshy zone present levels of Pb and Cd above the established in the Framework of the Subaé River. The site has levels up to 260.3 times the maximum allowed value for Pb and 84 times allowed for Cd;
c) groundwater is contaminated in the wetland area, however, upstream and downstream of this zone, the levels found for Pb and Cd are very close to the maximum limits established by current legislation;
d) hydromorphic sediments were deposited on the vertisol of the swampy zone, containing organic matter originating from the decomposition of vegetation and clays from the erosion of the vertisol of the hills of the valley. This sediment, with a thickness ranging from 10 to 30cm, occurs throughout the Plumbum wetland where vegetation classified as *Typha sp* develops.

Table 6.6 - CONCENTRATIONS OF Pb AND Cd IN THE SOIL

UPPER SAMPLING (SPP-01, 04 and 05) AND SOIL PROFILE (SPP-02 and 03)	Depth (cm)	Pb (µg/g)	Cd (µg/g)	CEC (Meq/100g)	MO %	pH
SPP-01.01	10 cm	50	1.0			
SPP-01-02	10 –30 cm	<5.0	<0.5			
SPP-02.01	10 cm	1,800	38.0	44.3	2.9	8.0
SPP-02.02	10 - 30 cm	1,300	18.1	41.0	0.7	8.1
SPP-02.03	30 - 50 cm	821	12.4	35.6	0.9	8.4
SPP-02.04	50 - 70 cm	307	3.7	38.6	1.1	8.5
SPP-02.05	70 - 90 cm	175	1.7	39.0	0.9	8.6
SPP-02.06	90 - 110 cm	<5.0	<0.5	23.7	0.4	8.6
SPP-02.07	110 - 130 cm	<5.0	<0.5	53.0	0.9	8.4
SPP-02.08	130 - 150 cm	<5.0	<0.5	20.0	0.3	8.7
SPP-02.09	150 - 170 cm	182	2.2	41.7	0.9	8.6
SPP-02.10	170 - 190 cm	157	2.1	40.4	0.6	8.6
SPP-03.01	10 cm	2,000	27.9	32.2	4.5	8.0
SPP-03.02	10 - 40 cm	390	5.0	37.4	1.3	8.4
SPP-03.03	40 - 70 cm	89	1.3	35.6	0.8	8.6
PP3-03.04	70 - 100 cm	256	2.5	39.0	0.7	8.6
SPP-03.05	100 - 130 cm	3,000	39.9	45.4	3.6	8.2
SPP-03.06	130 - 160 cm	1,400	20.4	45.1	4.9	7.9
SPP-03.07	160 - 190 cm	78	1.1	46.4	4.3	8.1
SPP-04.01	10 cm	8,200	117.0	47.1	10.9	8.0
SPP-04.02	10 - 30 cm	1,200	38.9	42.5	4.5	8.0
SPP-05.01	10cm	<5.0	<0.5			

Source: ANJOS (1998)

e) Most of the Pb and Cd are retained in the wetland sediment, possibly through the chemical processes of precipitation, sorption and complexation. These processes are especially developed due to the basic pH, which favors the precipitation of metals, their adsorption by clays and the formation of metallic organic complexes;

f) there is a risk of contamination of animals that graze freely on the contaminated site, especially cattle, which use the contaminated waters of the wetland to drink and feed on contaminated grasses, allowing the spread of contamination (bioaccumulation of metals) for populations that are using the milk and meat of these animals.

6.5 - The coating of the slag carried out by the Plumbum Co.

The technical project developed at the Plumbum site, as well as the execution of the work, was carried out by MORSA ENGINEERING CO. The project developed by the company deals only with a “proposal for the supply of labor and equipment necessary to cover with 30 cm (thirty centimeters) of earth, all the existing slag in the open” (GONÇALVES 2001).

The project executed by MORSA and presented to the Public Ministry, consists of 9 pages, and includes as “Obligations of MORSA Engineering Co. to carry out the works in accordance with the regulations and norms existing in the country” (GONÇALVES op. cit.) page 9.

The proposal developed by MORSA presents, exclusively, a list of photos of the places where the soil should be removed, the thickness of the coating and the total amount of soil removed for each area. In total, MORSA moved 170,000 m^2 of potentially contaminated soil, such as:

- in the slag dam area, called the upper area with slopes in the project, it was proposed to cover 30 cm of the area's own soil and place bamboo screens on the slopes to fix the land, in a total of 20,000 m^2 . pgs. 01 and 02 (GONÇALVES op. cit.) (Photos 6.2), and
- Completion of the lowering of the hill and execution of a slope with earth in the dimensions ≅ 2m high x 5m wide x 250m long, totaling 8,000 m^2. It was proposed to cover other points where there was slag in a total of 26,000 m^2. The total covered area is 85,000 m^2 (GONÇALVES op. cit.) pgs. 06, 07 and 08 (Photo 6.3).

Photo 6.2 - Slag bus with red signs indicating area to be worked on. Source: GONÇALVES (2001).

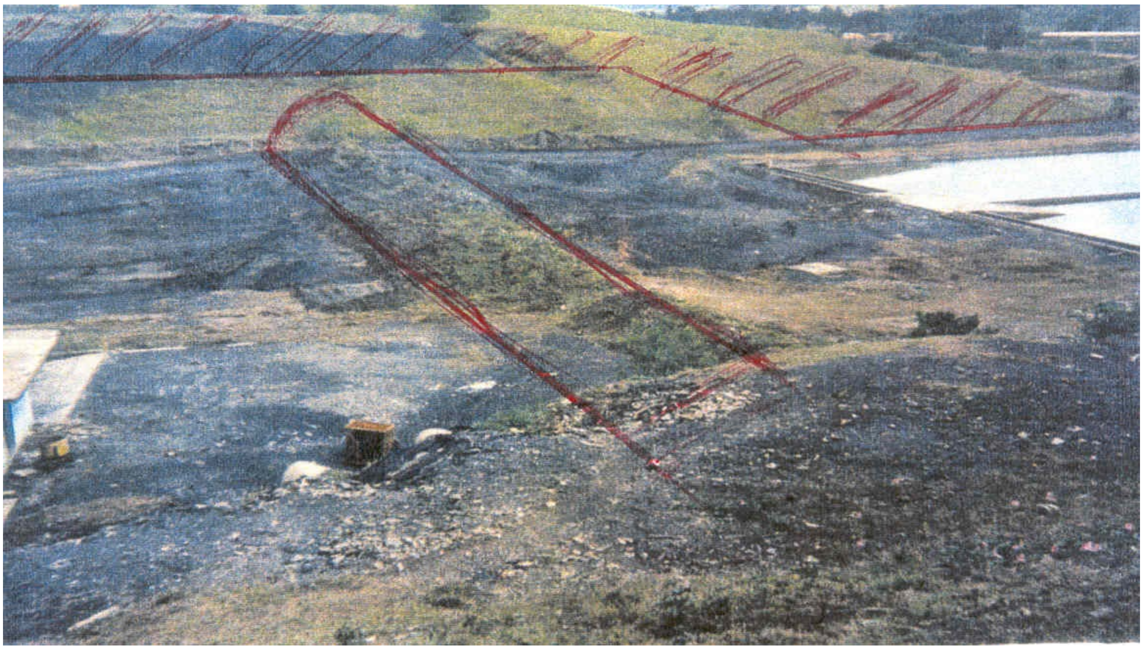

Photo 6.3 – Indication of lowering of the hill and construction of the dike. Source: GONÇALVES (2001).

6.6 Analyses of the expert report in civil action No. 302/98

The expert report on the quantification and evaluation of environmental and population contamination with lead and cadmium in the municipality of Santo Amaro da Purificação (CUNHA and ARAUJO 2001) was a study carried out between December 2000 and June 2001 in compliance with the determination contained in the records of Public Civil Action No. 302/98 of the local District Court.

The expert report, according to NETO (2001), presents partiality and methodological contradictions that nullify it. This objection by the Public Prosecutor accompanying the matter is given to the fact that the expert did not act with the necessary impartiality, especially in technical matters that are not inherent to his profession.

As the expert and his assistant are physicians, the following methodological contradictions related to the technical aspects of "encapsulation" were found in the expert report contracted by the local court:

1) "works under the responsibility of Engineer Paulo Roberto Riscado were started and are nearing completion by Morsa Engineering Co., with costs paid by Plumbum, with the purpose of encapsulating the slag. To this end, thousands of cubic meters of earth were mobilized from the region, suitable for its geological constitution, for the proposed purposes" pg 89 (CUNHA and ARAUJO op. cit.)".

   The encapsulation project did not present a study on the chemical characteristics of the soil used to cover the slag, so it cannot be said that the soil used is suitable for this situation.

   The term "ground" is very comprehensive, not specific for this work, because soils for encapsulation projects must have specifications that define their physical characteristics, such as the use of different types of compacted clays for waterproofing the soil. system.

2) "three embankments were built to prevent contaminated water from reaching the Subaé River" pg 89 (CUNHA and ARAUJO op. cit.).

   Initially, slope means an inclined land surface at the base of a hill or a valley slope, where there is a deposit of debris (MOREIRA 1992) or inclined land, escarpment, ramp, surface of an excavation, of an embankment (AURELIO 1986). While dyke means a natural or artificial structure that controls the water level of a river, lake or sea (MOREIRA op. cit.), solid construction, to dam running water, dam, dam or obstacle or barrier (AURELIO op. cit.), or earth masses or concrete walls or other suitable material, forming a containment basin (NBR 12235/92).

Faced with such concepts, it is evident that the term slope is used incorrectly. In addition, dykes would not prevent the migration of surface water, as they migrate through the pipe that runs under the dyke construction.

3) "it should be emphasized and reaffirmed that the measures adopted for the encapsulation of the slag, according to several specialists, were and are the only plausible solution to be adopted, which cannot be labeled palliative" pg 61 (CUNHA and ARAUJO 2001).

Initially, the project was executed without proper knowledge of the term "encapsulation". According to investigation carried out by NEDER (1998), encapsulation has been used worldwide as a technology for treating residues used in the solidification and stabilization processes of pollutants. That is, they are macro or microencapsulation mechanisms that physically imprison the residue within a larger matrix or within the crystalline structure of the solidified matrix (NEDER op. cit.).

However, if the project had been developed within the procedures of the technical standard for the storage of hazardous waste, which establishes the ways of storing hazardous waste, various types of efficient waste confinement projects could have been used in controlling pollution. However, this did not happen, the project developed by Plumbum only deals with a surface coating without any standard technical procedure.

Any remediation project at the Plumbum site has to take into account the slag and contaminated soil. Therefore, even surface covering would have to evaluate the recovery of this soil and not remove it inappropriately. For this there are other remediation techniques that could be carried out in the area, just see all the bibliography available for site remediation, such as CONSOIL (1998 and 2000), see Chapter 5.6 – Remediation Technologies.

The project developed by MORSA will only delay the solution of the problem, even if the slag were really confined, a project should be foreseen in the medium term to make the slag available in industrial landfills, or treated and recycled.

4) “back in 1992, three years after the total acquisition of the industry by Plumbum, production began to decline at such a way that culminated in the closure of activities in December of the following year” pg. 82 (CUNHA and ARAUJO 2001).

All lead alloy produced by Plumbum depended on processed ore from the Boquira mines or elsewhere. The reserve of a mine is controlled by the DNPM (National Department of Mineral Production) and its exhaustion is predicted well in advance by the shareholders. Note what the 1973 Lead Analytical Profile says: “The Boquira mine reserves, on 01/01/73, presented by Mineração Boquira in annual mining reports to the DNPM, will allow the life of the mine for a period of approximately 6 (six) years, at the current production rate, as in 1972, with the withdrawal of 274,800 tons of ores", that is, twenty years before, the useful life of the mine had already been estimated at six years with production made at the time.

Furthermore, in 1993, before the abandonment of metallurgy, the following events occurred: CRA issued a new Operating License for metallurgy with dozens of mitigating measures that were never fulfilled; precautionary action no. 180/92 and public civil action no. 264/93 began to be processed in the courts against Plumbum. There was also a publication, by the Pan American Health Organization, placing the city of Santo Amaro da Purificação as a reference on lead contamination in Brazil.

Therefore, to say that production only started to decline in 1992 and that this fact alone led to the closure of the metallurgy is at odds with the facts mentioned.

5) “in the year 1995, Plumbum Mining and Metallurgy Co., through a contract, leased part of its facilities for the implementation of a napkin manufacturing industry that, among other obligations, should take

> care of environmental liabilities. None of the contracted measures was effectively adopted" pg. 93 (CUNHA and ARAUJO 2001).

The Boka Loka napkin factory operated irregularly until its facilities were closed by the CRA. Therefore, it was not responsible for Plumbum's environmental liabilities, as these are not transferred under a temporary lease agreement, therefore the expert is not in a position to state that Boka Loka is responsible for the failure to remediate the site.

6) "from the analyses related to the environment, we can conclude that: a) There is environmental contamination with heavy metals (lead and cadmium) in the regions where slag is deposited, on the site where Plumbum Mining and Metallurgy Co. operated; it should be noted that such contamination is restricted to the aforementioned site" pg. 90 (CUNHA and ARAUJO op. cit.)

The authors are incoherent when, in the expert document itself, they indicate another place where metal contamination occurs. On pg. 85 (CUNHA and ARAUJO op. cit.) say "In the area in front of the DERBA Department, the slag irresponsibly distributed there, has, although in smaller quantities, high levels of lead and cadmium, which can represent a serious risk for children who go barefoot, and play in those places".

CHAPTER 7: FIELD AND LABORATORY RESULTS

7.1 First stage - Before coating the slag

The transfer of metals in the Plumbum wetland comes, initially, from rainwater that leaches and/or solubilizes the main source of contamination (slag dam) disposed immediately upstream of the wetland (Figure 7.1). Then, metals from the source of contamination are introduced into the wetland by surface runoff and interact with water and surface sediments, macrophyte vegetation and microorganisms, until the exit from the wetland to the river and Subaé estuary.

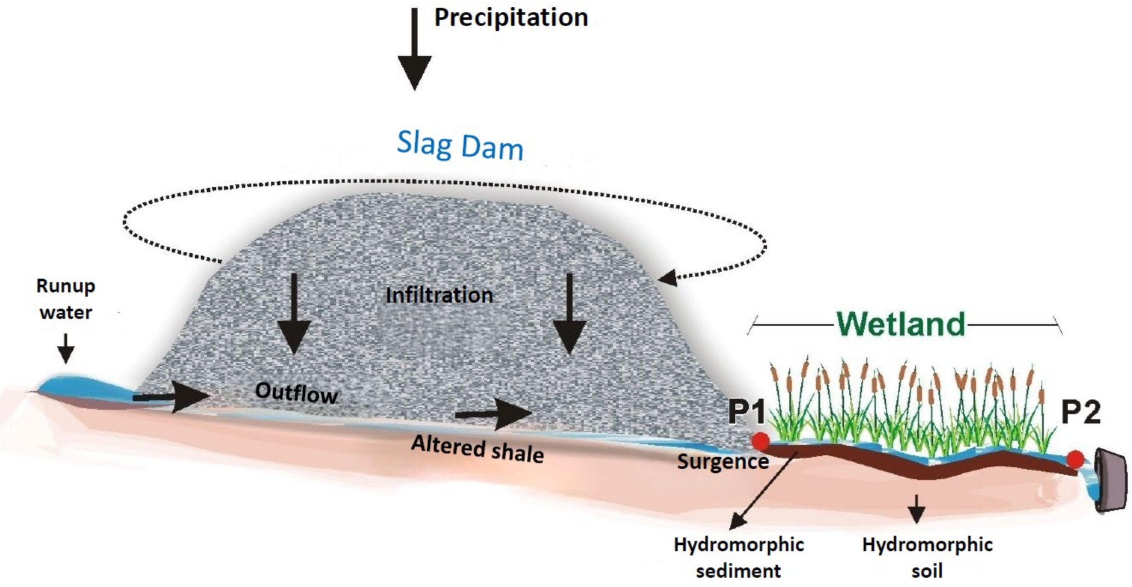

Figure 7.1 - Schematic section showing the slag barrier before the overlay and sampling points 01 and 02.

The parameters surveyed were related to rainfall, the source of pollution characterized by the damming of slag, the concentrations of metals in the entrance and exit of surface waters in the wetland, and the levels of metals available in the sediments of the area and in the soil.

7.1.1 - Evaluation of rainwater

Weekly survey of rainfall volumes and pH readings carried out in the vicinity of the Plumbum wetland during the first 5 (five) months of 2001 (Supplement 1) quantified the weekly precipitation in the area. During this period (22 weeks) low weekly rainfall, below 30 mm, predominated; however, these values were above 30mm in the ninth and eighteenth weeks, with values greater than 50mm of weekly rainfall (Figure 7.2), while in the seventh, tenth and thirteenth weeks there was no precipitation.

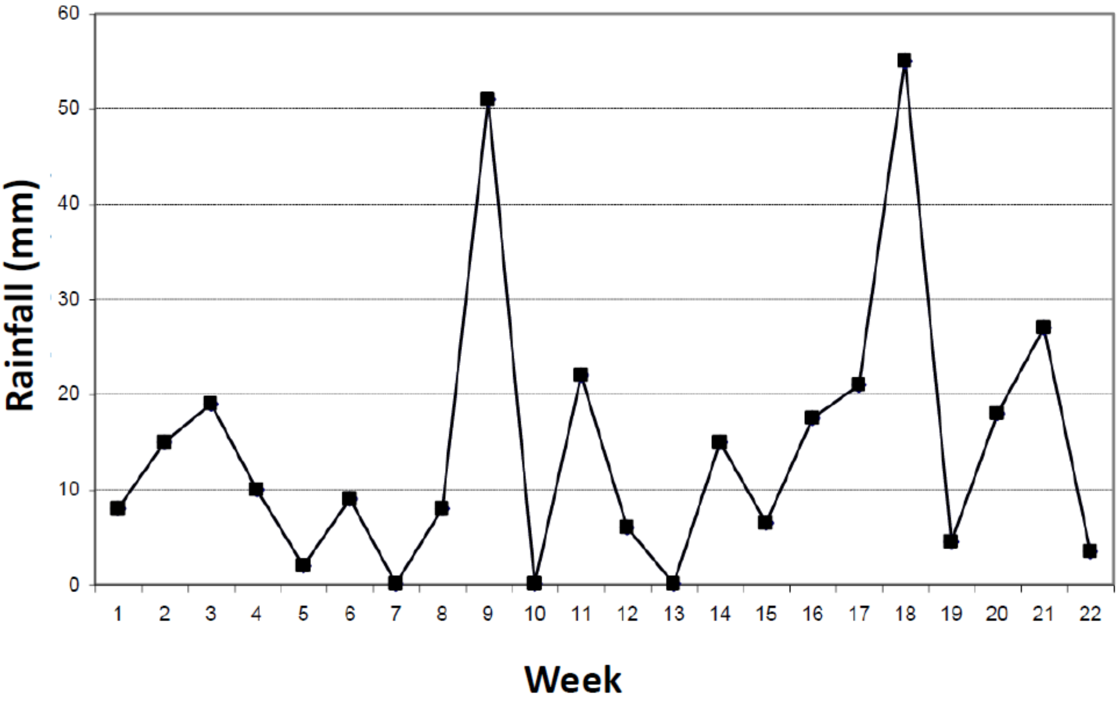

Figure 7.2 - Values of weekly rainfall.

As for the pH of the rainwater (Figure 7.3), it can be observed that in the seventh, tenth and thirteenth weeks the values were not measured due to the lack of precipitation. In this period the pH ranged from 5.2 to 8.3 and, until the ninth week, we can observe a correlation between small and high values of precipitation with small and high values of pH.

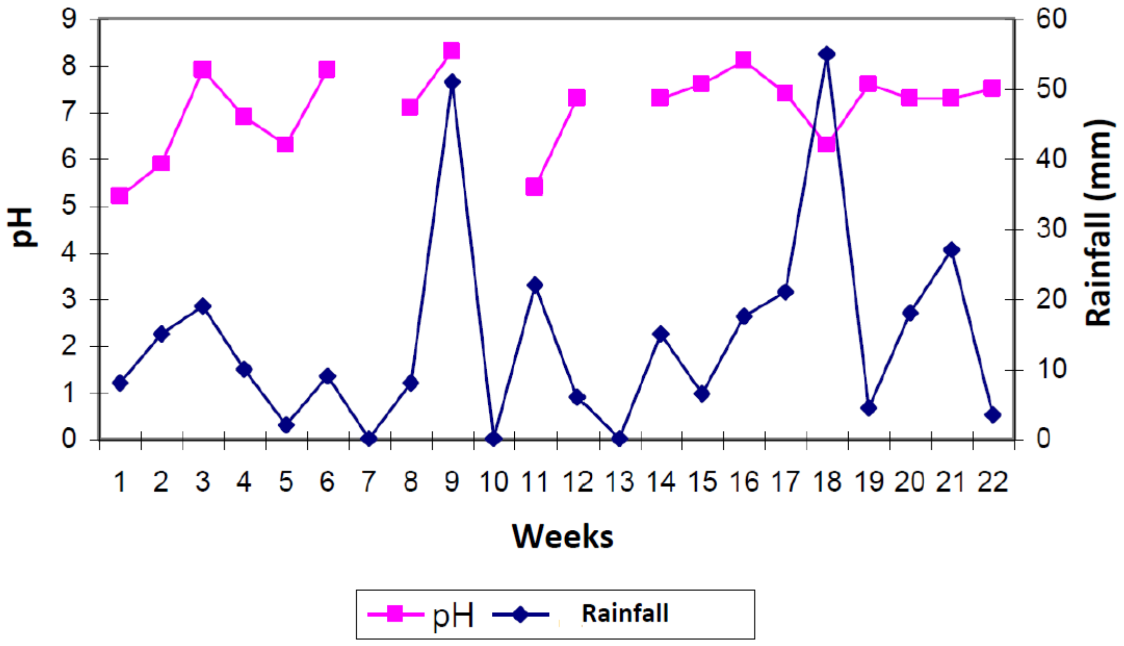

Figure 7.3 – Weekly pH and rainfall values in the Plumbum area.

The total volume of rainwater measured during the investigation was 318mm, while the value measured throughout 2001 was 1,270mm. Water functions as the main agent in the process of leaching and/or solubilization of metal-contaminated slag. The pH values found in the survey ranged from neutral to alkaline and, according to the vast literature on the subject, the pH in these conditions makes it difficult to trigger the processes of metal availability.

7.1.2 - Characterization of the slag

Chemical analyses by X-Ray Fluorescence were done on six samples to determine the current chemical composition of the slag (Table 7.1). As most of the slag was deposited and mixed in the valley in the form of a dam and as no information was available on the year of its production, sampling was carried out in two holes in the center of the dam to determine an average of its current chemical composition.

Table 7.1 – ANALYSES OF THE SLAG BY X-RAY FLOURESSENCE, IN %.

	Hole 33 SMP 02	Hole34 SMP 02	Hole 33 SMP 03	Hole 34 SMP 04	Hole 33 SMP 06	Hole 34 SMP 07
Depth (m)	1 – 1.99	1 – 1.99	3 – 3.99	3 – 3.99	6 – 6.99	6 – 6.99
MgO	7.29	3.37	7.97	4.10	8.04	6.52
Al_2O_3	2.18	2.60	2.16	2.53	2.28	2.58
SiO_2	23.70	21.5	25.5	21.8	25.1	25.1
P_2O_5	0.08	0.14	0.10	0.13	0.16	0.11
SO_3	1.41	3.09	1.07	3.72	1.41	0.81
K_2O	0.31	-	0.37	0.42	0.42	0.36
CaO_2	20.5	21.3	21.2	20.4	20.2	23.2
TiO_2	0.26	0.30	0.26	0.28	0.23	0.24
MnO	0.67	0.91	0.48	0.89	0.58	0.39
Fe_2O_3	26.6	25.4	23.3	25.4	23.3	22.6
CuO	0.15	0.51	0.11	0.61	0.08	0.19
ZnO	12.5	15.3	11.6	15.2	12.8	11.3
As_2O_3	0.09	0.44	0.18	0.36	0.25	0.06
Sb_2O_3	0.16	0.23	0.24	0.17	0.28	0.17
BaO	0.19	0.13	0.21	0.09	1.11	0.17
PbO	3.43	3.80	4.46	3.25	3.40	5.35
CdO	-	-	-	-	-	-

High concentrations of MgO, SiO_2, CaO, Fe_2O_3, ZnO and PbO can be observed in all six samples analyzed, however, cadmium was not detected in any of the samples in this research. Also, medium values were detected for Al_2O_3 and SO_3, and very low values for MnO, CuO, As_2O_3 and BaO.

7.1.3 - Concentrations of physical and chemical parameters of the surface water

In the first stage of the research, the surface waters were evaluated for 22 weeks, when the following in situ parameters were measured: pH (Figure 7.4), Redox Potential (Figure 7.5), Conductivity (Figure 7.6), Dissolved Oxygen (Figure 7.7) and Water Temperature (Figure 7.8) (Supplement 2).

Hydrogenionic Potential (pH)

The pH values found in the surface waters of the wetland were between 6 and 8 and established the condition of slightly acidic to slightly acidic water, except for the first two weeks for the entry point and the eleventh for the exit point. The values observed in Figure 7.4 show that the entry points (pH-01) have higher pH values than the exit points (pH-02) of the wetland.

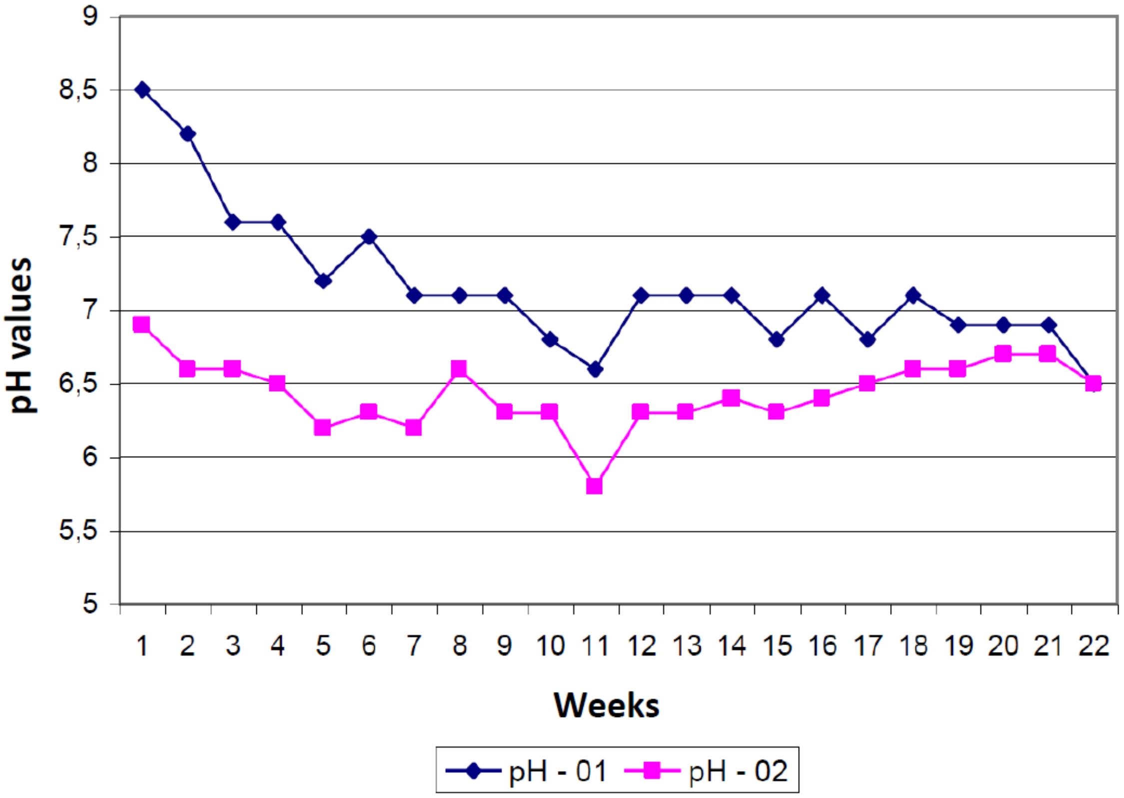

Figure 7.4 - Weekly pH values of surface water

Redox Potential (Eh)

The oxidation-reduction readings found in the surface waters of the Plumbum wetland zone in the first stage of the survey (Figure 7.5) show concentrated values, mostly between 50 and 350 mV (oxidation zone), with the exception of the last two weeks, when they were measured reducing values for the system.

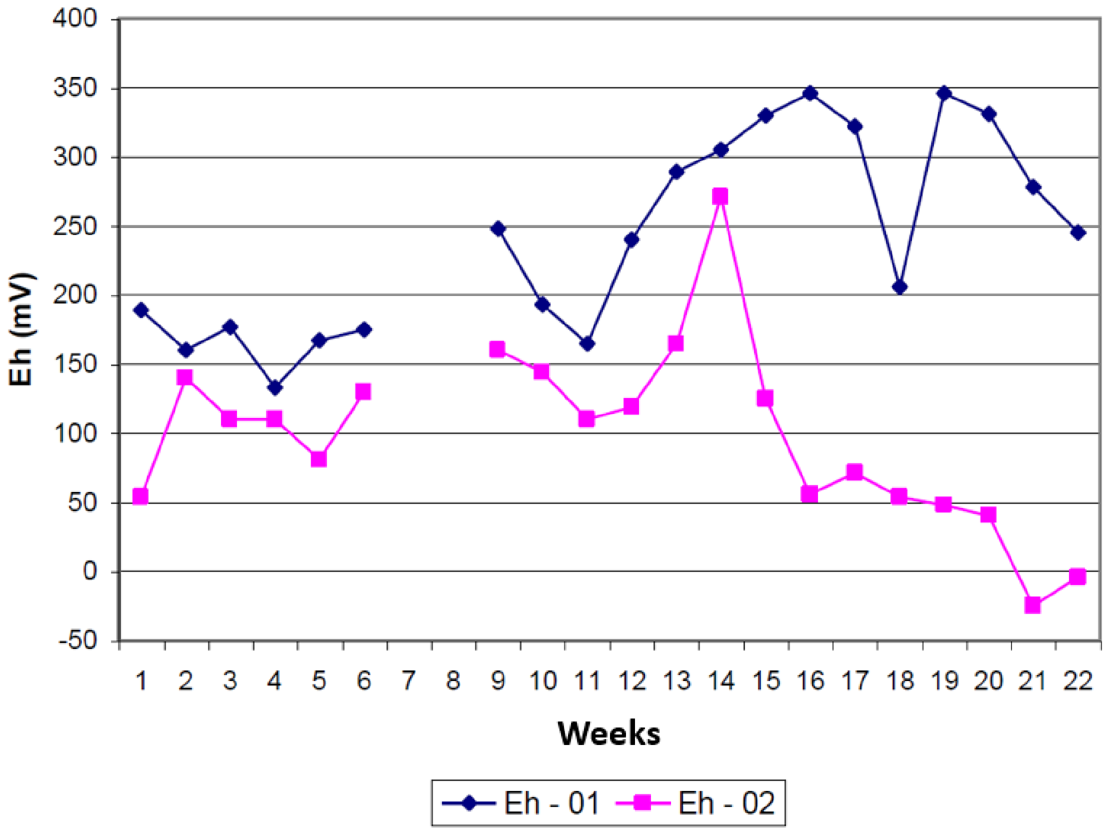

Figure 7.5 - Weekly values of redox potential in surface waters

The redox potentials measured at the entry point of the system (Eh – 01) show levels consistently higher than at the exit point (Eh - 02) of the wetland. This difference reflects processes inherent to the consumption of oxygen within the system by vegetation and microorganisms. In the seventh and eighth weeks, the Eh was not surveyed because the cell that measures this parameter was under revision.

Conductivity (CD)

It can be observed that the surface waters of the Plumbum wetland present conductivity varying between 600 and 1200 μmho/cm (Figure 7.6). The entry point of the wetland (CD – 01) presents lower values than at the exit point (CD – 02), except for the eighth week. These high values are related to the high concentrations of calcium and magnesium oxides found in the composition of the slag and in the sediments of the wetland (ANJOS and RIBEIRO 1999), in addition to the reduced volume of water in the flooded system providing a greater concentration of conductive species.

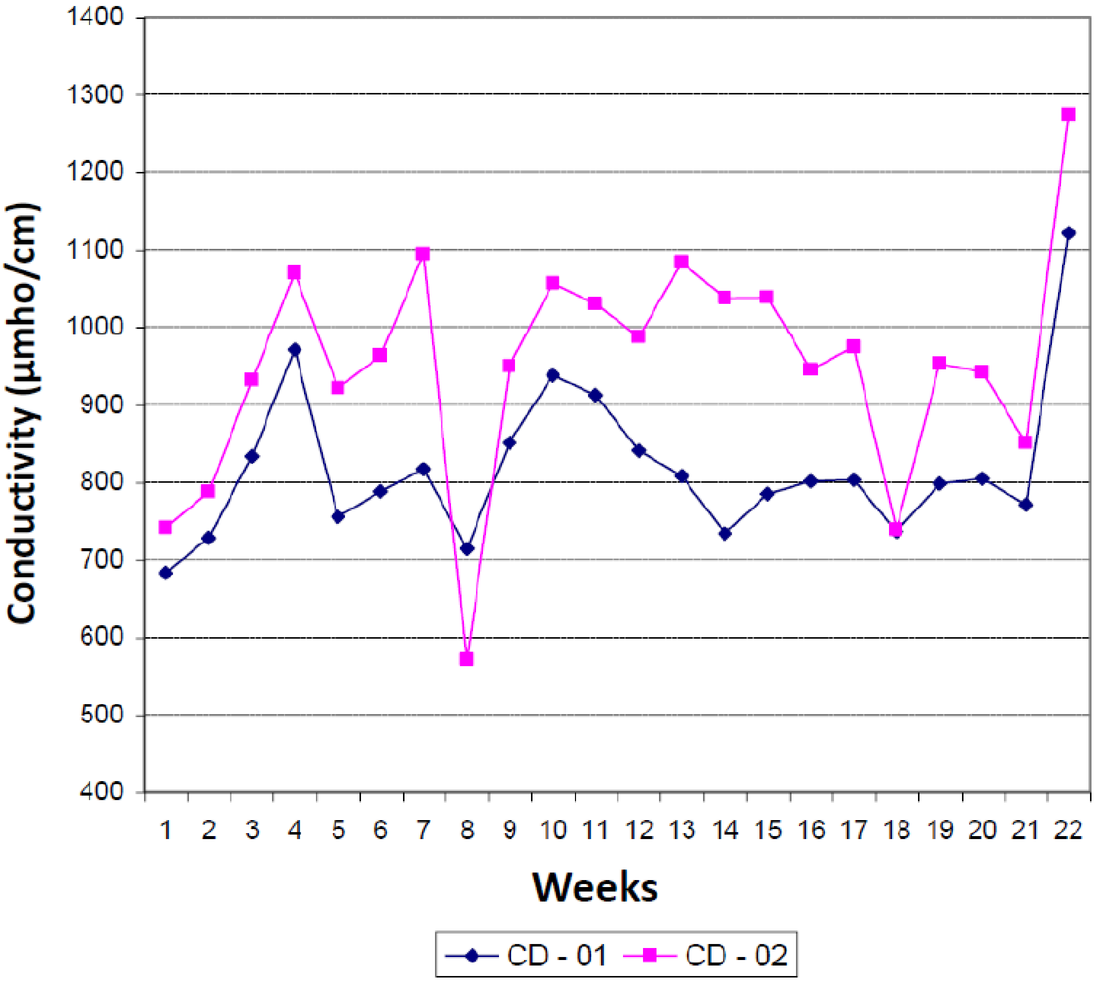

Figure 7.6 - Conductivity values in surface waters in the wetland area

Dissolved Oxygen (DO)

The levels of dissolved oxygen found in the surface waters of the Plumbum wetland present values below 2.5 mg/l. The highest values were found at the entry points of the wetland zone (OD – 01) in the second and ninth week, while from the eleventh week onwards, low DO values predominated, but with higher concentrations at the exit point of the wetland zone (OD – 02) (Figure 7.7).

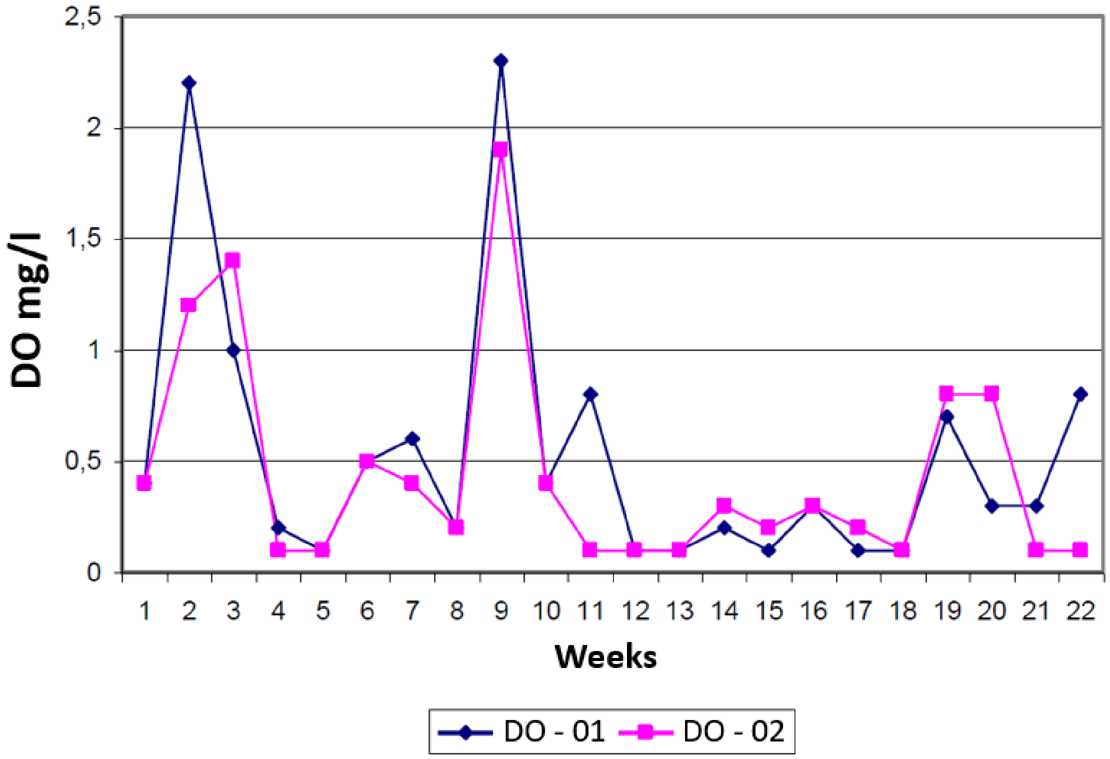

Figure 7.7 - Values of dissolved oxygen in surface waters of the wetland

Temperature

The surface water temperature in the Plumbum wetland area (Figure 7.8) varies between 24 to 30 °C. The values measured at the entry point (T – 01) always show higher values than the system exit points (T – 02). These high temperatures promote the development of biological processes and accelerate biochemical reactions.

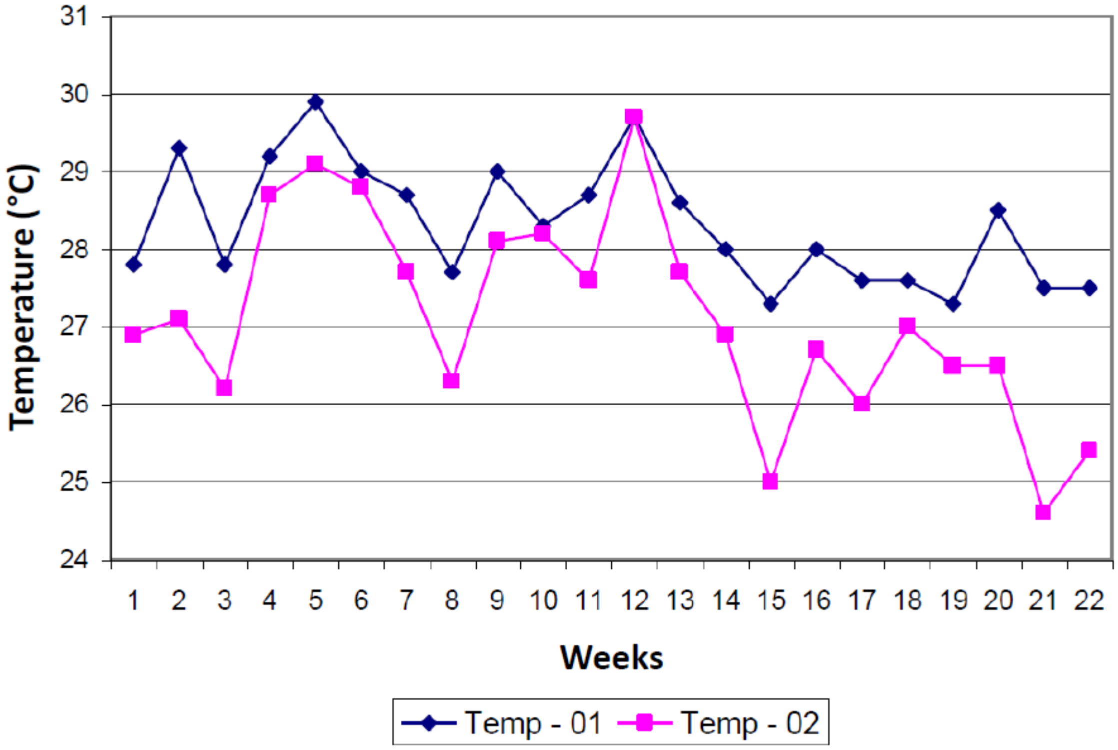

Figure 7.8 – Temperature values in surface waters.

7.1.4 - Levels of heavy metals in surface water

The surface water survey carried out in the first five months of 2001, before the slag was covered, at the wetland entry and exit points, had the objective of evaluating the levels of metals introduced in the wetland and the amount of metals removed by the system. The heavy metals showing expressive results were cadmium, lead, copper and zinc, while cobalt, chromium and nickel were not detected in the chemical analyses. Aluminum, calcium, iron, magnesium and manganese were also evaluated (Supplement 3).

7.1.4.1 Cadmium

Figure 7.9 presents a weekly survey for points Cd – 01 (entrance to the wetland zone) and Cd – 02 (exit of the wetland zone). The green dots represent the value established by CONAMA Resolution 01/86, Class 2 (0.001 mg/L Cd), while Table 7.2 presents the percentage of points that exceeded the tolerance limits established in the mentioned resolution.

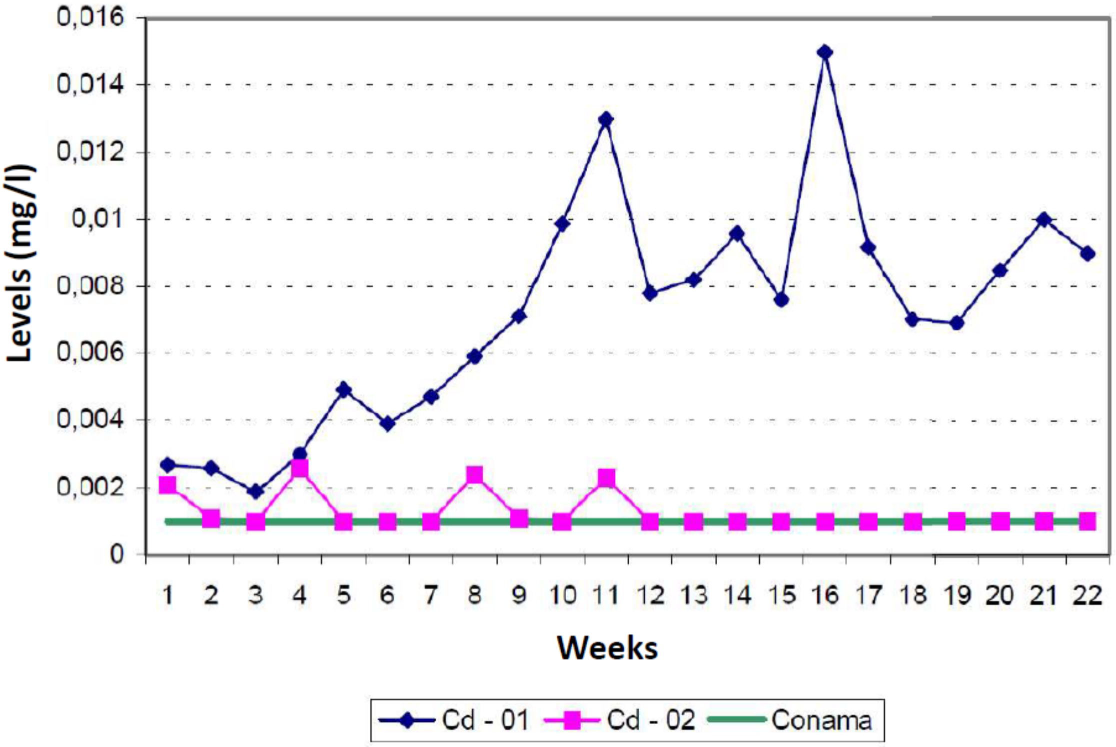

Figure 7.9 – Cadmium concentrations in the surface waters of the wetland

Table 7.2 - Percentage of weekly cadmium samples exceeding CONAMA Guidelines.

	YES	NO	TOTAL
Cd - 01	22 (100%)	0 (0%)	22 (100%)
Cd - 02	6 (27%)	16 (73%)	22 (100%)

The cadmium results in the Plumbum wetland reveal that this heavy metal has been leached and/or solubilized continuously from the slag into the surface waters of the wetland (Cd – 01). And that, mostly, it has been retained in the wetland system by geochemical and biological processes (Cd – 02). It is noteworthy that, during the five months of the survey, in just six weeks, 27% of the evaluated points had their values at the exit of the wetland zone with concentrations higher than those established by the CONAMA Resolution.

7.1.4.2 Lead

Figure 7.10 presents a weekly survey for points Pb – 01 (entrance to the wetland zone) and Pb – 02 (exit of the wetland zone). Green dots represent the value established by CONAMA Resolution 01/86, Class 2 (0.03 mg/l Pb). Table 7.3 presents the percentage of points that exceeded the tolerance limits established in the mentioned resolution.

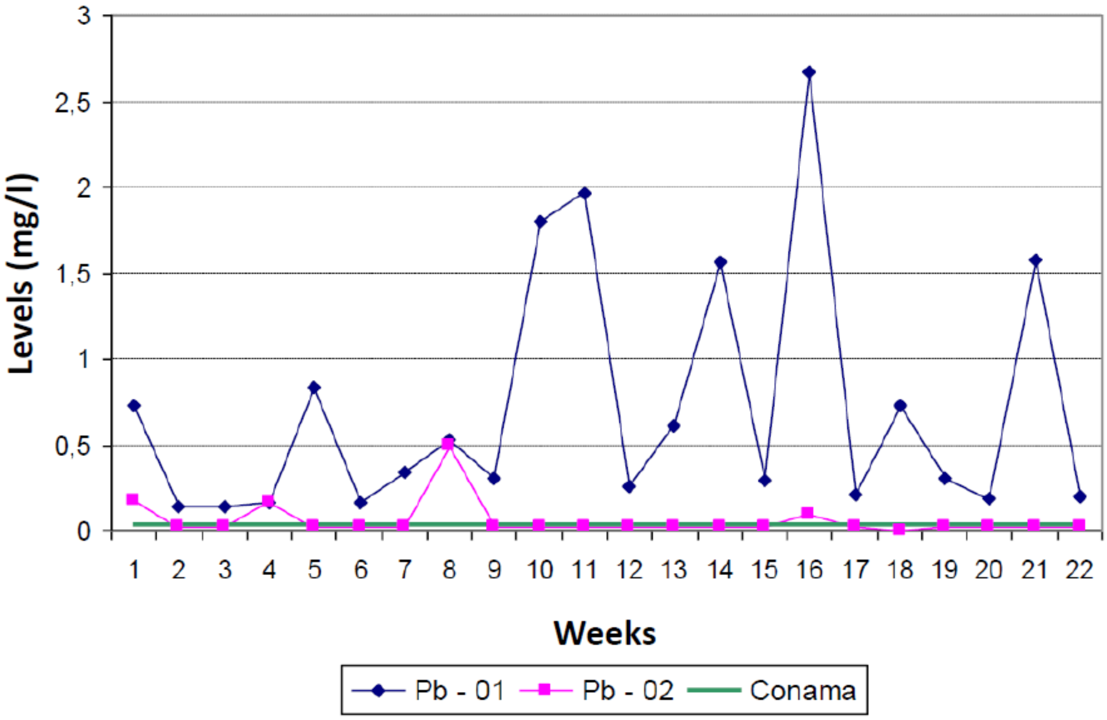

Figure 7.10 – Lead levels in the surface waters of the wetland

Table 7.3 - Percentage of weekly lead samples exceeding CONAMA Guidelines.

	YES	NO	TOTAL
Pb – 01	22 (100%)	0 (0%)	22 (100%)
Pb – 02	4 (18%)	18 (82%)	22 (100%)

The concentration of lead in the surface waters of points 01 (Pb – 01) shows a great leaching and/or solubilization of the metal in the source of contamination, while point 02 (Pb – 02) at the exit of the wetland demonstrates that lead has been intensively retained by the swampy zone.

Only in four (18%) of the twenty-two weeks did concentrations exceed the limits established by CONAMA Resolution.

7.1.4.3 Copper

Figure 7.11 presents a weekly survey for points Cu – 01 (entrance to the wetland zone) and Cu – 02 (exit of the wetland zone). The green dots represent the values established by CONAMA Resolution 01/86, Class 2. (0.02 mg/l Cu), while Table 7.4 presents the percentage of points that exceeded the tolerance limits established in the aforementioned resolution.

Copper values in the surface waters of points 01 (Cu – 01) shows high leaching and/or solubilization of the contaminated slag, while point 02 (Cu – 02) at the exit of the wetland demonstrates that copper has been completely removed by the wetland. At the entry point, 82% of the samples exceeded the limit, while at the wetland exit point, all twenty-two weeks showed concentrations below the limits established by the CONAMA Resolution.

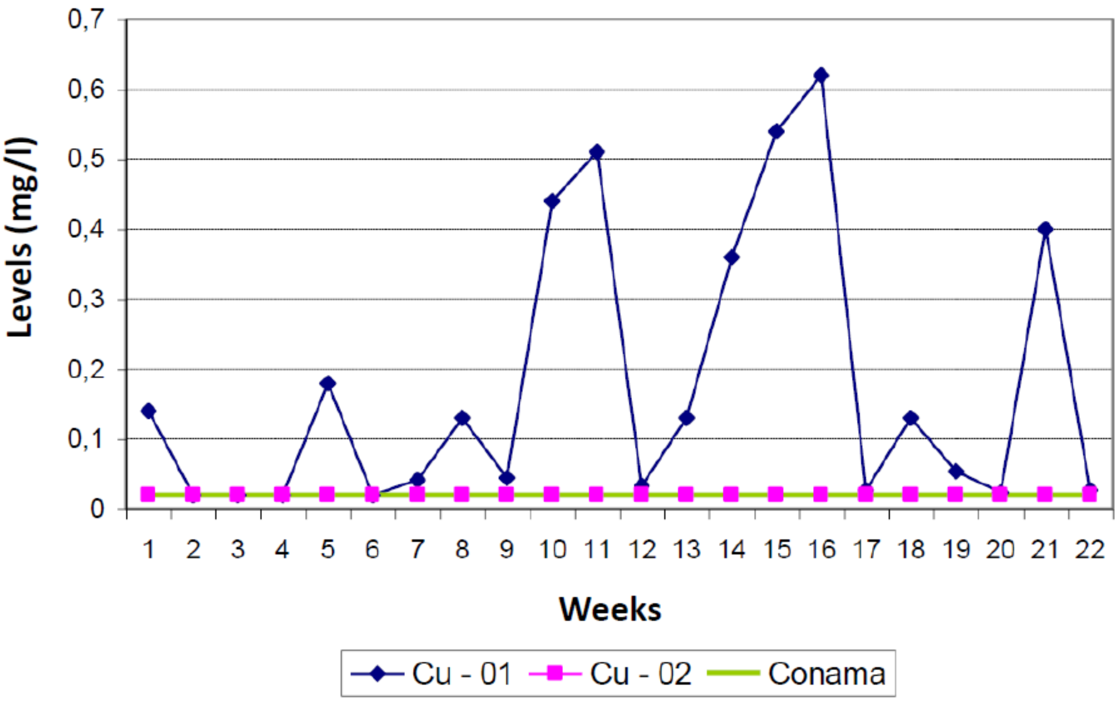

Figure 7.11 - Copper levels in the surface waters of the wetland

Table 7.4 - Percentage of weekly copper samples exceeding CONAMA Guidelines.

	YES	NO	TOTAL
Cu – 01	18 (82%)	4 (18%)	22 (100%)
Cu – 02	0 (0%)	22 (100%)	22 (100%)

7.1.4.4 Zinc

Figure 7.12 shows the weekly survey for points Zn – 01 (entry of the wetland zone) and Zn – 02 (exit of the wetland zone). The green dots represent the value established by CONAMA Resolution 01/86, Class 2. (0.18 mg/L Zn). Table 7.5 presents the percentage of points that exceeded the tolerance limits established in the mentioned resolution.

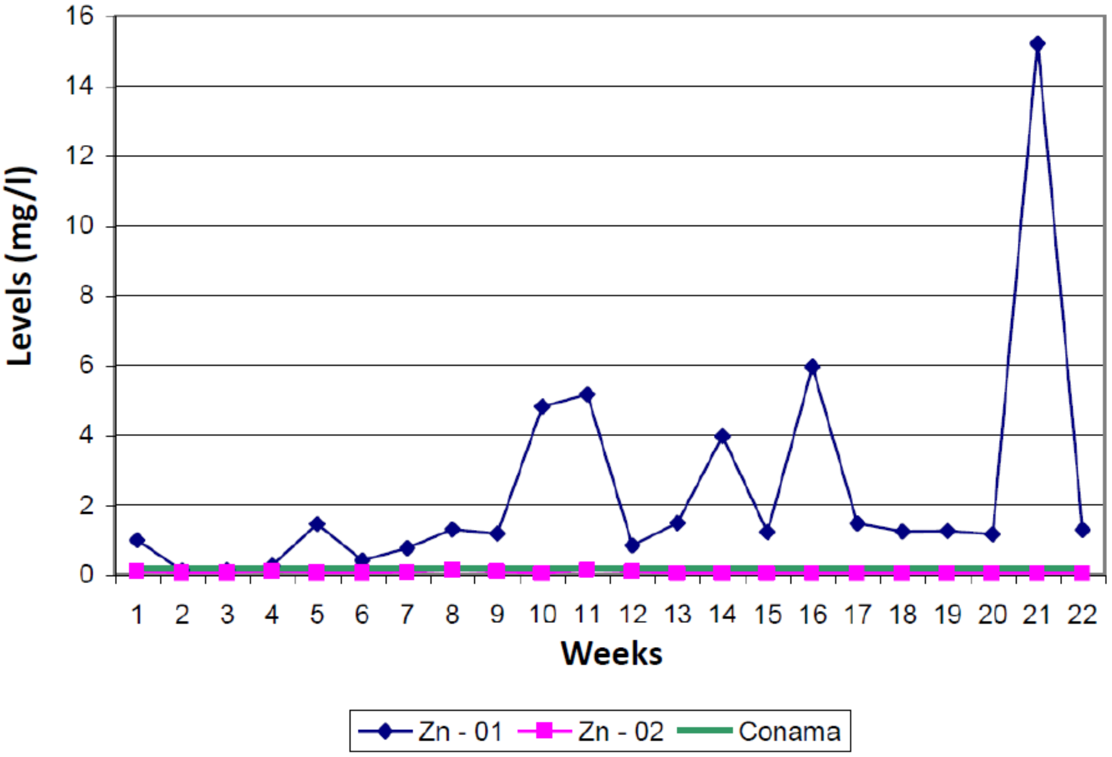

Figure 7.12 – Zinc levels in surface water in the wetland area

Table 7.5 - Percentage of weekly zinc samples exceeding CONAMA Guidelines.

	YES	NO	TOTAL
Zn - 01	20 (91%)	2 (9%)	22 (100%)
Zn - 02	0 (0%)	22 (100%)	22 (100%)

Zinc levels in the surface waters of points 01 (Zn – 01) shows a high leaching and/or solubilization, while point 02 (Zn – 02) at the exit from the wetland demonstrates that zinc, like copper, has been completely retained by the wetland. At the entry point, 91% of the samples exceeded the limit, while at the exit point of the wetland, all twenty-two weeks showed concentrations below the limits established by the CONAMA resolution.

7.1.5 - Levels of support elements in surface water

Support elements have been of great importance in understanding the processes of removal and availability of toxic metals in soil and water. The main elements investigated include aluminium, iron and manganese, due to their connection to clay minerals and iron and manganese oxides. In addition to these elements, calcium and magnesium were also evaluated due to their high concentrations at the source of contamination and of fundamental importance in pH variation.

7.1.5.1 - Aluminum

Figure 7.13 presents a weekly survey for points Al – 01 (entrance to the wetland zone) and Al – 02 (exit of the wetland zone). The green dots represent the value established by CONAMA Resolution 01/86, Class 2 (0.1 mg/l of Al).

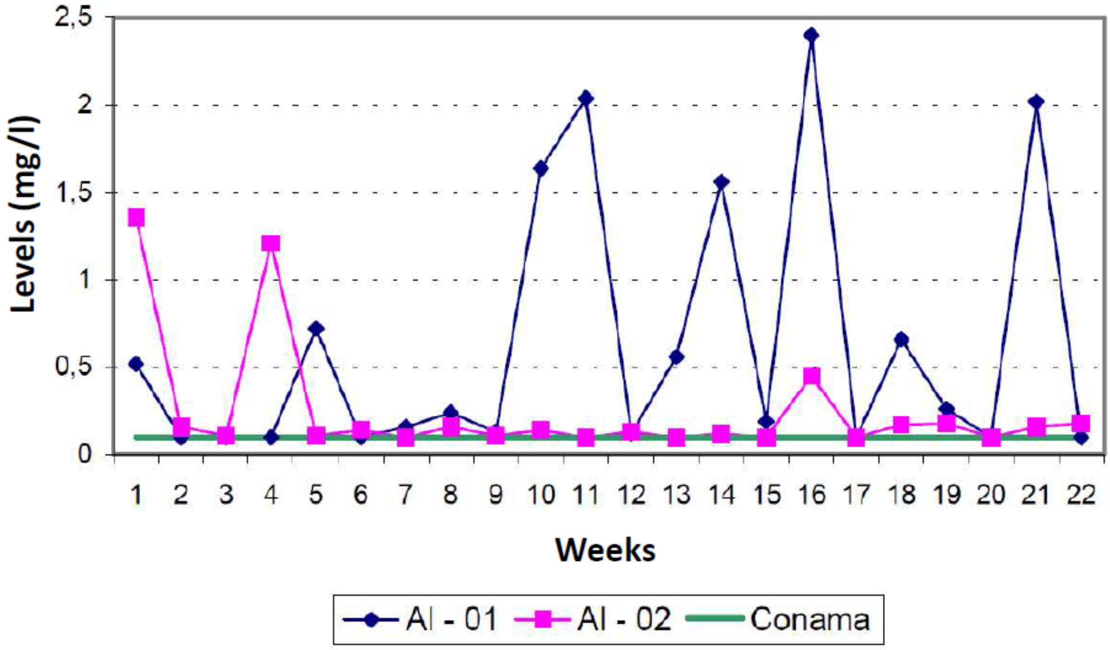

Figure 7.13 – Aluminum levels in the surface waters of the wetland

The levels of aluminum in the surface waters of points 01 (Al – 01) shows a great deal of leaching and/or solubilization of the slag, with the exception of the first four weeks where aluminum availability predominated in the wetland. While point 02 (Al – 02) at the exit of the wetland demonstrates that aluminum has been partially removed by the wetland, mainly from the fifth week.

7.1.5.2 - Calcium

Figure 7.14 presents a weekly survey for points Ca – 01 (entrance to the wetland zone) and Ca – 02 (exit of the wetland zone). Calcium does not have any use restriction for surface waters according to CONAMA.

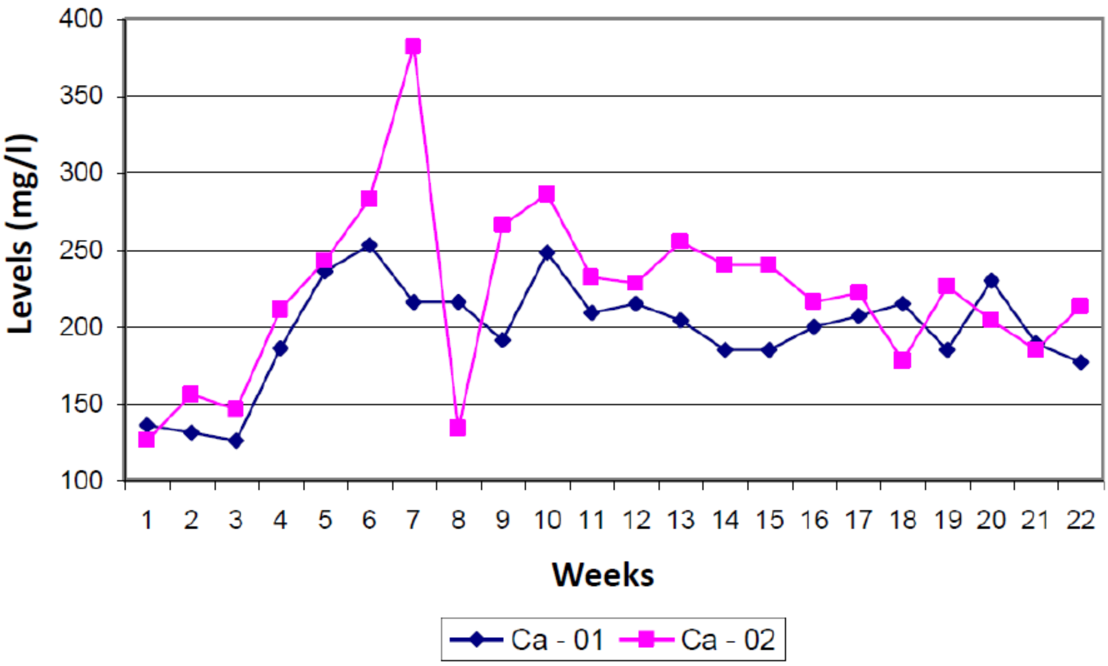

Figure 7.14 – Levels of Calcium in the surface waters of the wetland

Levels of calcium in the surface waters at points 01 (Ca – 01) shows a great leaching and/or solubilization of the slag, however with a great contribution of calcium in the wetland zone. Higher concentrations of this element can be observed at point 02 (Ca – 02) during the twenty-two weeks, except for the first, seventh, eighteenth, twentieth and twenty-first, when the values for entry into the wetland were greater than outgoing ones.

7.1.5.3 - Iron

Figure 7.15 presents a weekly survey for points Fe – 01 (entrance to the wetland zone) and Fe – 02 (exit of the wetland zone). The green dots represent the value established by CONAMA Resolution 01/86, Class 2 (0.3 mg/l of Fe).

The levels of iron in surface waters shows a small predominance at the outlet of this element, point 02 (Fe – 02), where until the fifteenth week the available values were mostly lower than 2 mg/l. While the highest concentrations of point 01 (Fe – 01) found from the ninth week onwards with values of up to 15 mg/l.

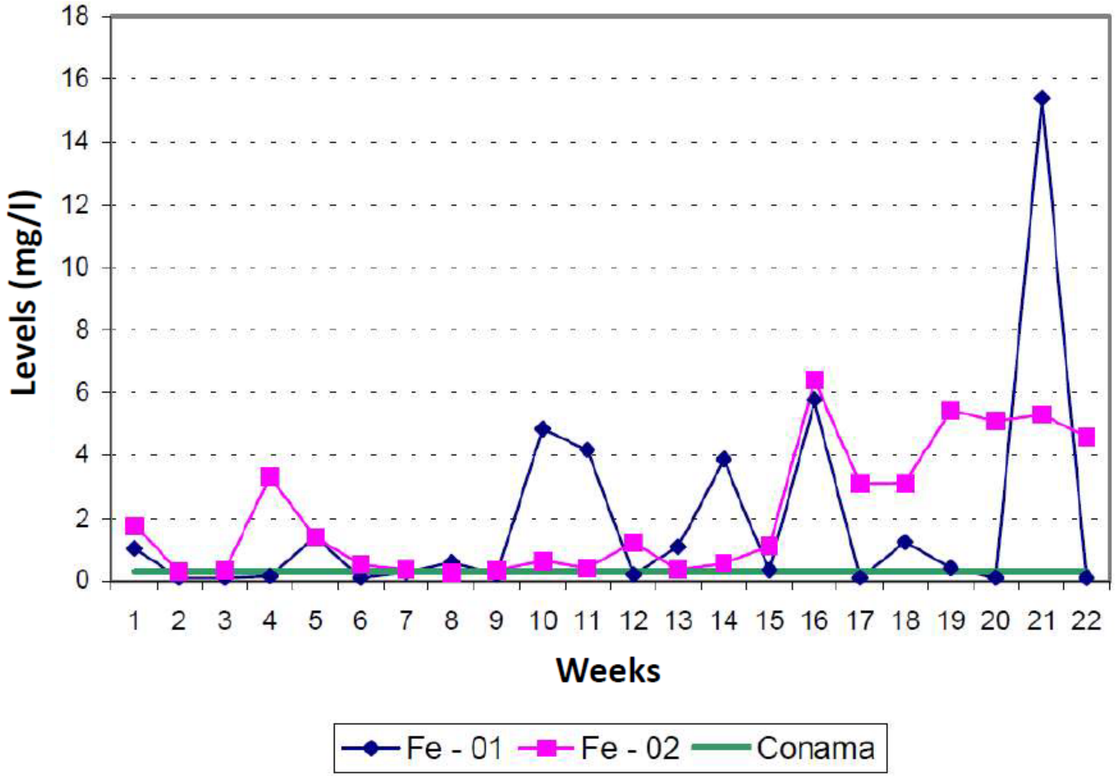

Figure 7.15 – Levels of iron in the surface waters of the wetland

7.1.5.4 - Manganese

Figure 7.16 presents the monthly survey for points Mn – 01 (entry of the wetland zone) and Mn – 02 (exit of the wetland zone). The green dots represent the value established by CONAMA Resolution 01/86, Class 2 de.(0.1 mg/l Mn).

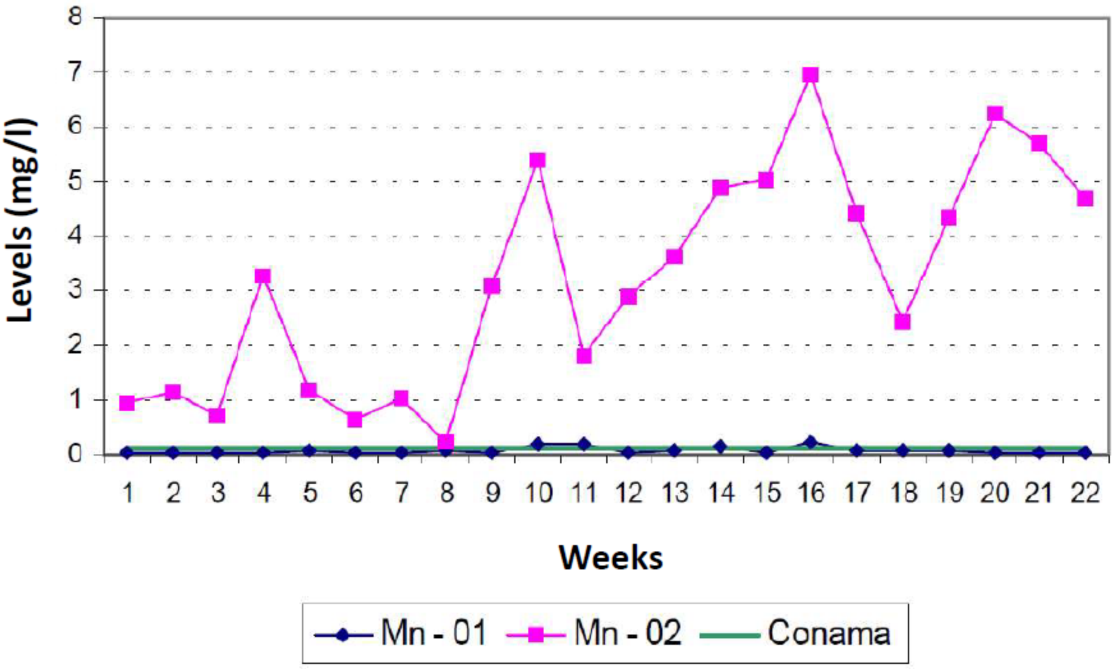

Figure 7.16 – Levels of manganese in surface waters of the wetland

The values of leached and/or solubilized manganese from the slag, point 01 (Mn – 01), were predominantly below the limits established by CONAMA, while point 02 (Mn – 02) which occurs at the exit of the wetland zone shows a high availability of manganese.

7.1.5.5 - Magnesium

Figure 7.17 presents the monthly survey for points Mg – 01 (entry of the wetland zone) and Mg – 02 (exit of the wetland zone). Magnesium does not have any use restrictions for surface waters, according to CONAMA.

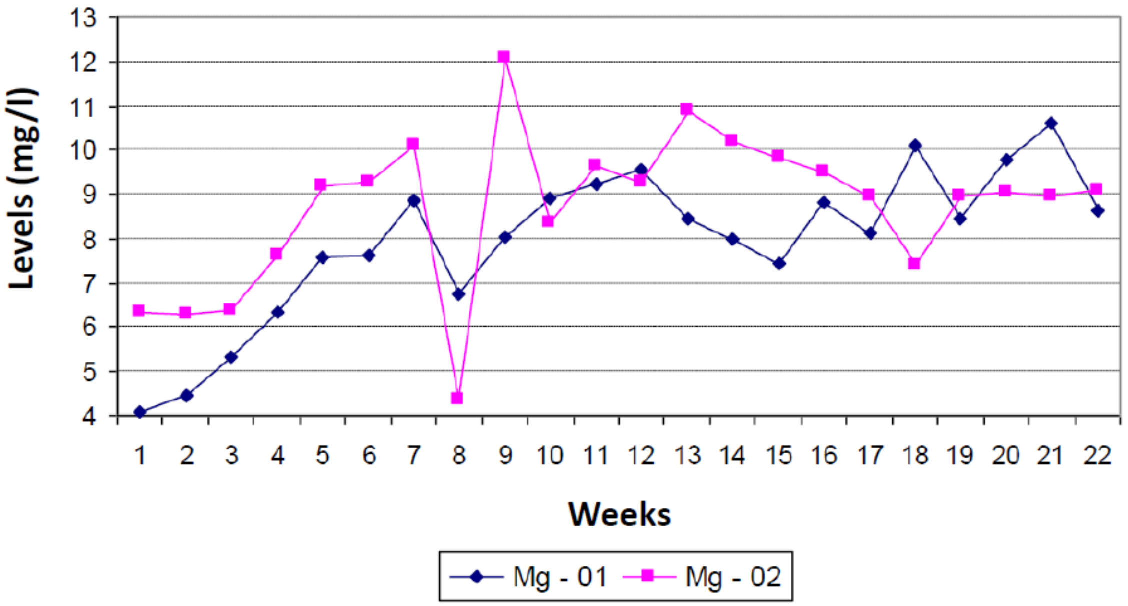

Figure 7.17 – Levels of magnesium in the surface waters of the wetland area

The levels of magnesium found at the exit of the wetland zone, point 02 (Mg – 02), are mostly higher than the leached and/or solubilized values of the slag, showing that there is a migration of magnesium to the flooded system.

7.1.6 - Levels of heavy metals in soil and sediment

For the development of this investigation, 5 sediment samples from the Plumbum wetland and a soil sample from its surroundings were collected, in addition to a sediment sample from a wetland collected 7 km from the investigation area.

Analyses were carried out by sequential extraction of lead, cadmium, copper, and zinc metals. The choice of these metals was based on the concentrations of Zn, Pb and Cu found in the composition of the slag and Zn, Cd and Pb verified in previous studies for soil and water at the Plumbum site (ANJOS 1998).

The main objective of this analyses was to evaluate the amount of metals potentially available to the environment, in addition to investigating in which geochemical phase these metals are preferably concentrated. The analyses will support the preparation of the remediation project for the Plumbum site.

The results obtained in the exchangeable, carbonate, reducible, oxidizable and residual phases of the sediment and soil were as follows (Supplement 4):

7.1.6.1. Exchangeable Phase

Sediment samples from the Plumbum wetland zone (AW1 to AW5) show high percentages (Figure 7.18) and concentrations (Figure 7.19) for lead at all surveyed points, followed by zinc, while the AW1 point close to the emergence of the slag leachate presents the highest concentrations for all analyzed metals.

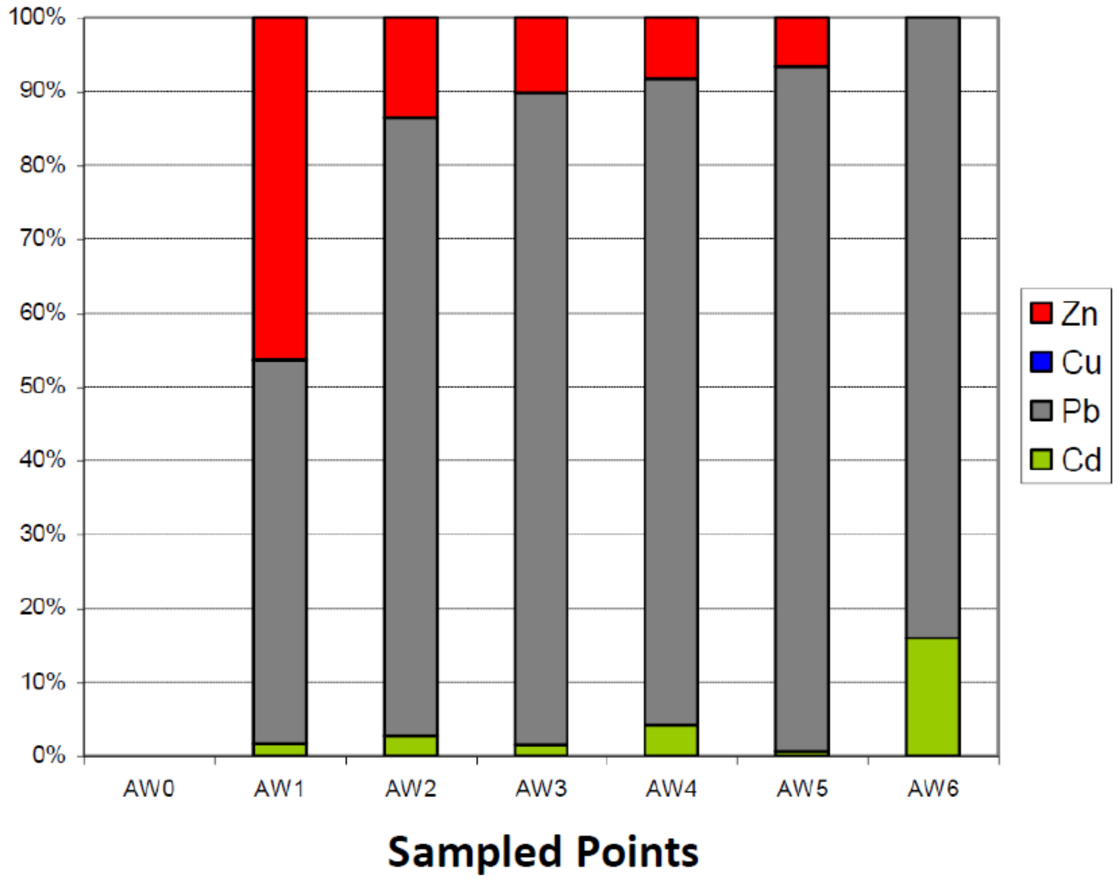

Figure 7.18 - Percentages of metals in the exchangeable phase

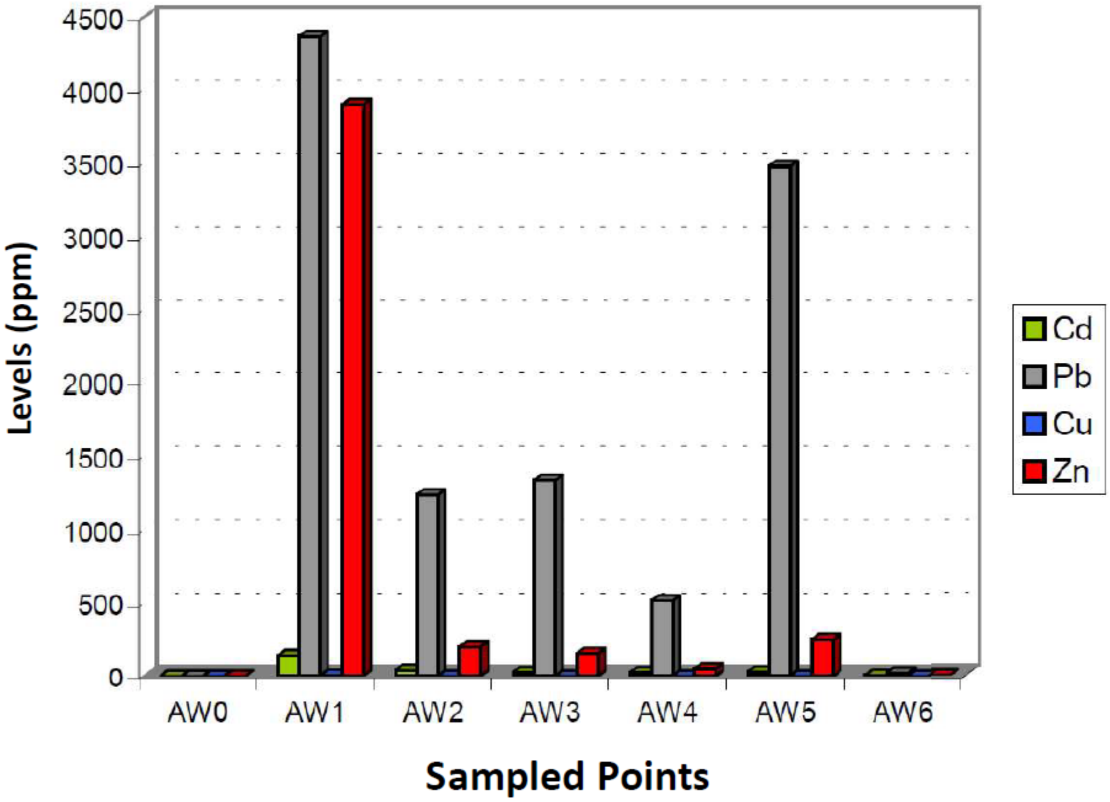

Figure 7.19 - Concentrations of metals in the exchangeable phase

The soil sample (AW6) presents concentrations of lead and cadmium much lower than the sediment samples. While in the control point AW0 the metals Cd, Pb, Cu and Zn were not detected.

7.1.6.2. Carbonate phase

Sediment and soil samples (AW1 to AW6) (Figure 7.20 and 21) show high concentrations and percentages of lead and zinc and, to a lesser extent, cadmium, while the AW1 point close to the emergence of the slag leachate continues to show the highest concentrations of lead , zinc and copper. The AW0 point shows only measurable concentration for zinc.

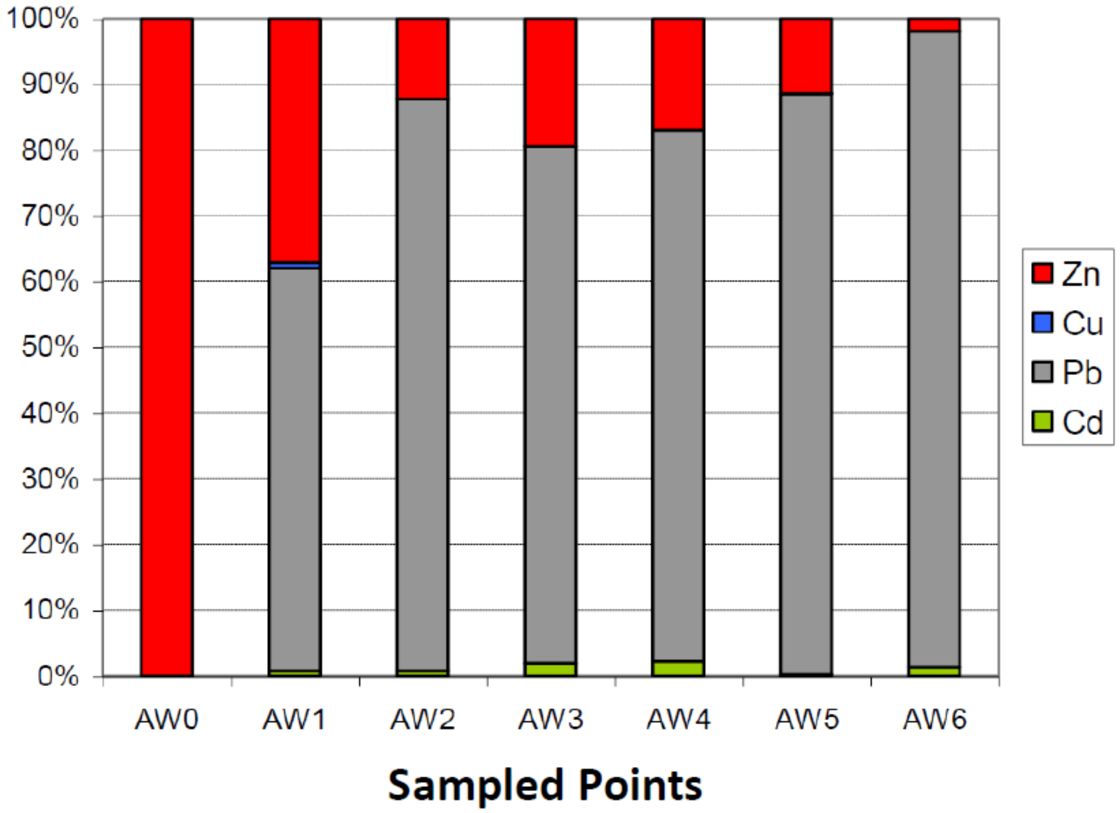

Figure 7.20 - Percentages of metals in the carbonate phase

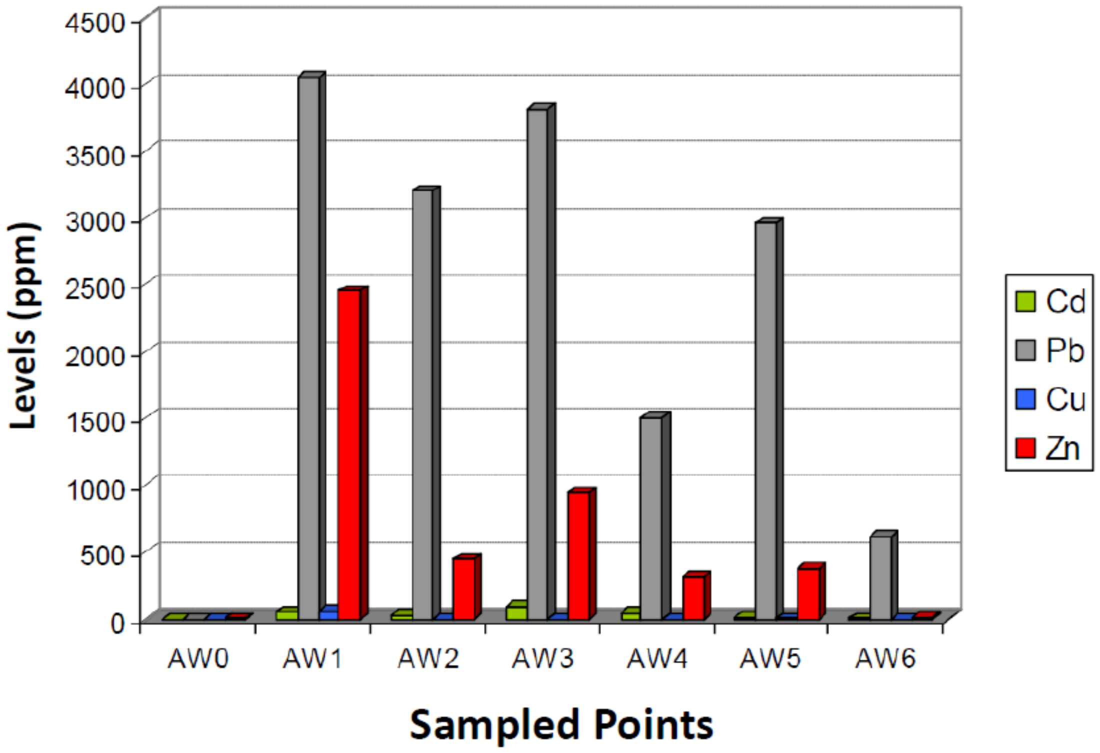

Figure 7.21 - Concentrations of metals in the carbonate phase

7.1.6.3. Reducible Phase

Sediment and soil samples (AW0 to AW6) (Figure 7.22 and 23) show high percentages of lead and to a lesser extent zinc. While point AW1 continues to show the highest levels for lead, zinc and copper, and point AW3 has the highest concentrations for cadmium. At point AW0, low levels of lead and zinc were detected.

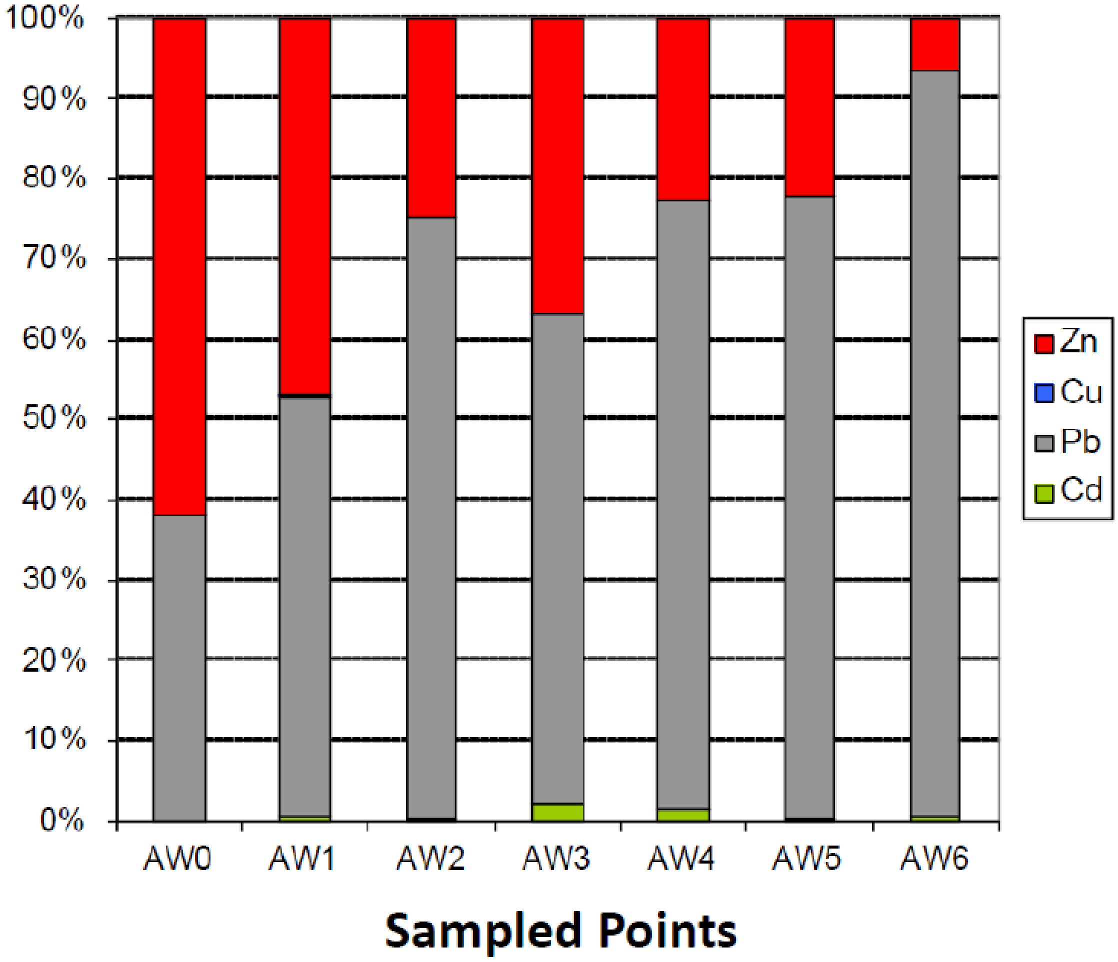

Figure 7. 22 – Percentages of metals in the reducible phase

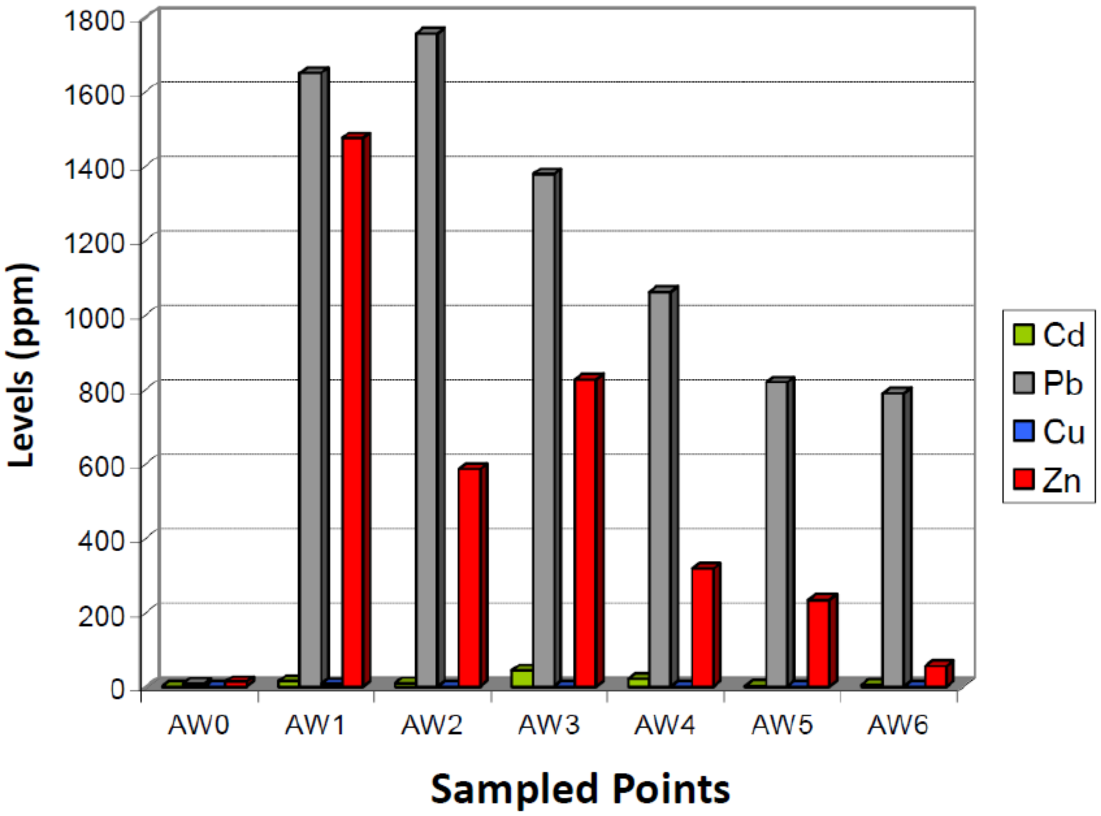

Figure 7. 23 – Concentrations of metals in the reducible phase

7.1.6.4. oxidizable phase

The levels of lead, copper and zinc show very similar values at point AW1, while at all other points in the sediment (AW2 to AW5) the levels follow the order Pb>Zn>Cu>Cd. Copper occurs for the first time in high concentrations, mainly at the AW1 point, demonstrating a high affinity with the organic matter phase (Figure 7.24 and 25).

As in the reducible phase, lead and cadmium have low levels at the AW0 point. While in the soil sample (AW6) it presents concentrations of the four metals always lower than those of the sediments.

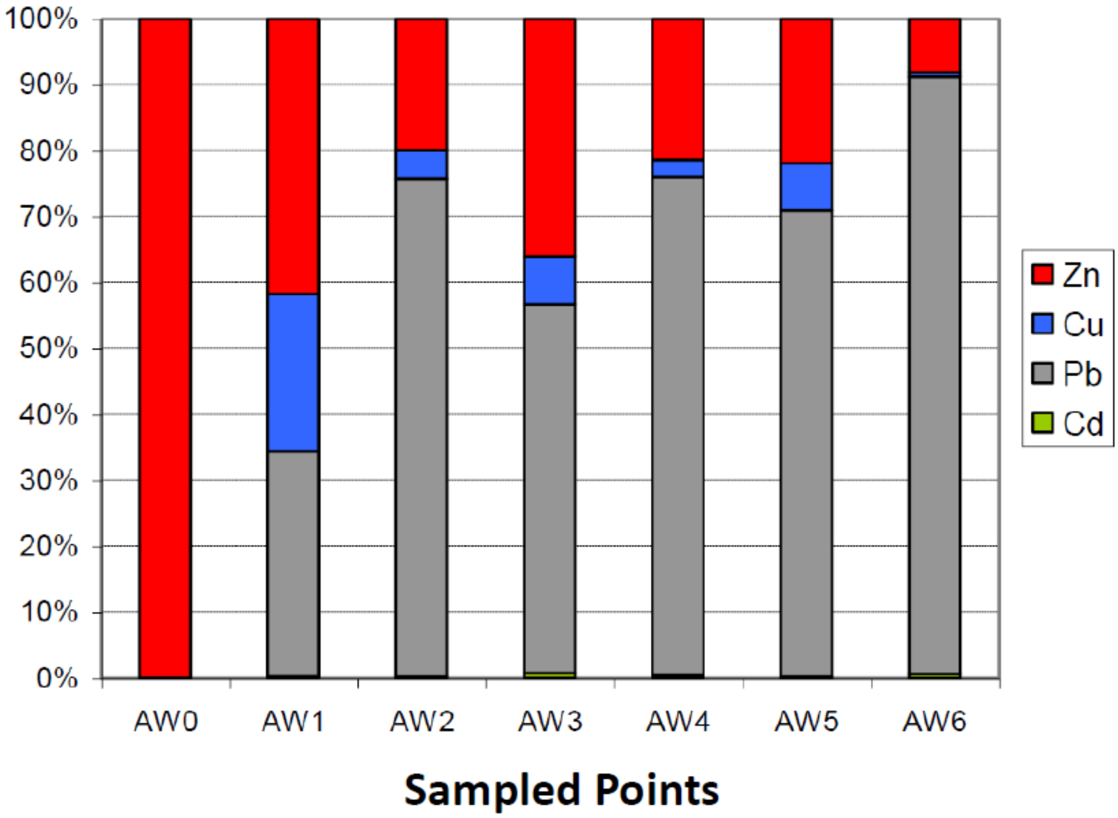

Figure 7.24 - Percentages of metals in the oxidizable phase

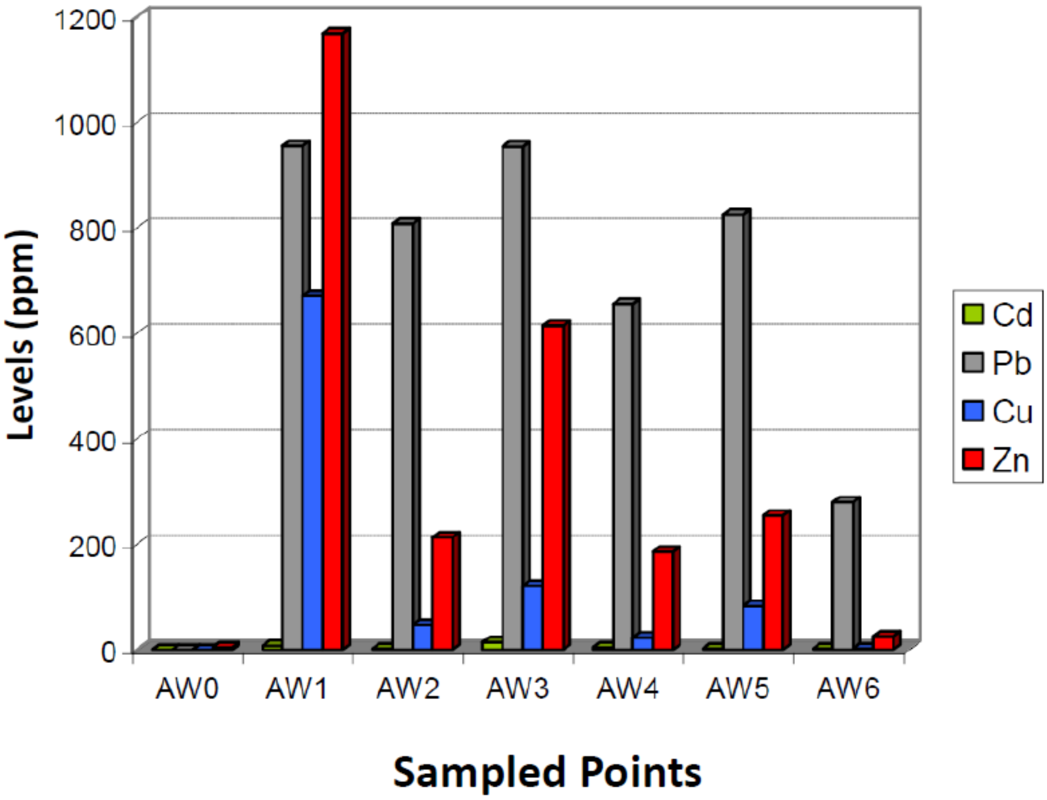

Figure 7.25 - Levels of metals in the oxidizable phase

7.1.6.5. residual phase

Lead percentages in residual phase sediment samples also occur in higher levels. Once again, point AW1 presents the highest values for lead, zinc and copper. Copper concentrations in all samples demonstrate its affinity for this phase (Figure 7.26 and 27).

Lead continues to be the main metal to concentrate in the sediments, with values higher than the oxidized phase, while cadmium shows lower levels than the exchangeable, carbonate, reducible and oxidizable phases.

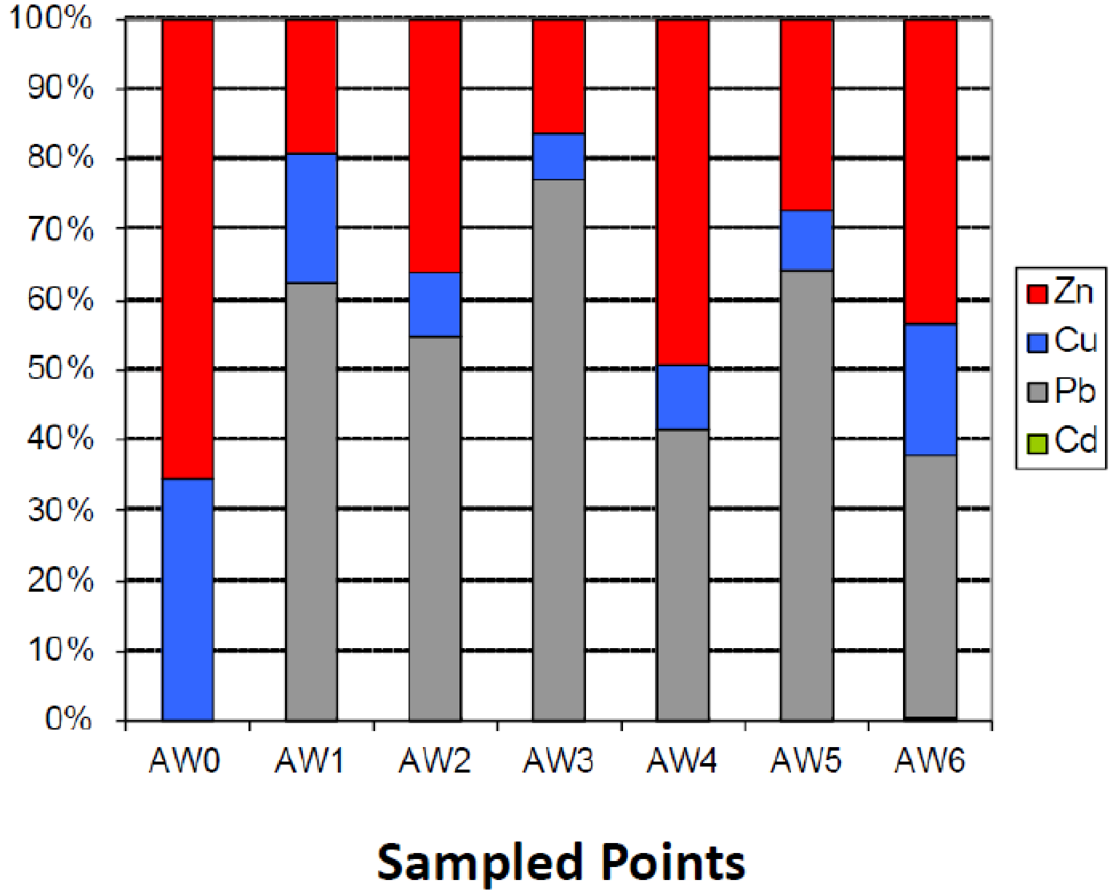

Figure 7.26 - Percentage of metals in the residual phase

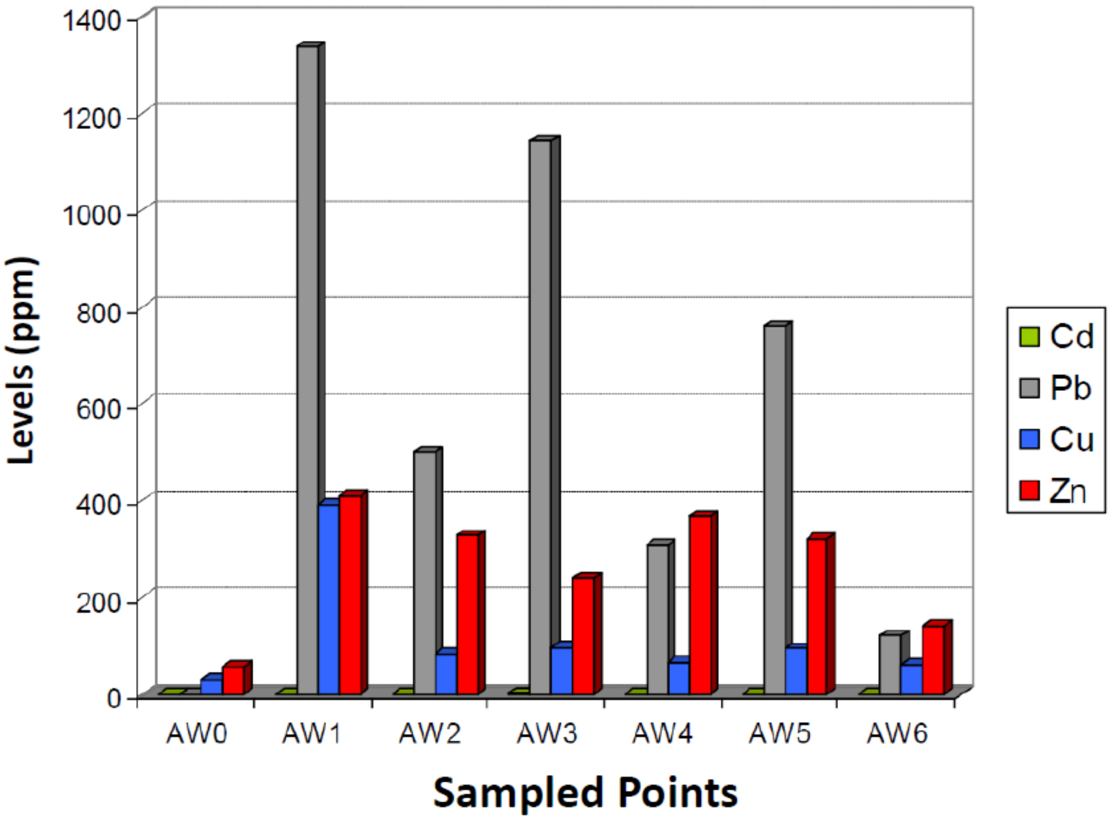

Figure 7.27 - Levels of metals in the residual phase

7.2. – Second Stage – During slag coating

During the period from June to July 2001, a survey was carried out in the Plumbum wetland area, after the slag coating covered the fixed point P1 for sampling the waters arising from the slag (Figure 7.28). The main purpose of the project developed by MORSA was not fulfilled, that of confining the waste so that it would not be leached and/or solubilized by rainwater, as the water continued to migrate through the slag dam. In this way, it was possible to continue measuring surface water at the exit point of the wetland (P – 02).

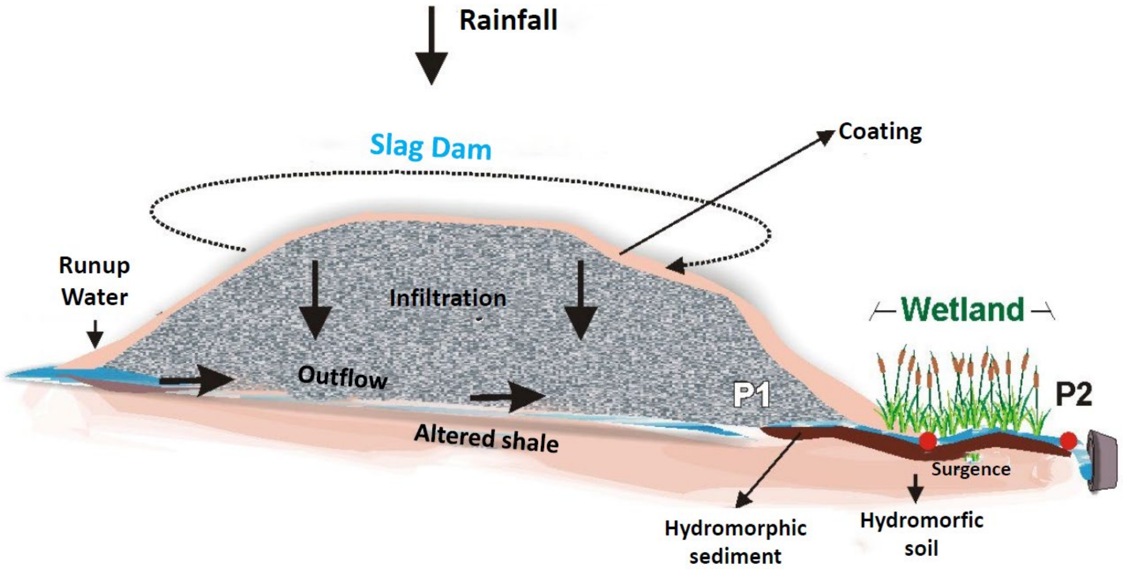

Figure 7.28 - Schematic section with the covering of the slag dam and the landfill at point 01.

7.2.1 - Levels of rainwater

The weekly survey of the volume of rain and pH carried out in the vicinity of the Plumbum wetland during the 2 months of slag covering (June and July), quantified the rainfall precipitation and weekly pH values in the area (Supplement 1) (Figure 7.29) . During this period (8 weeks) average weekly rainfall, greater than 50 mm, predominated; however, these values reached up to 90mm in the twenty-seventh week, while in the twenty-eighth and thirtieth weeks it was below 15 mm. As for pH, there was an increasing trend and a slight variation from 6.9 to 7.4.

During the period of covering the slag dam, the total volume of precipitation was around 430mm, much higher than the initial 5 months when only 318mm of rainwater were measured.

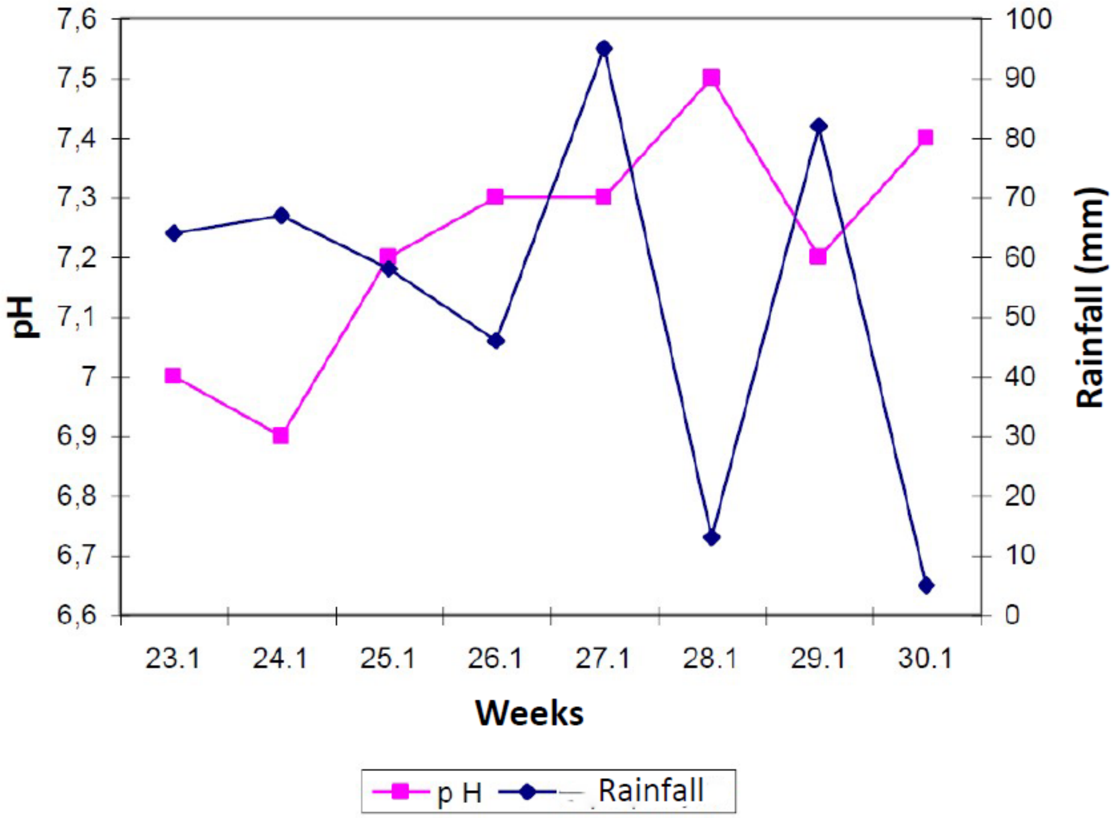

Figure 7.29 - Weekly pH and precipitation values during coating

7.2.2 - Concentrations of physical and chemical parameters of surface water

In this second stage of the investigation, the surface waters were evaluated for 8 weeks, when the following parameters “in situ” were measured: pH, Redox Potential, and Water Temperature (Figure 7.30) (Supplement 2).

The pH values ranged from 6.7 to 7.6 demonstrating an increase in the alkalinity of surface waters. The oxidation-reduction potential shows values ranging from 88 to 344 mV and a growing tendency to oxidation of the system, while the surface water temperature varies from 23.4 to 26 °C. The three parameters showed an increasing variation during this period of slag coating.

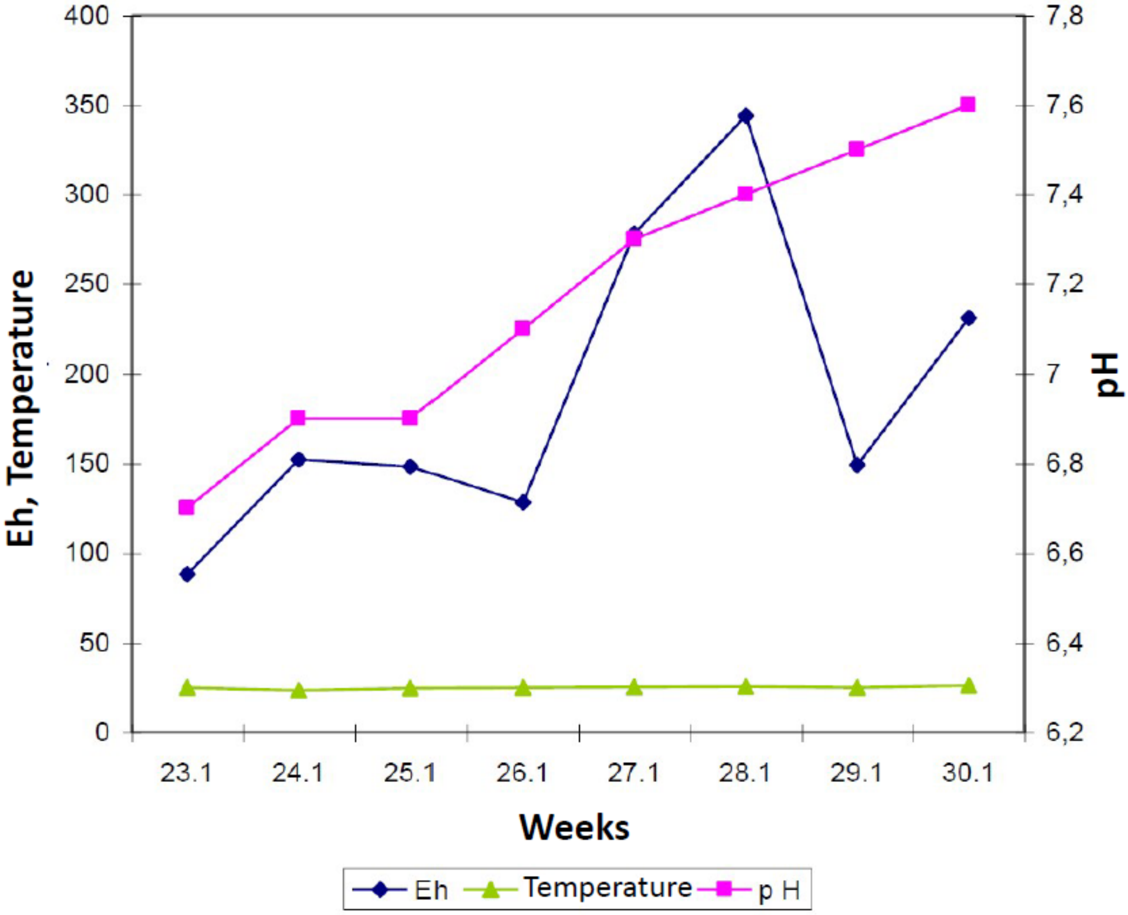

Figure 7.30 - pH, Eh and Temperature values during coating

7.2.3 - Levels of heavy and support metals in surface water

The evaluated heavy and support metals (Supplement 3) remained the same as in the first stage, that is, cadmium, lead, copper and zinc, and the results showed that Cu and Zn are below detection limits, while cadmium and lead present small values above the CONAMA Resolution, respectively in weeks 27 and 29 and in week 30 (Figure 7.31).

Support metals Al, Ca, Fe, Mg, and Mn continued to be detected while heavy metals Cobalt, Nickel, Silver, and Vanadium did not reach detection limits (Figure 7.32). Aluminum values ranged from <0.1 to 0.22 mg/l during this phase, while calcium continued to obtain high values from 208 to 353 mg/l. Iron, magnesium and manganese presented values, respectively, from 0.24 to 3.28 mg/l of iron, from 9.19 to 32.5mg/l of magnesium and from 0.19 to 2.82 mg/l of manganese.

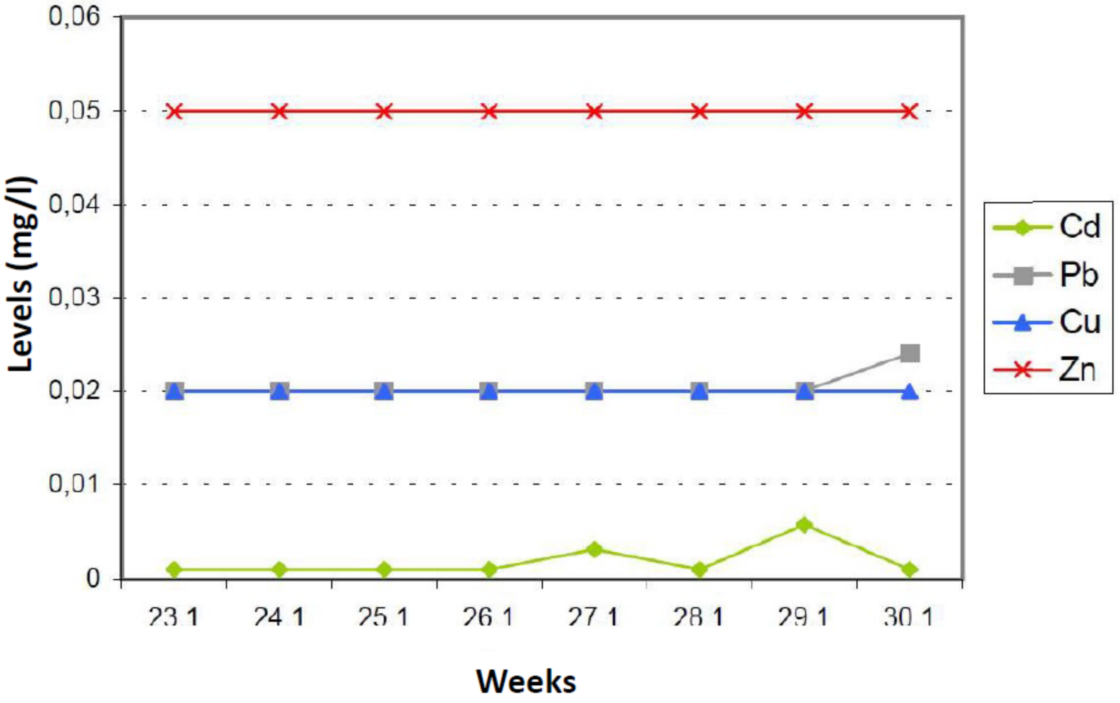

Figure 7.31 – Heavy metals at the exit point of the wetland. CONAMA 01/86, Class 2: Cd = 0.001; Pb = 0.03; Cu = 0.02; and Zn = 0.18.

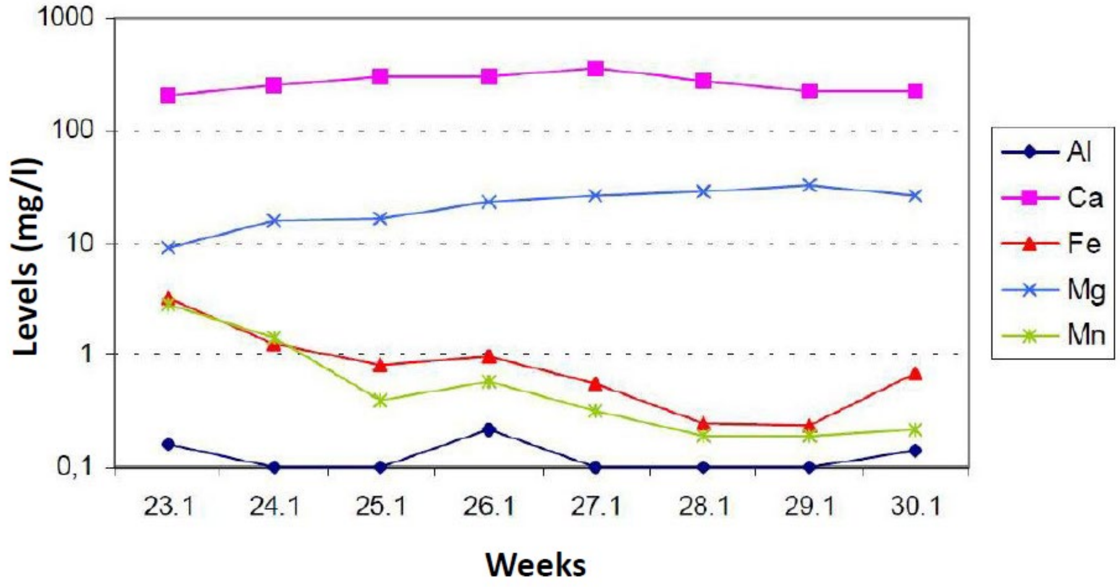

Figure 7.32 – Support metals found in surface water during slag coating.

7.3 Third Stage – After slag coating

After covering the surface of the slag, an attempt was made to evaluate the implanted project and its consequences in the wetland. As Plumbum's project did not include a schedule of activities, the end of activities was assumed when the mobilization of tractors and soil was completed, that is, after the total covering of the slag carried out by the Morsa Company.

During this phase, the effect of rain on the surface covering was noticed, through the development of an erosion process (Figure 7.33). This led the company to redo some areas that were heavily affected by this process.

A survey was carried out of metals and support parameters in surface waters at point P – 02 at the exit of the wetland and a new point P – 03 at the confluence of the drainage with the Subaé river, which continued to migrate, now from the dam covered with soil .

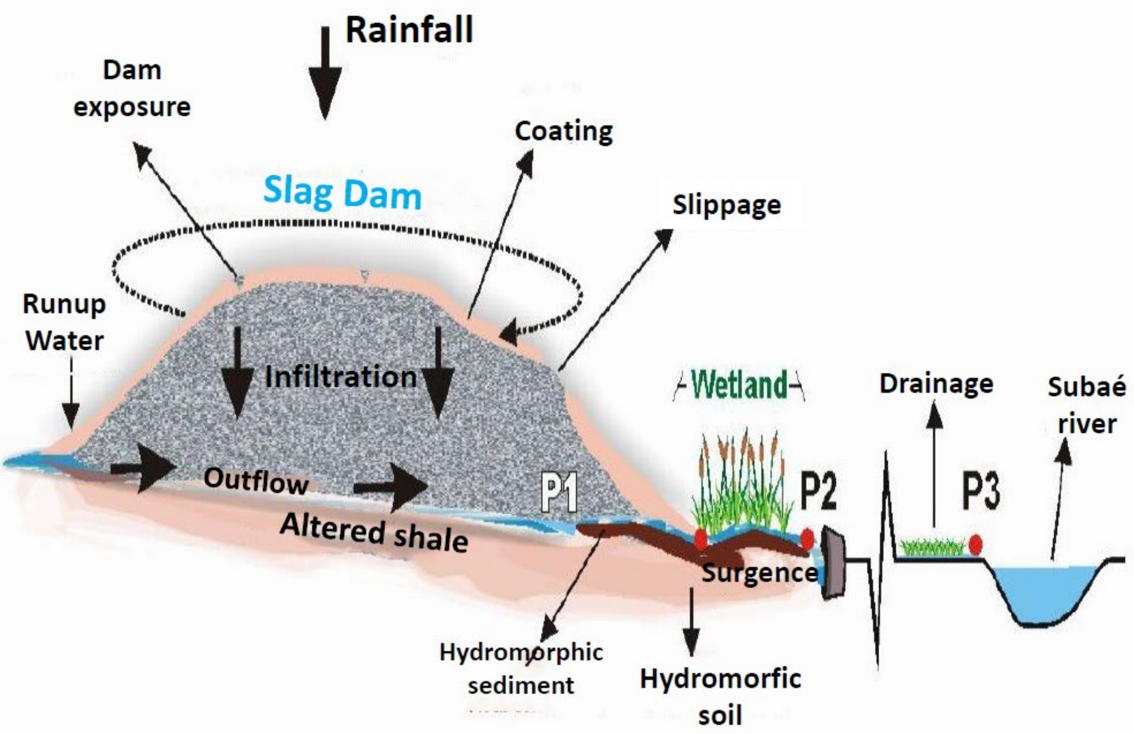

Figure 7.33 – Schematic section showing the surface covering area of the slag dam and sampling points 02 and 03.

Due to the inexistence of a monitoring[52] plan in the project carried out by Plumbum, we established a survey of parameters, until the end of 2001, with the aim of evaluating the behavior of the metals after surface coating, comprising measurements of the metals at the point of leaving the swampy area and an additional point, immediately close to the Subaé river.

7.3.1 – Monitoring of support parameters and heavy metals.

The pH and volume of rainwater (Figure 7.34) (Supplement 01) and the metals lead, cadmium, copper and zinc (Supplement 3) were surveyed.

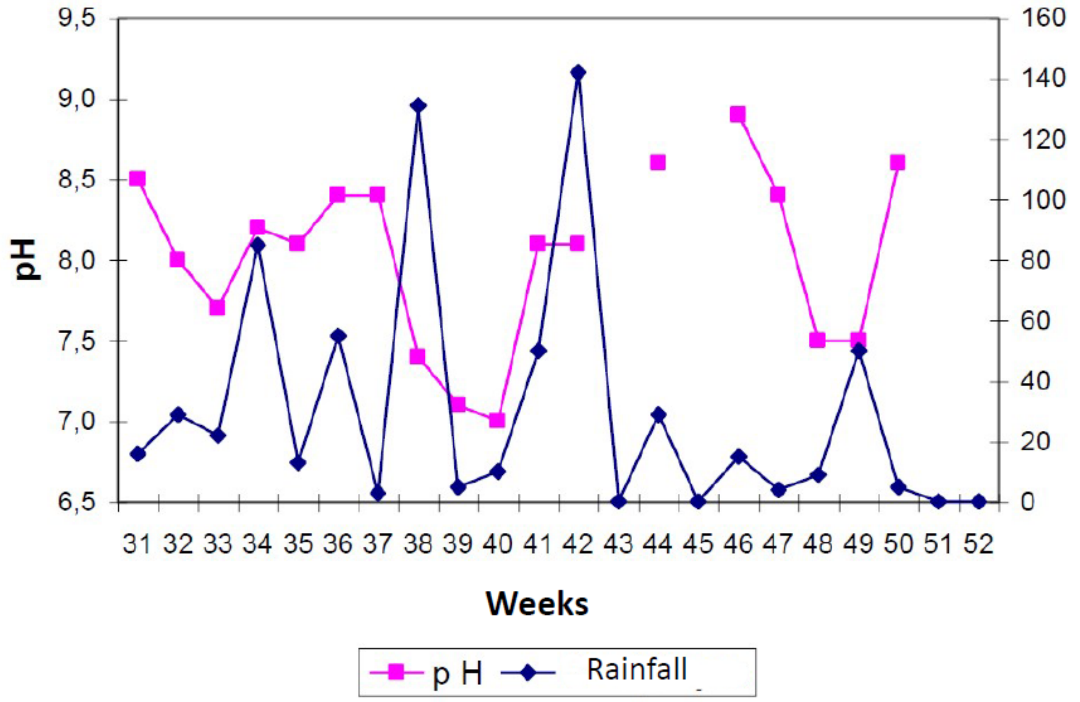

Figure 7.34 – Rainfall volumes and pH

The pH values for this phase ranged from 7 to 8.9, i.e., the waters became more alkaline, while the rainfall volume ranged from zero (43rd,

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[52] The term environmental monitoring, according to LEAL FILHO (1994), means a set of norms and procedures systematically used to control the impact generated by human activities. However, the English establish basic differences between two types of environmental monitoring, the term monitoring is associated with measurement over time (pre-operational, at the moment and post-operational), while the term “Survey”, without translation in Brazil, would be associated with measures of the immediate nature of its objectives. However, in this work we will follow the term monitoring in accordance with the Contaminated Areas Manual, which establishes the following, the term monitoring means “continuous or periodic measurement of the quality or characteristics of a medium” (CETESB 1999).

45th, 51st and 52nd weeks) to 142mm in the 42nd week. However, only in the months of August, September and October there was a total of 590mm of rainfall out of the 673mm recorded in this stage.

Cadmium

From the 36th to the 47th week, the cadmium values at point Cd-2 (at the exit of the swampy area) showed values always above the established by the Conama resolution, while the point Cd-3, close to the Subaé river, presented values above of the Conama resolution, only in the 33rd and 41st weeks (Figure 7-35).

Lead

The lead values at the Pb-2 point at the exit of the wetland exceed the Conama resolution values in the 40th, 46th and 52nd weeks while the Pb-3 point only in the 33rd week (Figure 7-36).

Copper

The copper values at the Cu-2 point at the exit of the wetland exceed the Conama resolution values at the 46th week, while the Cu-3 point does not show lead migration into surface waters. (Figure 7-37).

Zinc

Zinc values at the Zn-2 point at the exit of the wetland zone and Zn-3 near the Subaé River did not show concentrations that exceeded the Conama resolution value. (Figure 7-38).

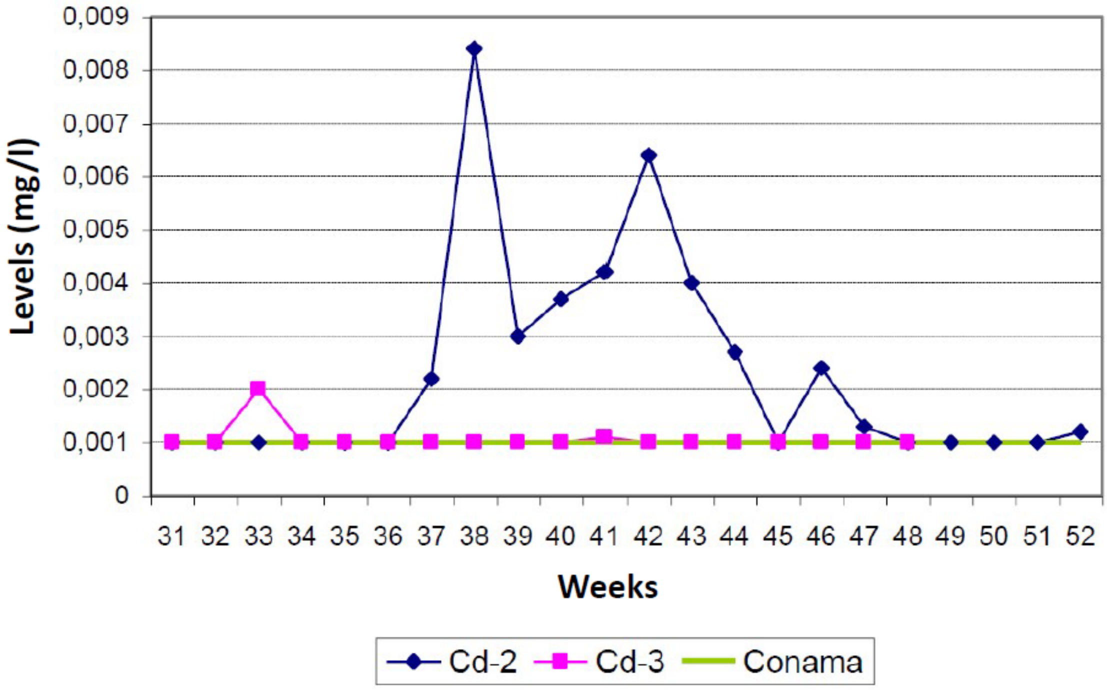

Figure 7.35 – Levels of cadmium at the exit of the wetland (Cd-2) and near the Subaé River (Cd-3).

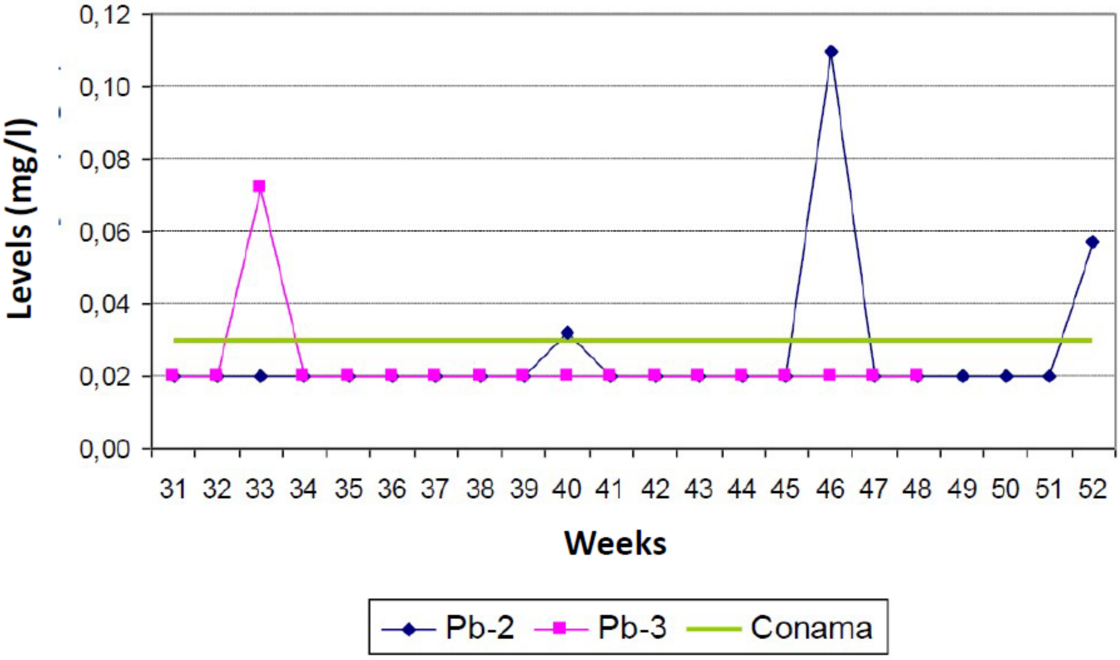

Figure 7.36 – Levels of lead at the exit of the wetland (Pb-2) and near the Subaé River (Pb-3).

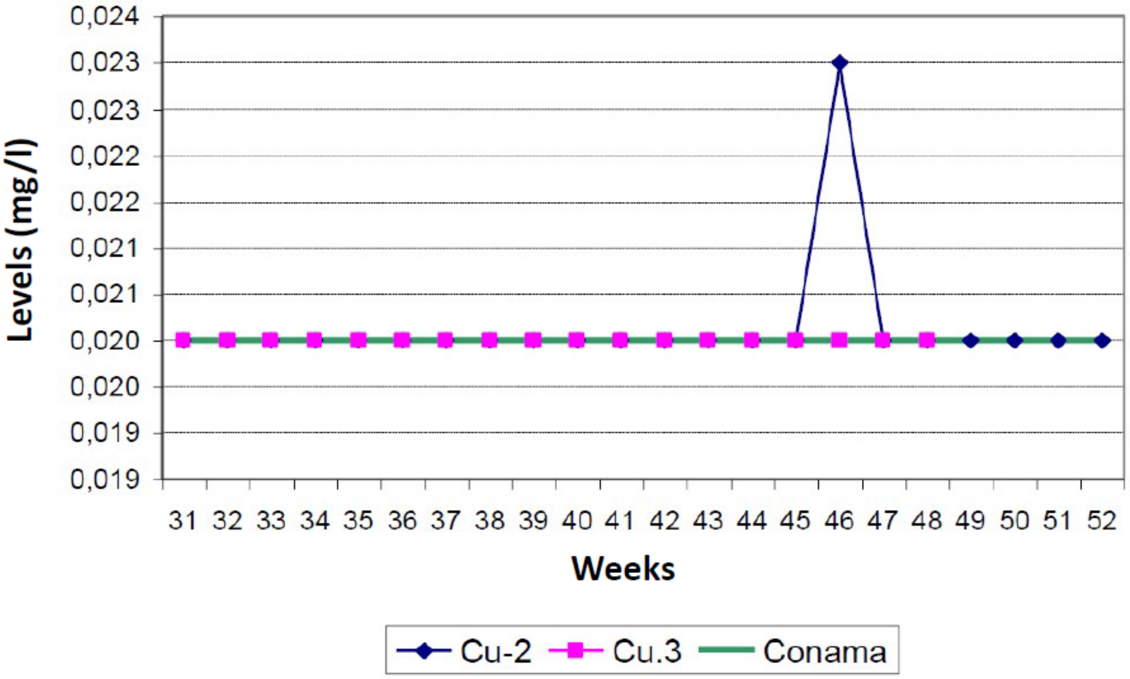

Figure 7.37 – Levels of copper at the exit of the wetland (Cu-2) and near the Subaé River (Cu-3).

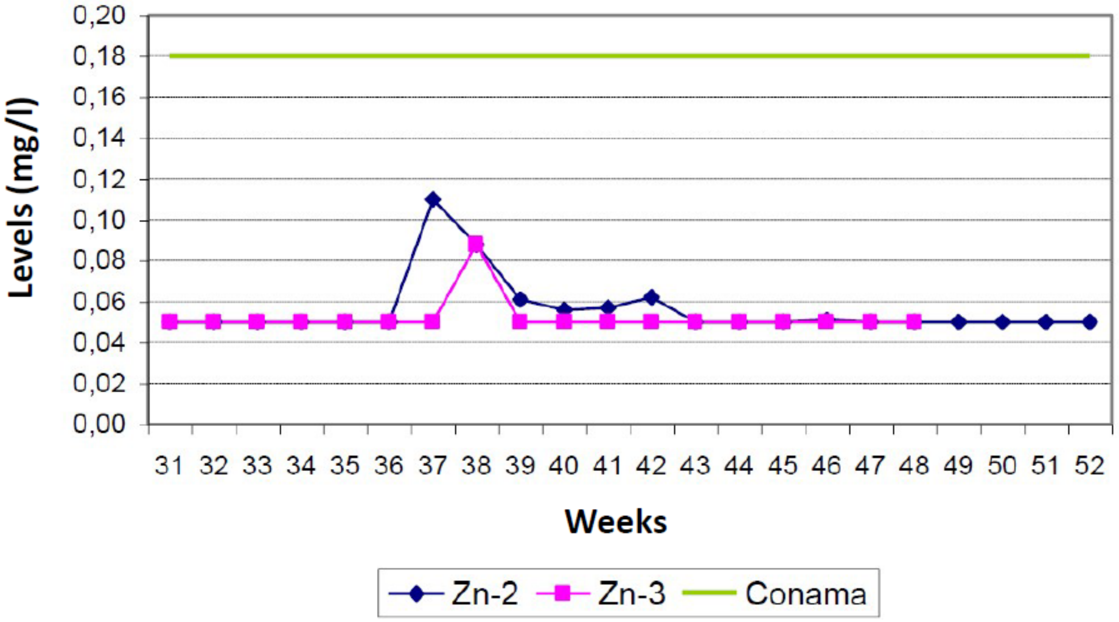

Figure 7.38 – Levels of copper at the exit of the Wetland (Zn-2) and close to the Subaé River (Zn-3).

CHAPTER 8: ANALYSIS AND DISCUSSION

8.1 - First stage - Before coating the slag

8.1.1 - Rainwater and its interference in the leaching and/or solubilization of the slag.

The pH of rainwater measured in the 22 weeks before covering the slag (Figure 7.3), predominantly alkaline, characterizes this parameter as the main natural control mechanism for leaching and/or solubilization of contaminated slag (SOLOMONS 1995, KABATA-PENDIAS 1995 and BORBA et al. 1996). This alkalinity condition of the system mildly leaches the metals Pb, Cd, Cu, Zn, Al, Mn and Fe and solubilizes the Ca and Mg carrying them to the wetland.

Comparing the monthly values collected in 2001 by the Plumbum rain gauge (Figure 8.1) with the average rainfall measured during the period 1913-1985 at the meteorological station operated by the National Institute of Meteorology (INMET), located in the municipality of São Francisco do Conde, close to Santo Amaro, we can observe that the values collected in the first five months and the following five months of the year in Santo Amaro were, respectively, lower and higher than the average for the region (BAHIA 1996).

The rainfall volume for the first five months of the first stage corresponds to 318 mm measured at Plumbum in Santo Amaro and compared with the average 894 mm at the São Francisco do Conde station, demonstrates that there was an atypical year of rainfall. These data are corroborated by the great drought that hit Brazil in 2001, causing the greatest energy control program directly caused by the extremely low water levels in Brazilian reservoirs.

The weekly precipitation volume shows outstanding values above 50 mm in the ninth and eighteenth weeks (Figure 8.1), which could contribute to a process of greater leaching and/or solubilization of the slag. However, for the surface water support parameters, only the DO (Figure 7.7) has a higher value in the ninth week, justified by the greater volume of water in the system, the same not happening in the eighteenth week when the DO is extremely low.

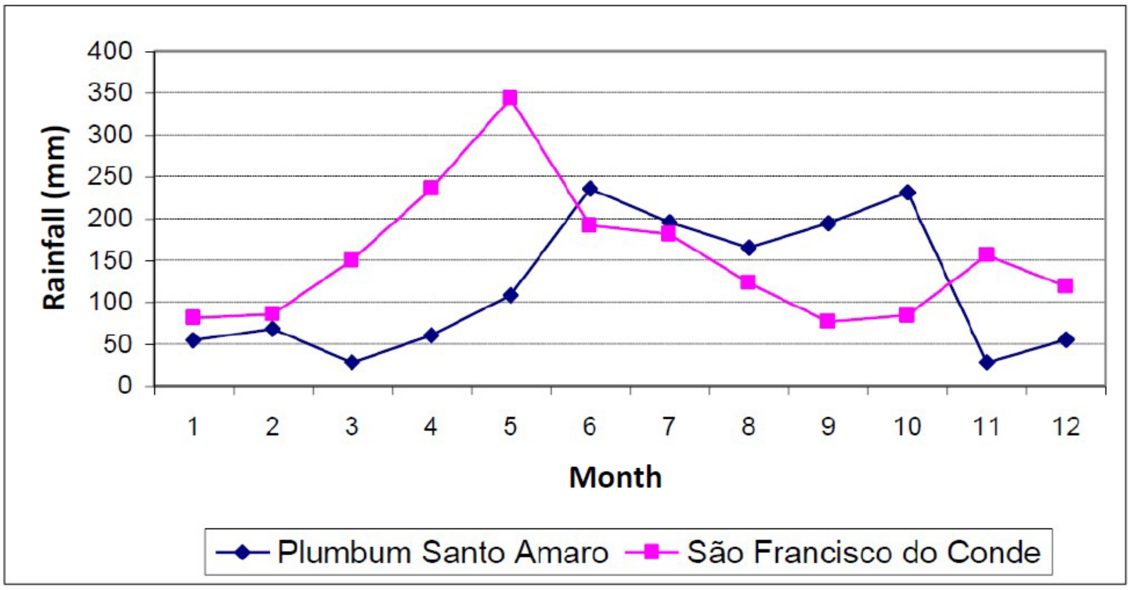

Figure 8.1 – Monthly rainfall values measured at the Plumbum site in 2001 and monthly average values for the region close to Santo Amaro. Source: Modified from BAHIA (1996)

By checking the pH values of rainwater in the first and eleventh weeks (Figure 7.3), when concentrations below six were measured, and therefore inducing a tendency towards greater removal of metals contained in the slag, it can be seen that this direct correlation is not observed in the first week. However, in the eleventh week, the concentrations of metals Cd, Pb, Cu and Zn (Figures 7.9; 7.10; 7.11 and 7.12) at the slag emergence point are among the three highest concentrations in the period.

As for the support elements Al, Ca, Fe, Mn and Mg (Figures 7.13; 7.14; 7.15; 7.16 and 7.17), it was observed that in the first week there was no correlation between the low pH and the higher concentration of these elements in the appearance of the slag skimming, while for the eleventh week, only aluminum shows significant concentrations. Ca and Mg, on the other hand, showed high concentrations at the entrance of surface waters, due to their high percentages in the slag and because they are very leached and/or solubilized even in a neutral to alkaline environment.

The four toxic metals and support metals evaluated at the entrance to the wetland zone show low concentration levels in the ninth and eighteenth weeks, demonstrating the lack of direct correlation between high precipitation volumes (Figure 7.2) and metals leached from the slag.

The average values of the chemical composition of the slag (Table 7.1) determined by X-ray Fluorescence were evaluated with the analysis presented by CRA (1992) and OLIVEIRA (1977) (Table 8.1):

Table 8.1 - PLUMBUM SLAG COMPOSITION

COMPOSIÇÃO	OLIVEIRA (1977)	CRA (1992)	ANJOS (2003)
SiO2	20 to 25%	20 to 25%	21.5 to 25.5%
FeO	28 to 35%	28 to 35%	23.3 to 26.6%
CaO	15 to 20%	15 to 20%	20.4 to 23.2%
Pb	1 to 3%	1 to 3%	(PbO) 3.25 to 5.35%
Zn	8 to 17%	8 to 12%	(ZnO) 11.3 to 15.3%
S	1 to 3%	1 to 3%	(SO3) 1.7 to 3.72%
Cd		25 g/t	Not detected
Cu			(CuO) 0.08 - 0.61%

However, CRA's (1992) and OLIVEIRA's (1977) propositions do not make any reference to the analytical method applied to determine the composition of the slag. Hence, it is not possible to compare these data due to the different results, possibly being correlated to different analytical methods (Scanning Electron Microscope; X-Ray Fluorescence, Graphite Furnace; Optical Plasma and Atomic Absorption by Flame).

From data on the volume and pH of precipitation, a statistical survey was carried out using Boxplots (TOLOI et al. 2002) in order to observe possible discrepant points in the data set. Figure 8.2 shows that the volume of precipitation did not present discrepant values in the 22 weeks of the first stage, leaving the discrepant points for values that occurred in the months of July, September and October of the same year, while in Figure 8.3 there is a very discrepant value low for precipitation pH in the first week of January.

Using the graph of smoothed series[53], it can be verified that the year 2001 was atypical in relation to the volume of precipitation, since the average of the region (Figure 8.1) in the rainy season ranges from April to July, while the smoothing graph it is clearly seen that the rainy season runs from June to October (Figure 8.4). The precipitation pH smoothing graph demonstrates that rainwater is changing from slightly acidic to alkaline (Figure 8.5).

However, since there are no emission of atmospheric particulates near the city of Santo Amaro that interfere with the pH of rainwater, it can be measured that this fact may be related to the direction of the winds (east-west) and emissions from the Landulfo Alves Refinery and Siderúrgica do Brasil Steel Co., located north of the Todos os Santos Bay and which in the summer, due to the small amount of cloud condensation, can concentrate mainly sulfur, interfering with the pH of rainwater in the region.

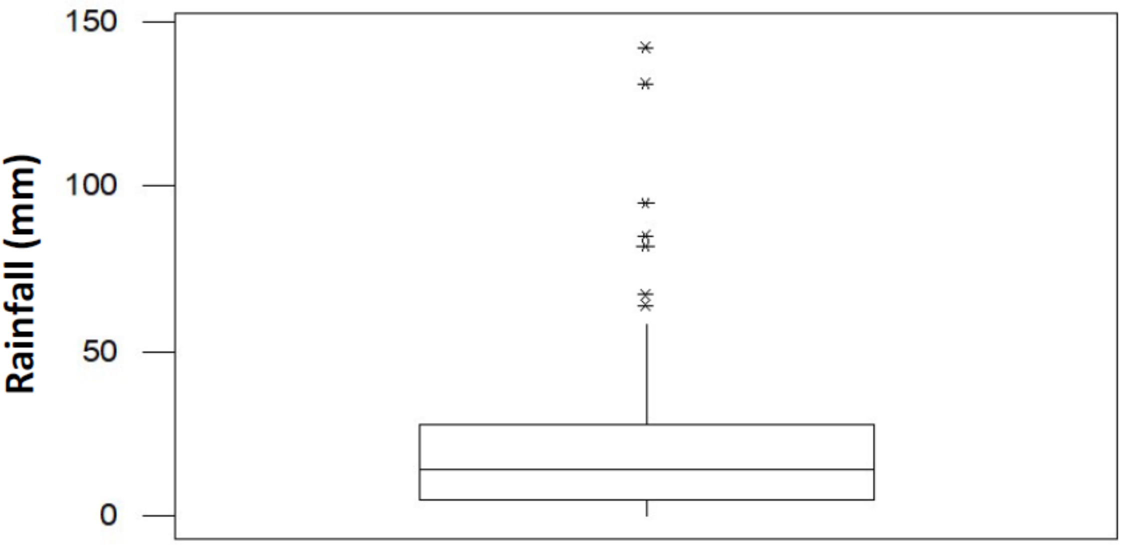

Figure 8.2. – BoxPlot of rainfall volume

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[53] Smoothing is obtained by taking the arithmetic mean of every four consecutive observations as a means to verify a trend in the series, through the decrease of data variability (TOLOI et al. 2002).

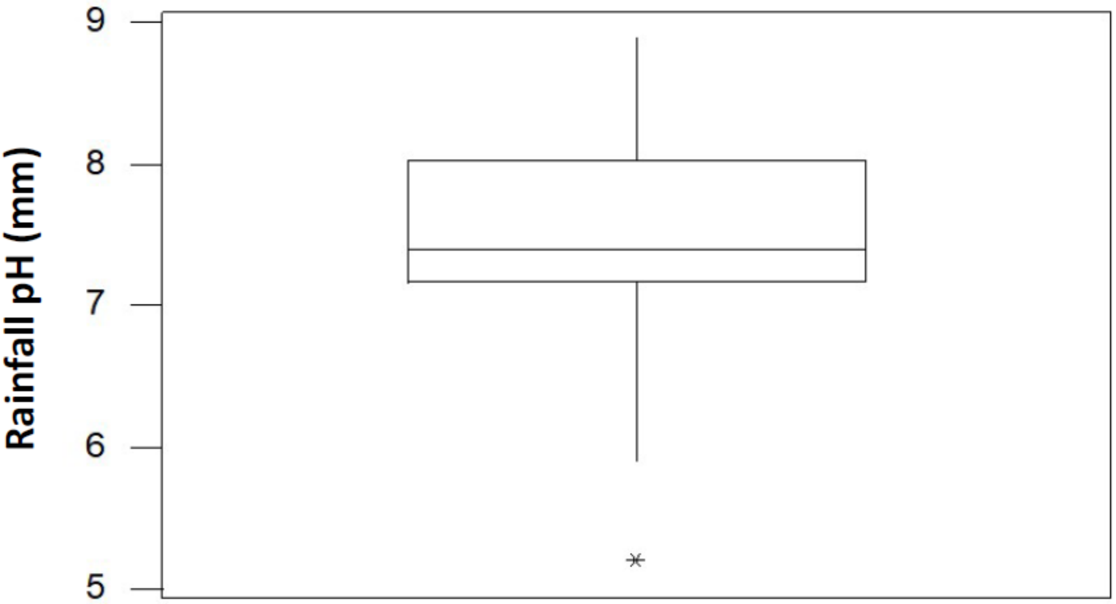
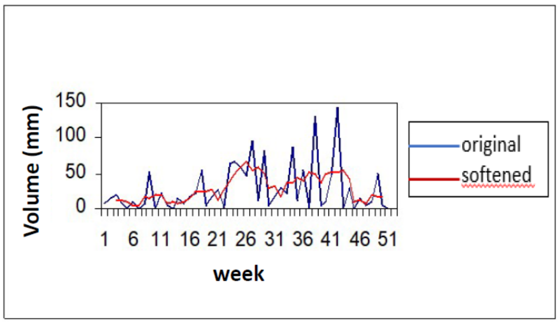


Figure 8.3. - BoxPlot of rainfall pH



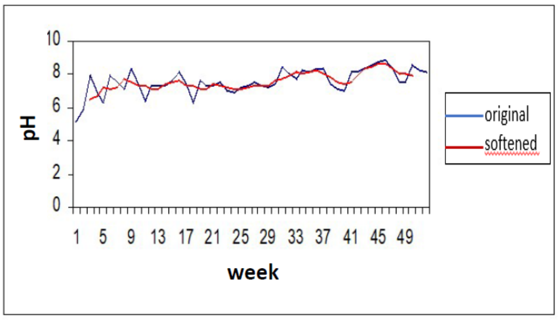


Figure 8.4. - Rainfall volume.

Figure 8.5. - Rainfall pH

8.1.2 - Behavior of metals in surface water entering and leaving the wetland zone

Surface water at the Plumbum site behaves as the main transport vector for metals. Understanding how metals are leached and/or solubilized from the slag to the flooded zone determines the main mechanisms and conditions for the removal and potential availability of the researched elements.

The measurement of metal concentrations and support parameters at the entrance and exit of the flooded zone allows evaluating the efficiency of this wet system as an environment conducive to the removal of metals and the possible interference of support parameters in the precipitation and/or solubilization of metals.

The levels of metals Cd, Pb, Cu and Zn represented in Figures 7.9; 7.10; 7.11 and 7.12 consistently show higher levels of these elements at the entrance of the wetland than at the exit. In this case, it is possible to observe (Figure 8.6) that there is a strong correlation between the levels of lead, copper and zinc and, to a lesser extent, cadmium. This fact may be due to the high solubility that cadmium presents when found in water with a pH between 6 and 9 (SMITH et al. 1995), as in the case of the Plumbum wetland (Figure 7.4), while for Pb, Cu and Zn, the pH found at the entrance to the wetland favors the precipitation of these metals.

As for heavy metals at the exit point of the wetland, their concentrations are strongly correlated with the biogeochemical processes that occur in surface waters and sediments, such as: precipitation, sorption, complexation and redox (BOURG and LOCH 1995).

As for the concentrations of support elements Al, Ca, Fe, Mn and Mg (Figures 7.13; 7.14; 7.15; 7.16 and 7.17) at the entrance to the wetland, aluminum, iron and manganese are correlated with each other and with toxic metals (Figure 8.7), while calcium and magnesium do not correlate with the other metals, but maintain a correlation between them.

However, research demonstrates that some metals present specificities such that the greater solubilization of aluminum is conditioned to pH from 7 (KADLEK and KNIGHT, 1996). Observing the pH found at the entrance to the wetland, an initial predominance of pH above 7 is noted until the 6th week, from this point the pH tends to values equal to or less than 7 (Figure 7.4). On the other hand, the aluminum concentrations verified at the entry point of the wetland tend, initially, to low values, increasing in concentration with the decrease in pH at the entrance of the wetland (Figure 7.13). Therefore, as aluminum, iron, manganese, lead, cadmium, zinc and copper are highly correlated with each other, it is possible that pH is the main control mechanism for the removal processes of these metals in slag.

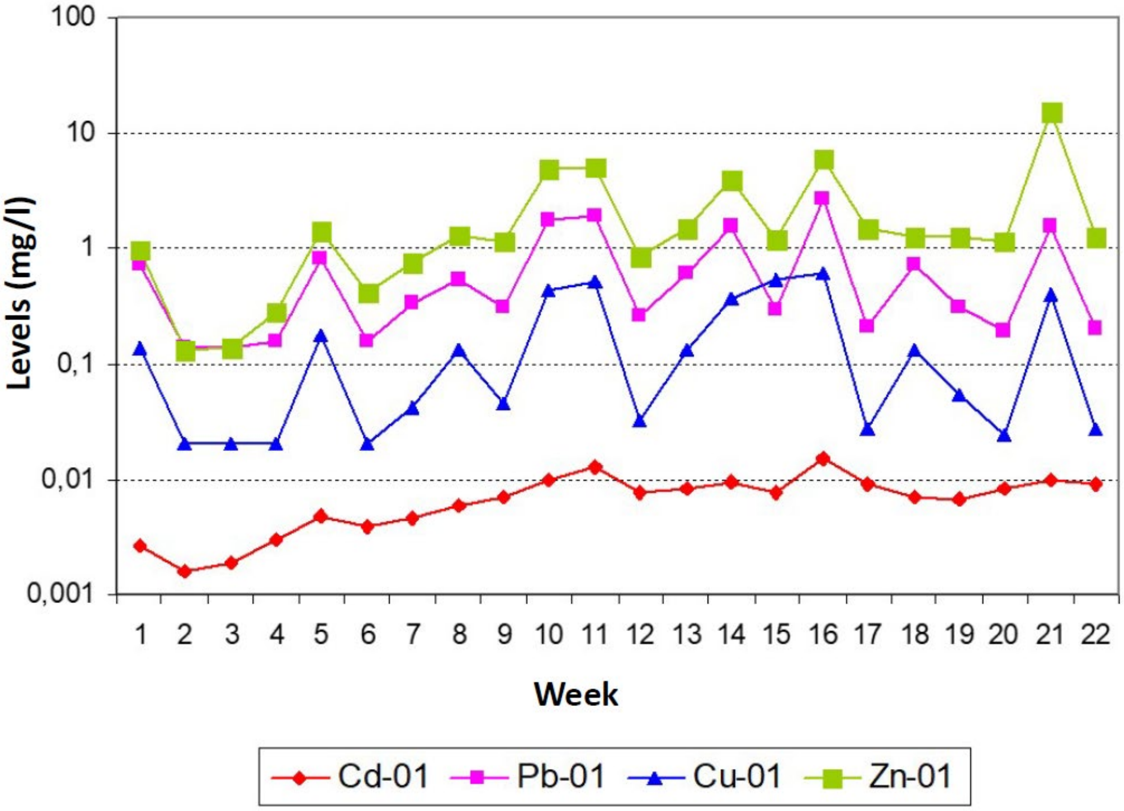


Figure 8.6 - Correlation of metal concentrations at the entrance to the wetland

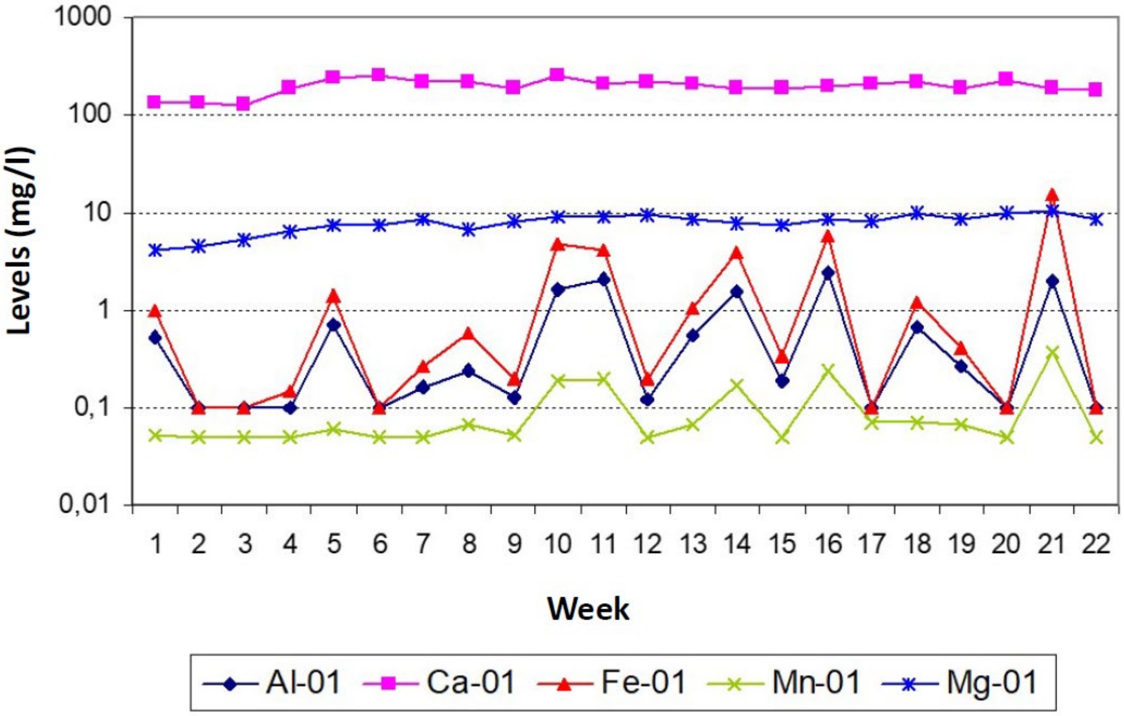


Figure 8.7 - Correlation between support elements at the entrance to the wetland

Iron can be found in wetlands in the oxidized state as Fe^{+2} or reduced as Fe^{+3}. At the entry point of the wetland, Eh ranges from 150 to 350 mV (Figure 7.5) and the predominant pH ranges from 7 to 8 (Figure 7.5). According to the iron and manganese stabilization diagram (Figure 8.8) (SENGUPTA 1993), the raised points would be concentrated in the Fe^{+3} precipitation zone.

In addition to pH and Eh, another important support parameter for the mobility of metals in the Plumbum wetland was water conductivity. The high conductivity can be strongly related to the high concentrations of calcium and magnesium. Although concentrations of these parameters at the exit of the wetland are higher than at the entrance, this must be understood as a function of the competition with iron and manganese in the hydromorphic sediment, causing the displacement of calcium and magnesium to the solution.

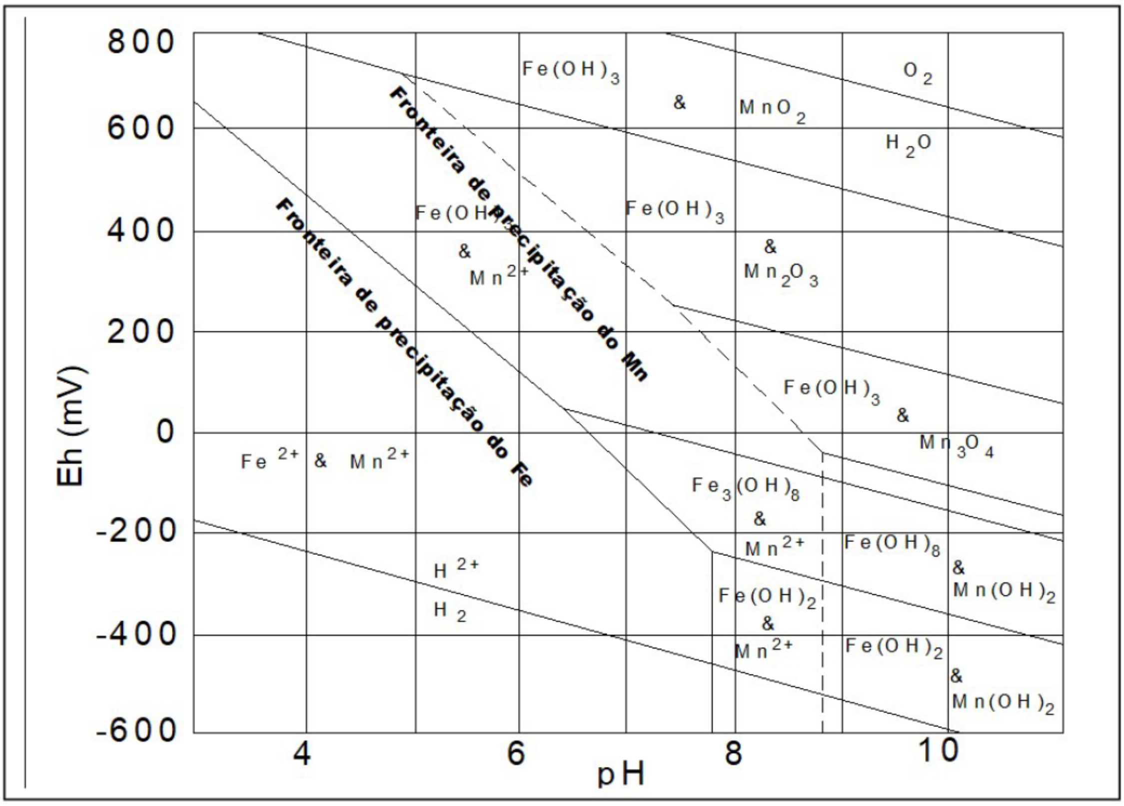


Figure 8.8 - Stability diagram of iron and manganese in composition with pH and the Eh. Source: Adapted from FAULKNER and RICHARDSON (1990) apud SENGUPTA (1993)

As for the water temperature (Figure 7.8), it was observed that the values at the inlet are always higher than at the outlet. This fact is due to the conditions of higher temperature that the water acquires when migrating through the dam of the slag that has a dark color and absorbs more solar energy, whereas when subject to the shading conditions produced by the vegetation of the wetland, they present lower temperatures.

The values found for pH and Eh at the entrance to the wetland are higher than those at the exit of the same zone. This fact is due to the consumption of oxygen and the presence of organic acids in the wetland system, hence the lower values at the exit from the wetland.

The levels of heavy metals - lead, cadmium, copper and zinc – found in the surface waters of the Plumbum wetland showed the following peculiarities:

- lead and cadmium present at the entry point (P1) of the wetland zone 100% of the samples above the limits established by the Conama resolution, while for zinc and copper there are, respectively, 91% and 82% of overruns;
- copper and zinc are being removed 100%, while lead is being retained 82% and cadmium 73%;
- the selectivity of metals at the exit of the wetland is: Cu and Zn > Pb > Cd. This selectivity is in agreement with SOUZA et al. (2000), which establishes that Cu and Zn are more likely to form low solubility compounds, such as hydroxides, carbonates and sulfides, explaining, in part, the decrease in the concentration of these elements in surface waters;
- cadmium was the least selective of the heavy metals (27%). This fact proves that Cd is the most soluble of the researched metals; and
- Lead concentrations were still above the Conama Resolution standard in 18% of the samples.

A statistical evaluation of the metals Pb, Cu, Zn and Cd at the entry and exit points of the wetland area using Boxplots showed that: cadmium (Figure 8.9) and copper (Figure 8.11) do not present any discrepant point in relation to the others , both at point 01 and at 02. In Figure 8.10, it is observed that, for lead at point 01 there was a concentration well above the others, which corresponds to the observation of the 16th week, while at point 02, three discrepant values appeared. For zinc (Figure 8.12), in point 01 there is also a high value in relation to the others, corresponding to the last week of May and, in point 02, all concentrations were very low, that is, lead and zinc have discrepant values many higher than the mean values found.

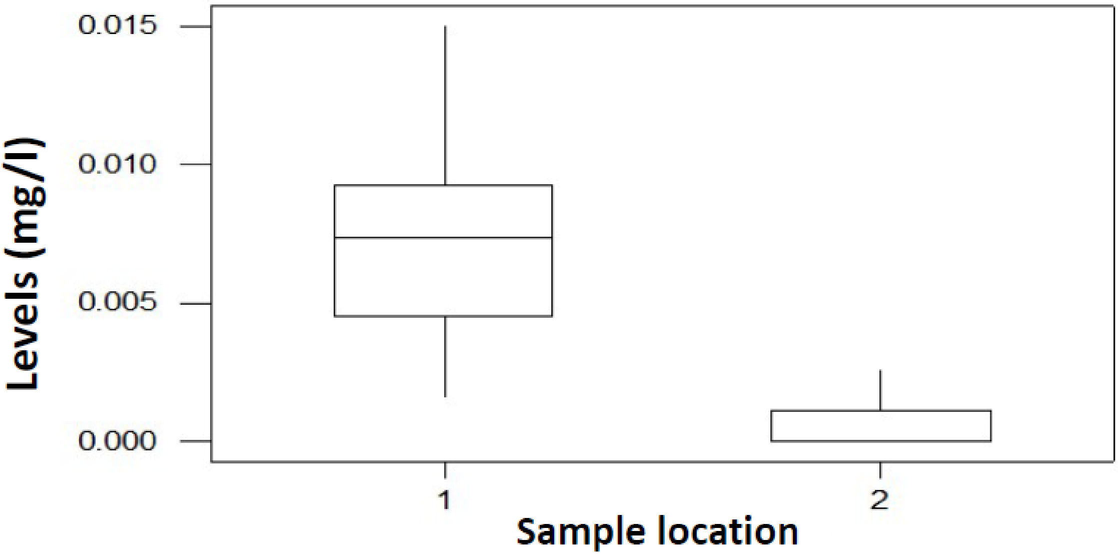


Figure 8.9. - BoxPlot of cadmium concentration

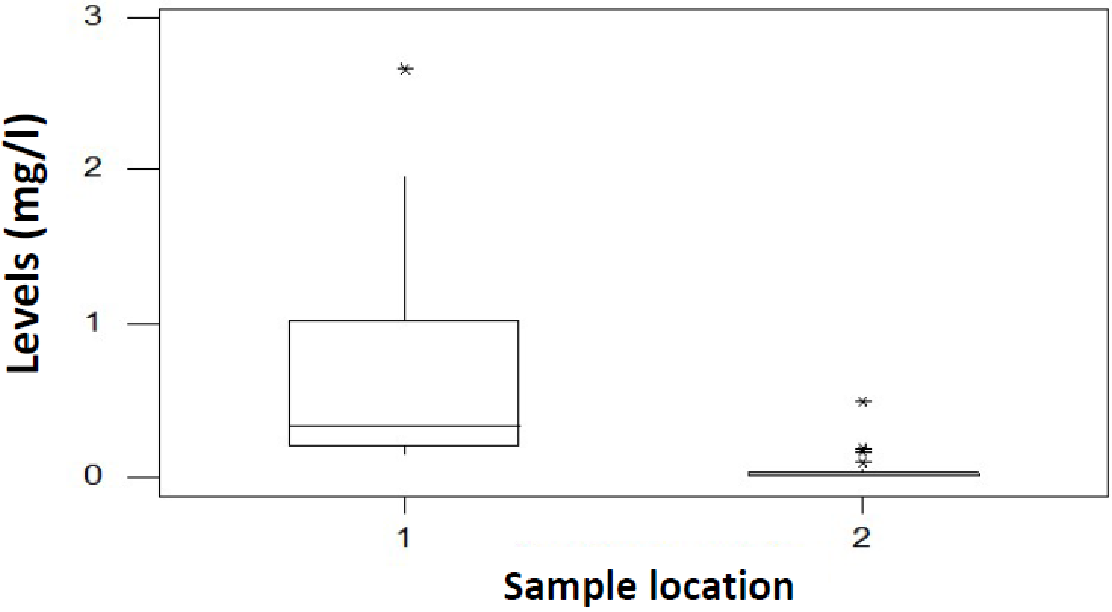


Figure 8.10. - BoxPlot of lead concentration

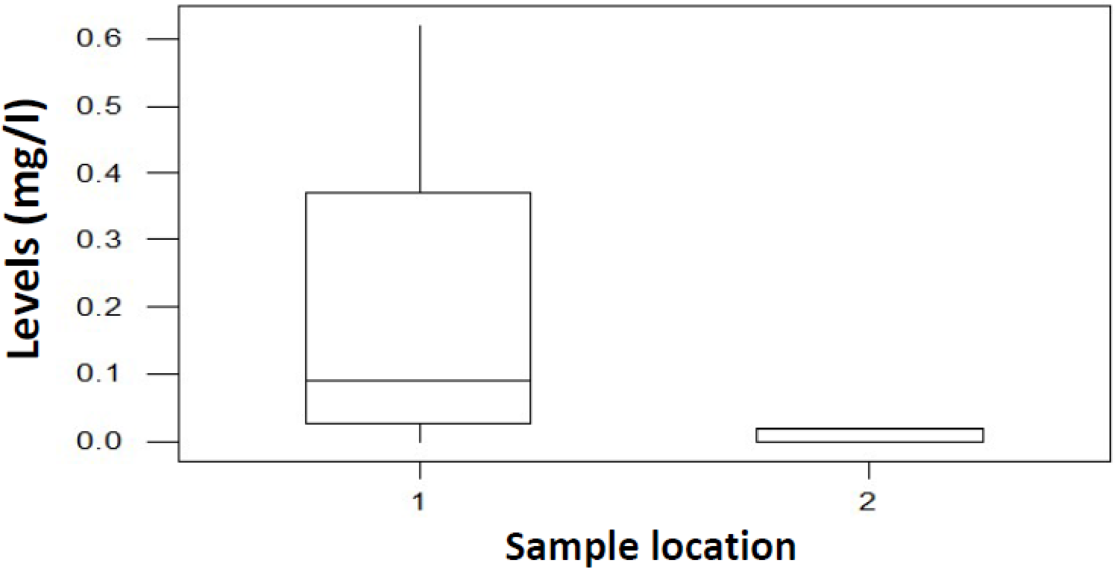


Figure 8.11. - BoxPlot of copper concentration

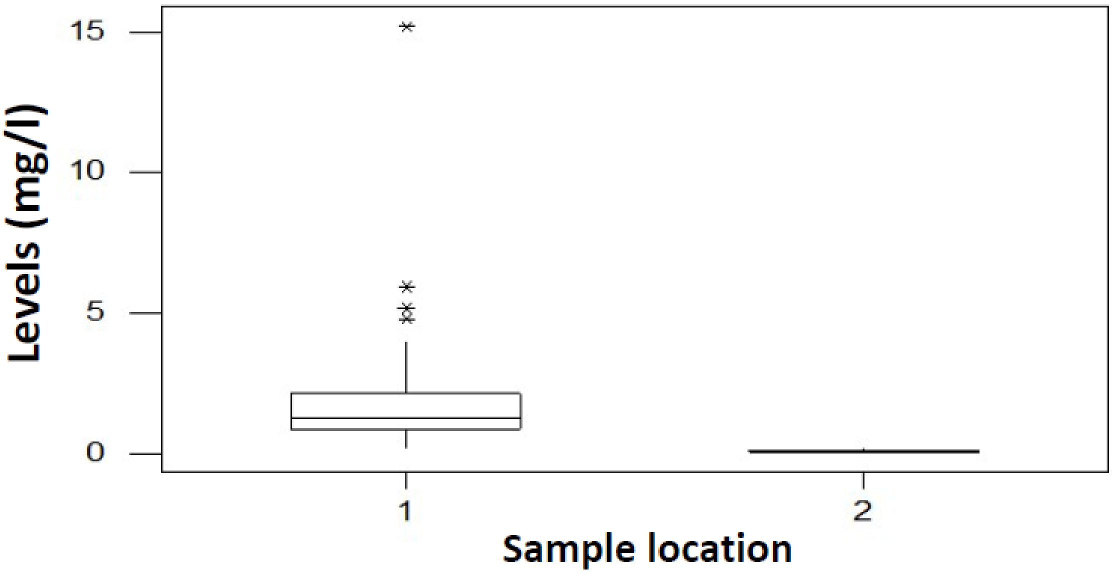
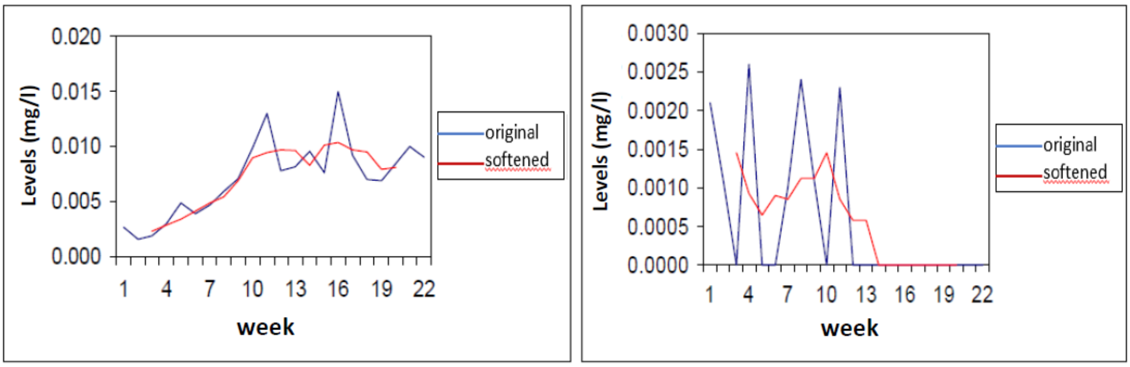
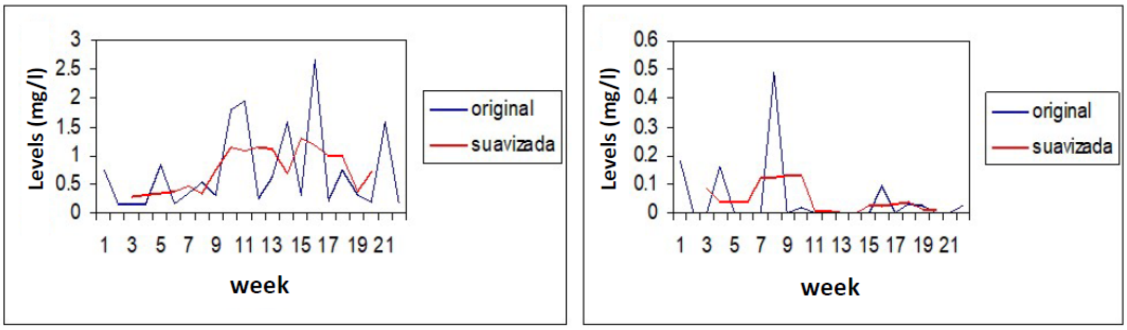


Figure 8.12. - BoxPlot of zinc concentration

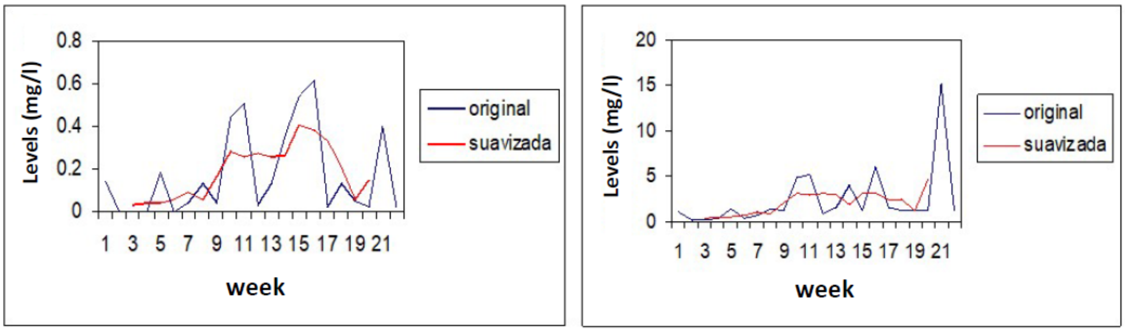
The graphs of the smoothed series were made for the metals cadmium (Figure 8.13 and 8.14) and lead (Figures 8.15 and 8.16) at the entry and exit points of the wetland, while for the metals copper and zinc (Figures 8.17 and 8.18) graphs were made only for the entry point, as all the values found at the exit of the wetland were below the limits established by CONAMA and also below the detection limit of the chemical analysis.



Figures 8.13 and 8.14 - respectively cadmium at points 01 and 02



Figures 8.15 and 8.16 - lead at points 01 and 02 respectively



Figures 8.17 and 8.18 - respectively copper at point 01 and zinc at point 01

The graphs of points 01 for cadmium, lead, copper and zinc show a tendency for these elements to increase, more specifically between the eighth and nineteenth weeks, while the exit points for cadmium and lead show a tendency for these metals to decrease over time.

This fact may be related to the increase in the volume of precipitated water, which increases the leaching and solubilization of metals, culminating in an increase in dissolved oxygen in surface water and, together with the alkaline pH, precipitation and removal of metals in the flooded system.

To check the existence of a correlation between the concentrations of metals at points 01 and 02 and the volume and pH of the precipitation, two statistical analyzes were carried out. The first called Pearson's correlation matrix (Table 8.2) with the purpose of finding whether there was a linear relationship between: Precipitation volume and its pH; pH of precipitation and concentration of metals at point 01; volume of precipitation and concentration of metals at point 01; and concentration of metals at points 01 and 02. Correlation coefficients above 0.5 are highlighted in bold.

Table 8.2 - Pearson correlation matrix

Variables	**Cd1**	**Cd2**	**Pb1**	**Pb2**	**Cu1**	**Cu2**	**Zn1**	**Zn2**	**Volume**
Cd2	-0.272								
Pb1	**0.730**	-0.032							
Pb2	-0.158	**0.630**	0.000						
Cu1	0.703	-0.081	**0.853**	-0.038					
Cu2	0.320	-0.476	0.087	-0.172	0.167				
Zn1	**0.574**	-0.147	**0.693**	-0.103	**0.624**	0.210			
Zn2	-0.084	0.084	0.024	**-0.614**	-0.020	**-0.563**	-0.106		
Volume	0.137	0.013	0.077	-0.126	-0.002	0.077	0.172	0.048	
pH	0.330	-0.453	-0.010	-0.201	-0.056	0.091	0.090	-0.303	0.039

As can be seen, there is no statistically valid correlation between the rainfall volume and its pH, between the rainfall pH and the levels at points 01 and 02, and between the rainfall volume and the levels of metals at points 01 and 02. However, for the levels of metals at points 01 and 02, it can be seen that zinc at point 01 showed a positive correlation with all other heavy metals (Pb1>Cu1>Cd1), as well as Cu1/Pb1 and Pb1/Cd1 show, respectively, the highest positive correlations between the metals, that is, it is possible that the leaching and/or solubilization processes that occur in the slag dam and that carry the metals to the point of emergence, are occurring simultaneously, without many expressive physicochemical changes.

As for the exit points from the wetland, there is only a positive correlation between Pb2 and Cd2 and a high negative correlation between Zn2 with Pb2 and Cu2.

The second statistical analysis between the metals was carried out to find out the linear relationship between the concentrations of the metals at points 01 and 02, and between the volume and the pH of the precipitation, using the causality analysis[54] (CUNHA 1997). To evaluate the causality between the researched parameters, the causality model in time series by CUNHA (op. cit.) was used.

The causality analysis was performed, initially, by determining whether any of the series presented any significant correlation between the autocorrelation and partial autocorrelation functions; then, the adjustment of time series models was performed using the auto-regressive model of moving averages (BOX et al. 1994); and ending with the determination of the cross-correlation.

The autocorrelation and partial autocorrelation functions for rainfall volume and pH (n=22 and 52 weeks) and metal levels at points 01 and 02 (n=22 weeks) (SUPPLEMENT 05), demonstrates that there was an autocorrelation (Figure 8.19) and partial autocorrelation for the volume of rainfall, when n=52 weeks, in “lag” 4. This autocorrelation means that there is a correlation between the volume of rain in one week and four weeks earlier.

---

[54] According to TOLOI et al. (2002), the concepts of causality consist of: as Xt and Yt represent two time series, Xt causes Yt if the present Yt can be better predicted using past values of Xt, than not using this information, that is, the correlation between two variables does not imply that there are cause and effect relationships between them, because these two variables may be associated with a third variable.

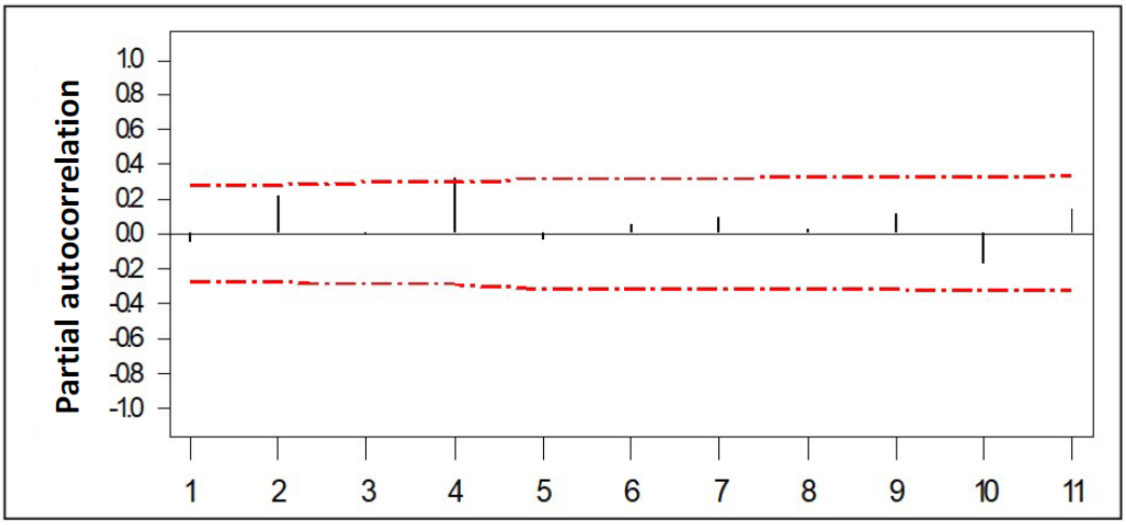


Figure 8.19 – Autocorrelation between rainfall volume for n = 52 weeks

For n = 22 weeks it was not possible to identify an autocorrelation and partial autocorrelation for the volume of rainfall.

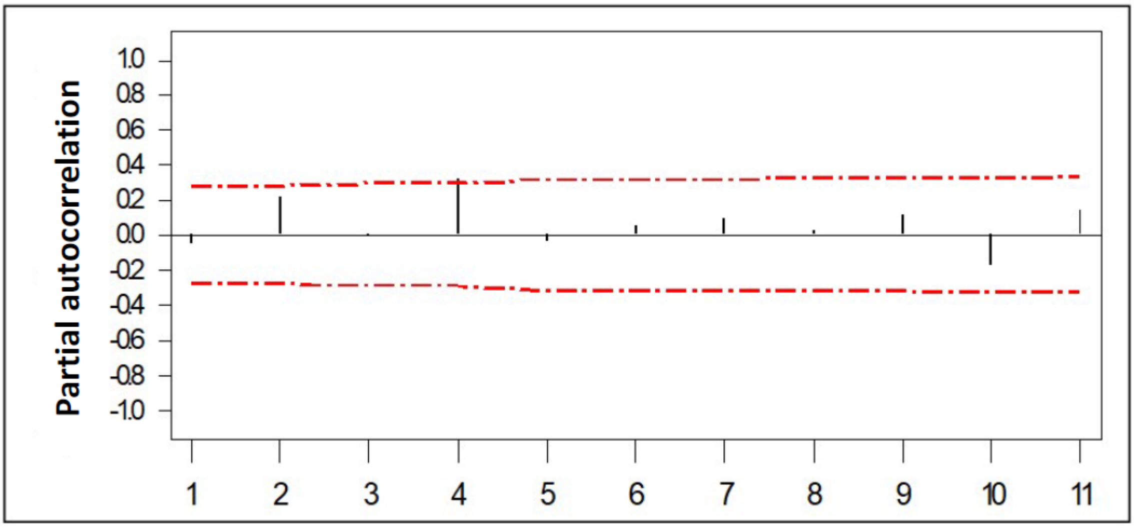


Figure 8.20 - Autocorrelation between rainfall pH for n=52 weeks

As for the rainfall pH for n=52 weeks, the autocorrelation (Figure 8.19) and partial autocorrelation could identify a significant autocorrelation in “lag” 1 and “lag” 3.

These results indicate the existence of an autocorrelation and partial autocorrelation between the pH of the rainfall in one week and the pH of the previous week, and with the pH of three weeks ago. There was no autocorrelation for rainfall pH when n=22 weeks.

The autocorrelation and partial autocorrelation functions were also performed for heavy metals for n=22 weeks and showed significant values for Cd at point 01 (Figure 8.21 and 8.22) and Cu at point 02 (Figure 8.23 and 8.24) in the “lag” 1.

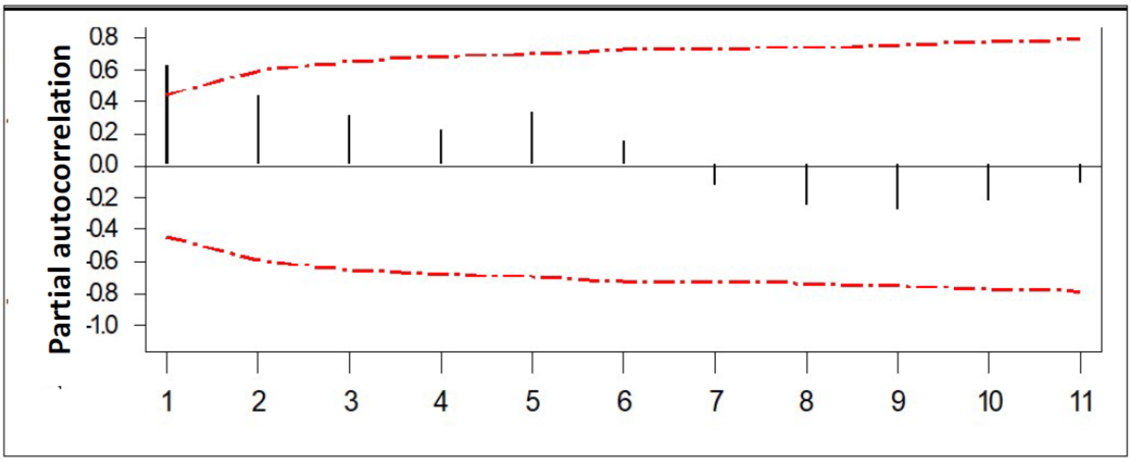


Figure 8. 21 - Autocorrelation of Cd at point 01

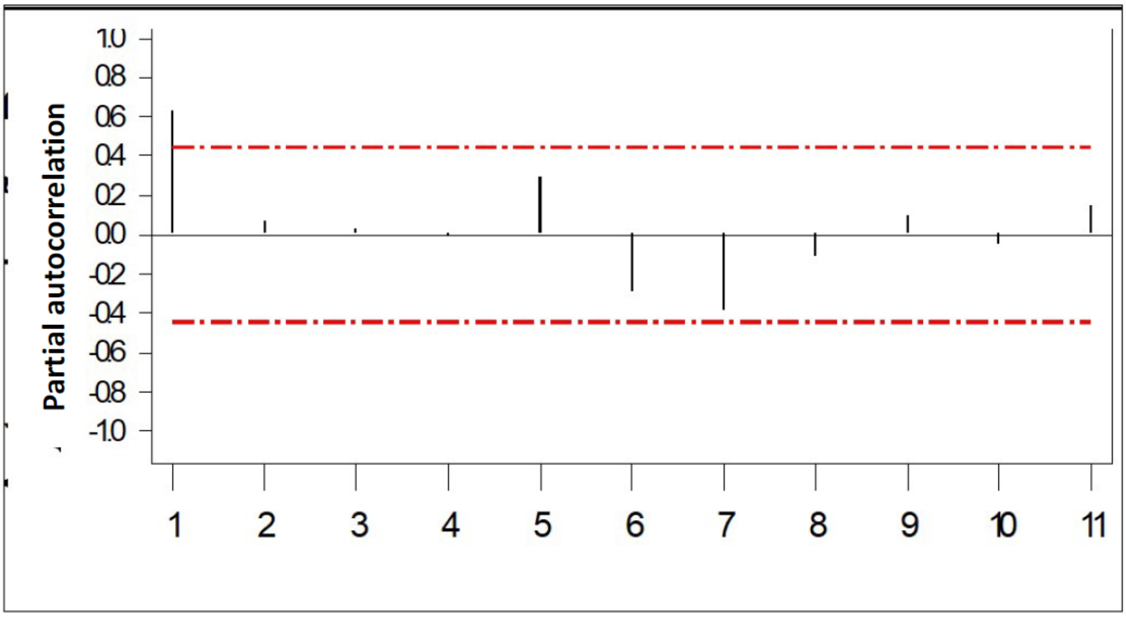


Figure 8.22 – Partial autocorrelation of Cd at point 01

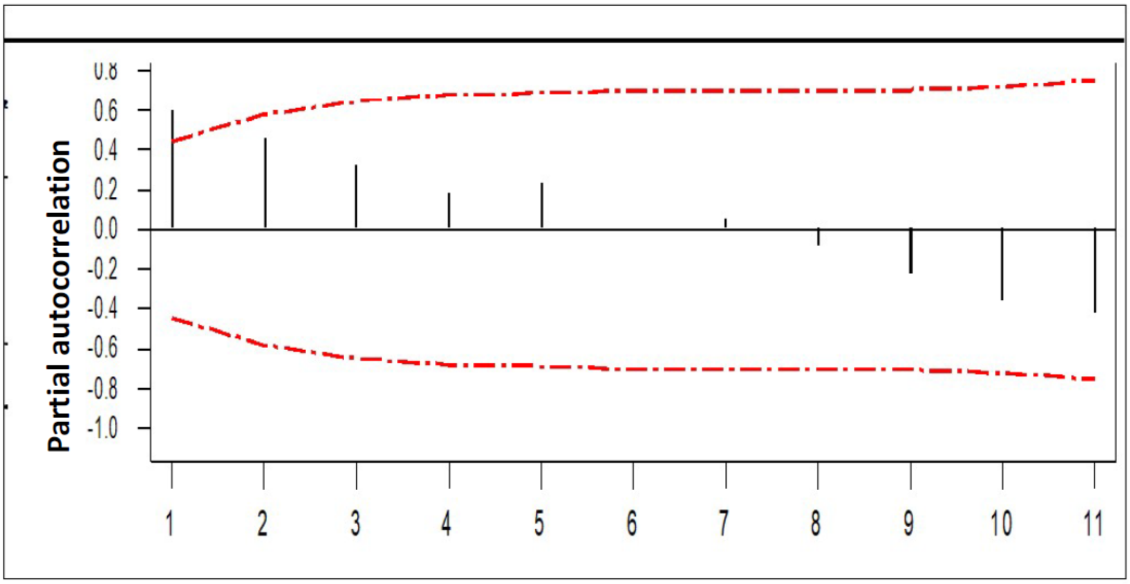


Figure 8.23 – Autocorrelation of Cu at point 02

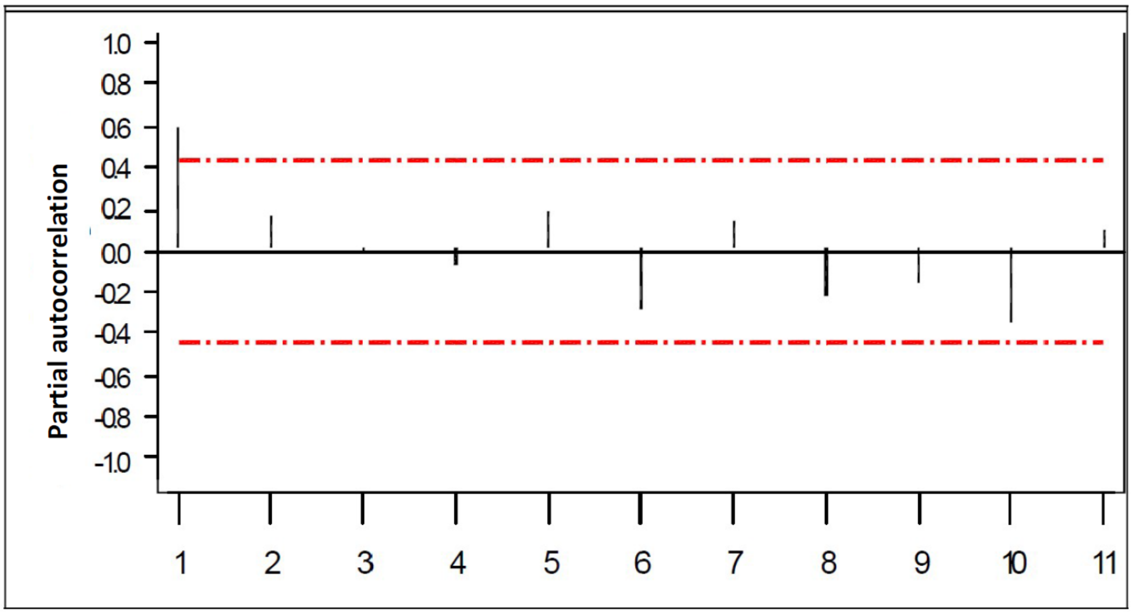


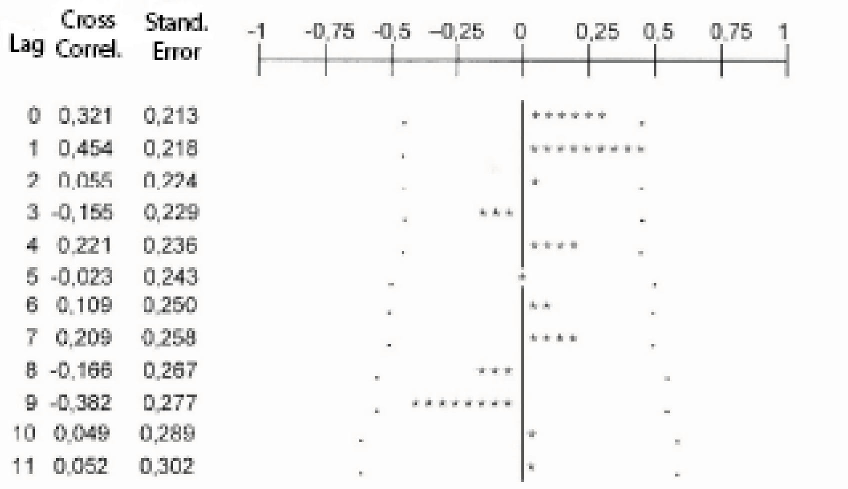
Figure 8.24 – Partial autocorrelation of Cu at point 02

The autocorrelation and partial autocorrelation functions for cadmium at point 01 and copper at point 02, which showed significant values in "lag" 1, indicate that the levels of each of these metals, observed in one week, was correlated with those from the previous week. For lead and zinc at points 01 and 02, cadmium at point 02 and copper at point 01 no significant autocorrelation was observed.

The second stage of the causality analysis was performed by adjusting the models and the functions of autocorrelations and significant partial autocorrelation. The result of the adjustment obtained through modeling demonstrates that significant autocorrelations were excluded, which means that the models are well adjusted (TOLOI et al. 2002).

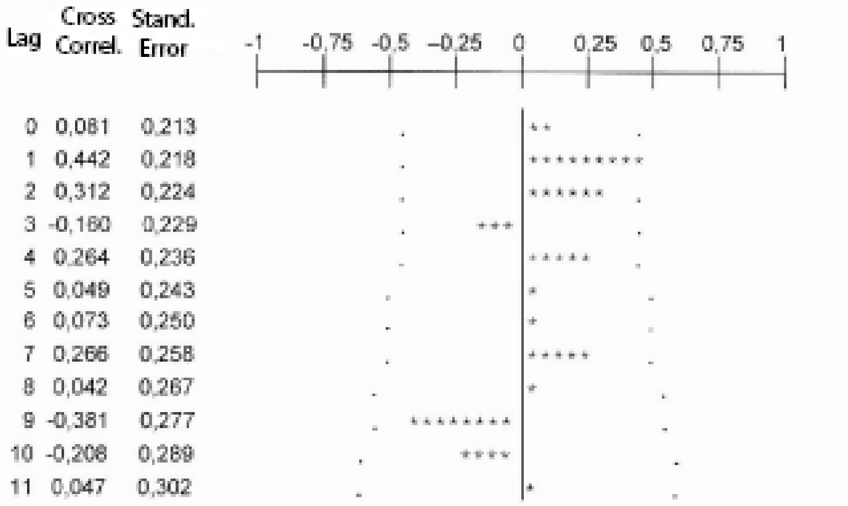
The third stage of causality analysis was obtained after adjusting the model and calculating the cross-correlations of interest to the investigation. The conclusions are as follows:

- cross-correlation between the volume of rainfall and each of the metals at the entry point of the wetland, to establish the metal levels at point 01 depends on rainfall volume. Figures 8.25, 8.26 and 8.27 denote that the levels of metals at point 01 does not have a linear relationship with the rainfall volume, as no causality was detected;
- Cross-correlation between rainfall pH and each of the metals at the wetland entry point, to establish the metal levels at point 01 depends on the rainfall pH. As can be seen from Figures 8.25, 8.26 and 8.27, there is a coincidence between the pH of the rainfall and the metals cadmium, lead and copper at point 01, through a correlation in the "lag"1, which indicates that the levels of these metals in the "lag"1 is linearly influenced by the pH of the rainfall of the previous week, or the higher the pH value of the rainwater, the greater the concentration of these three metals, which is in contradiction with what was expected, since the solubility of these metals is greater at acidic pH. Zinc levels did not show linear dependence with precipitation pH.
- cross-correlation between the same type of metal at point 01 and 02, it is noted that no causality was detected, therefore the levels of a metal at point 01 has no linear, positive or negative dependence on the levels at point 02, and
- cross-correlation between rainfall volume and pH (22 and 52 weeks), to find out if the rainfall pH depends on its volume. The correlations obtained demonstrate that there is no linear correlation between the volume and the pH of the rainfall.



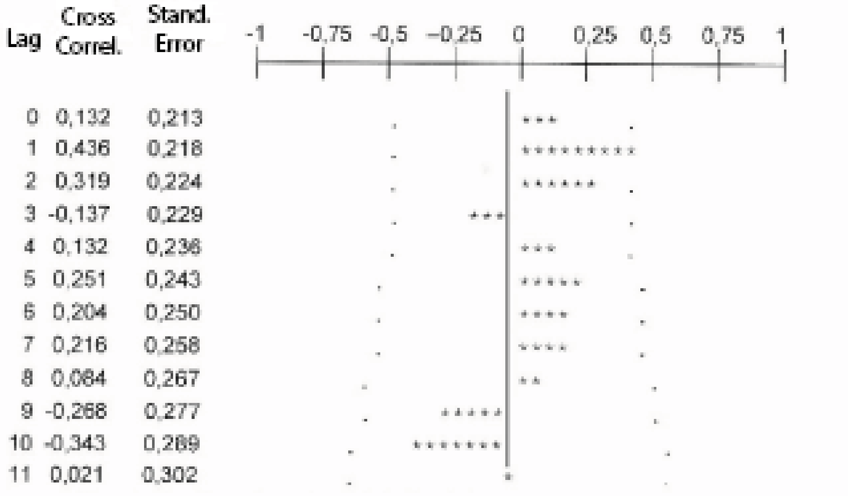
Lag	Cross Correl.	Stand. Error
0	0,321	0,213
1	0,454	0,218
2	0,055	0,224
3	-0,155	0,229
4	0,221	0,236
5	-0,023	0,243
6	0,109	0,250
7	0,209	0,258
8	-0,166	0,267
9	-0,382	0,277
10	0,049	0,289
11	0,052	0,302

Fig. 8.25 - Cross-correlation between rainfall pH and Cadmium levels (mg/l) at Point 1



Lag	Cross Correl.	Stand. Error
0	0,081	0,213
1	0,442	0,218
2	0,312	0,224
3	-0,160	0,229
4	0,264	0,236
5	0,049	0,243
6	0,073	0,250
7	0,266	0,258
8	0,042	0,267
9	-0,381	0,277
10	-0,208	0,289
11	0,047	0,302

Fig. 8.26 - Cross-correlation between rainfall pH and lead levels (mg/l) at Point 1



Lag	Cross Correl.	Stand. Error
0	0,132	0,213
1	0,436	0,218
2	0,319	0,224
3	-0,137	0,229
4	0,132	0,236
5	0,251	0,243
6	0,204	0,250
7	0,216	0,258
8	0,064	0,267
9	-0,268	0,277
10	-0,343	0,289
11	0,021	0,302

Fig. 8.27 - Cross-correlation between rainfall pH and Copper levels (mg/l) at Point 1

8.1.3 - Assessment of the removal and potential availability of metals in the soil and wetland sediment

The leached and/or solubilized metals from the contaminated slag are carried to the wetland and, depending on the alkaline pH and oxidizing Eh of the surface waters of the Plumbum wetland, are oxidized and precipitated under the hydromorphic sediment.

This process occurs with oxidation reactions, predominantly upon the oxidation of Fe^{2+} and Mn^{2+}, which, according to SCHACHELFORD (2000), are responsible for the precipitation of some heavy metals such as Pb, Cd, Cu and Zn, or the solubilization of other species such as Uranium (U), Molybdenum (Mo), Selenium (Se) and Arsenic (As).

Estimating the percentage of Potentially Available (PA) metals for the environment has become an essential tool for planning the recovery of contaminated sites. Depending on the toxicity of the metals and the contamination pathways at the site under study, it may be necessary to study the behavior of the metals involved and their potential risk to public health and goods to be protected.

The PA metals are the sum of the exchangeable, carbonate, reducible and oxidizable phases, while the Residual (R) phase is considered as the unavailable phase. At Plumbum, the potential availability of metals Cd, Pb, Cu and Zn was characterized.

Cadmium, due to its high solubility power, represents the metal with the highest percentage of availability among the four metals evaluated (Figure 8.28), from 95 to 97%, varying in the sediments of the wetland (WS1 to WS5) and soil (WS6) with concentration levels from 20 to 177 µg/g (Figure 8.29). These concentrations are much higher than CETESB's guideline values (2001) for soil, which presents 40 mg/kg as an intervention value for cadmium in soil in industrial areas (mg/kg = µg/g).

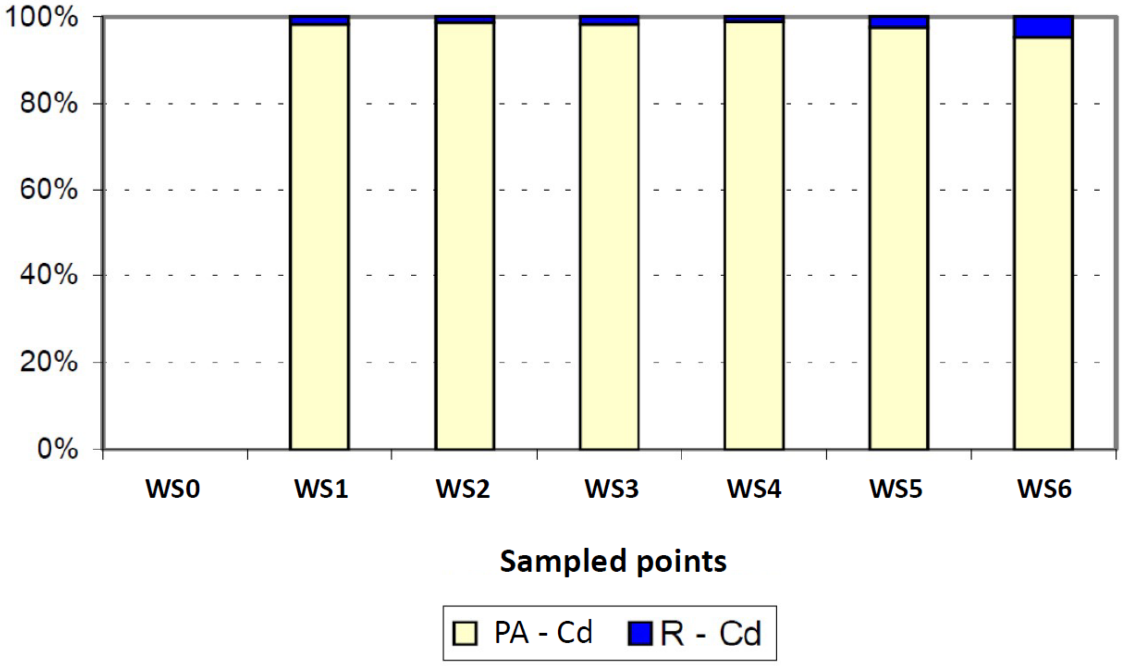


Figure 8.28 – Potentially available cadmium

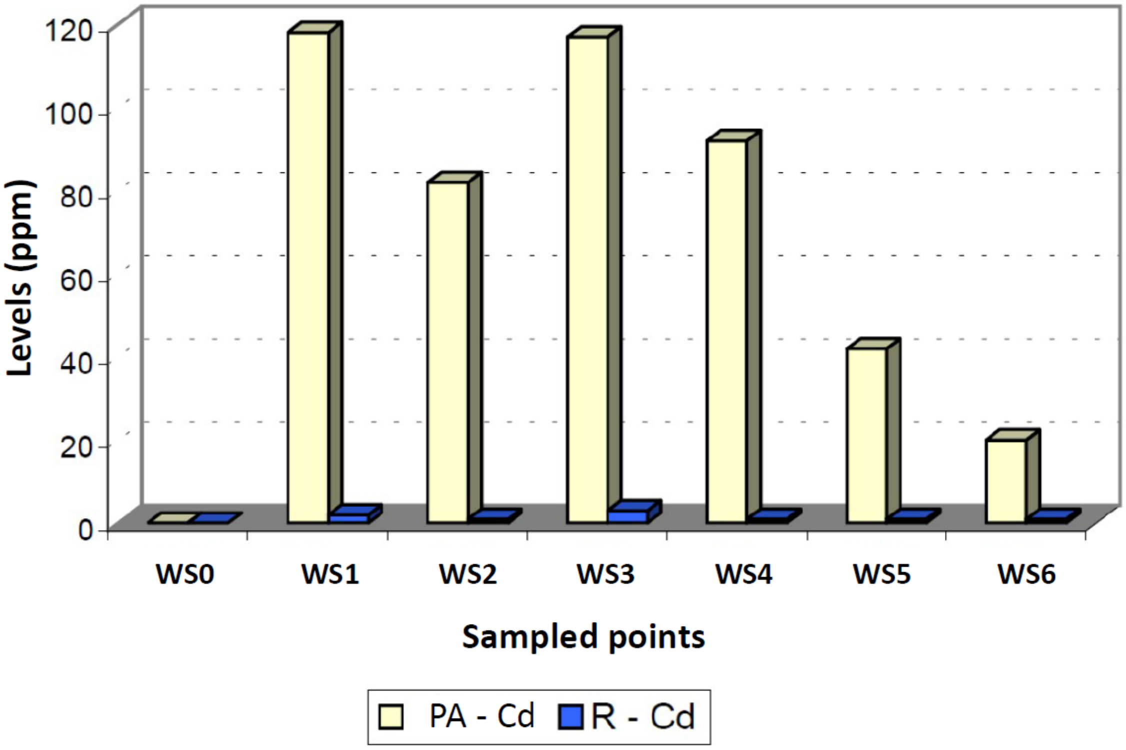


Figure 8.29 – Levels of Potentially Available Cadmium

The availability potential for lead is extremely high, although lower than cadmium (Figure 8.30). Initially due to the concentrations found in sediments and soil, with values ranging from 1,709 to 11,084 µg/g of lead (Figure 8.31), and for representing in almost all samples percentages above 85% of potential availability.

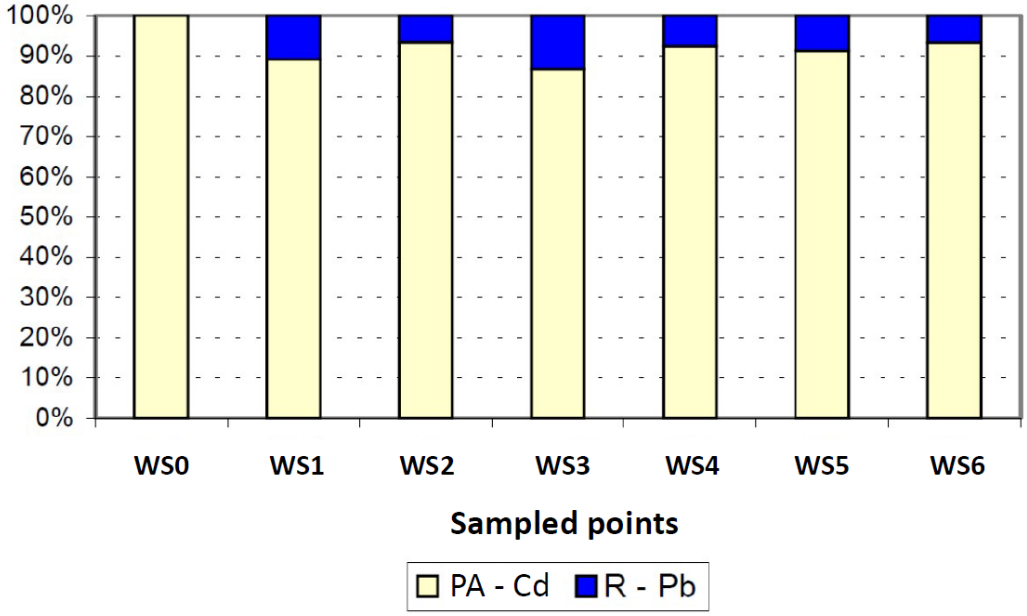


Figure 8.30 – Potentially available lead

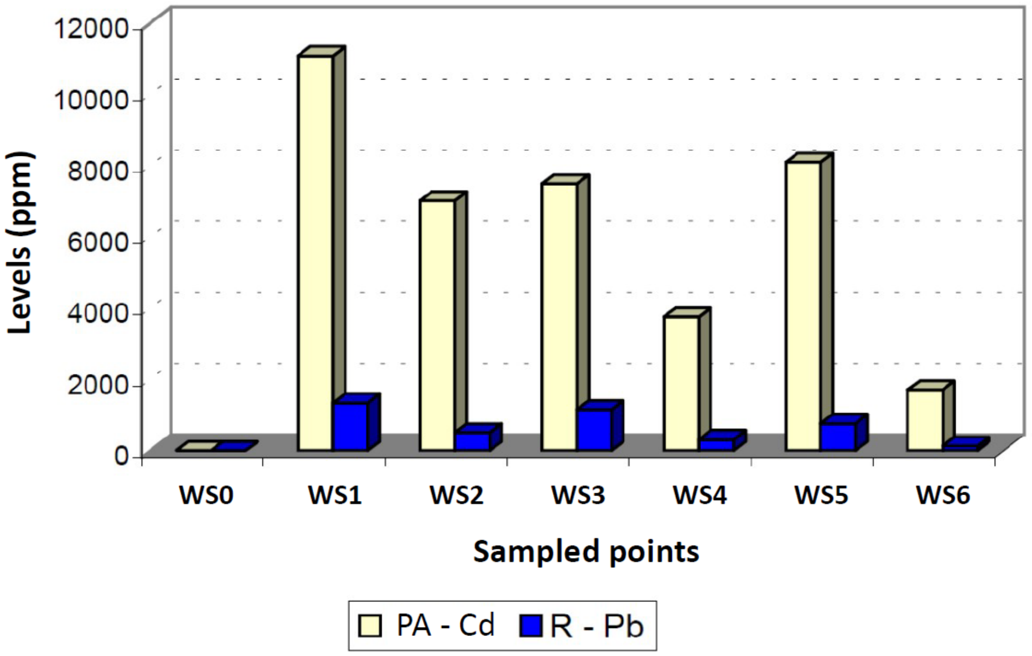


Figure 8.31 – Potentially available lead levels

The reference value for lead-contaminated soils is 15 mg/kg, while the guideline values for intervention in agricultural, residential and industrial areas are, respectively, 200, 350 and 1200 mg/kg. That is, the values found at the Plumbum site shows concentrations 10 times greater than that required for remediation. The availability potential of lead varies from 85 to 92%, and after cadmium it is the metal that presents the highest percentage of availability.

Copper has potential availability levels ranging from 70 to 30% in sediment samples (Figure 8.32), with the highest concentrations found in sample WS1, which has a value higher than that established by CETESB (2001) for industry intervention (700 mg /kg), while in the sediment a potentially available 742 μg/g was found (Figure 8.33).

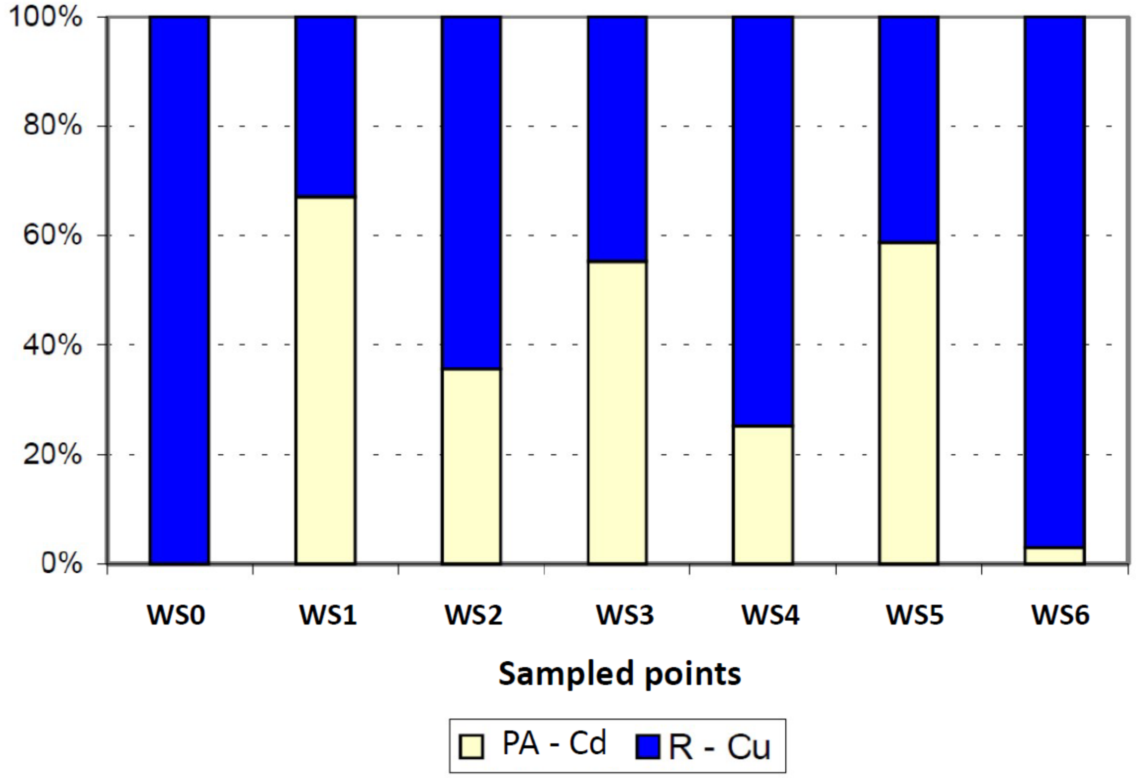


Figure 8.32 – Potentially available copper

Copper shows at sampling points WS2, WS4 and WS6 concentrations of residual metal higher than potentially available values, that is, most of the metal has not been available to the food chain.

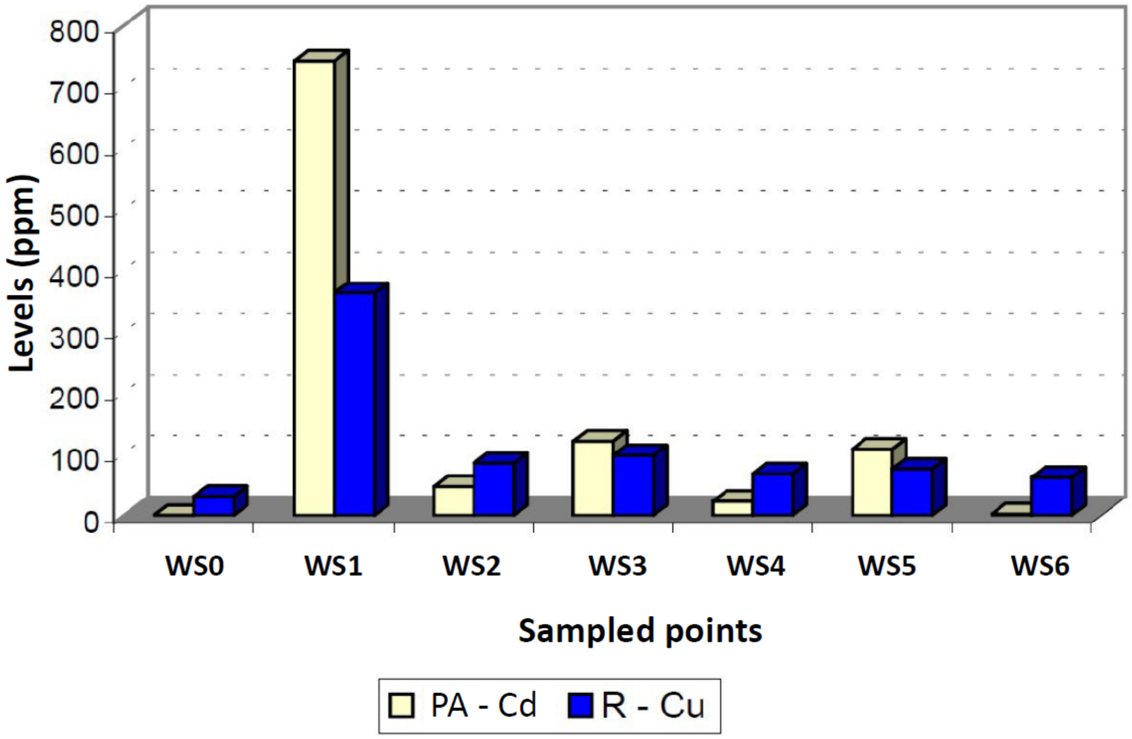


Figure 8.33 – Potentially available copper concentration

Zinc shows a variation of 95 to 70% of potential availability in the sediment samples, while the soil shows a value above 40% (Figure 8.34).

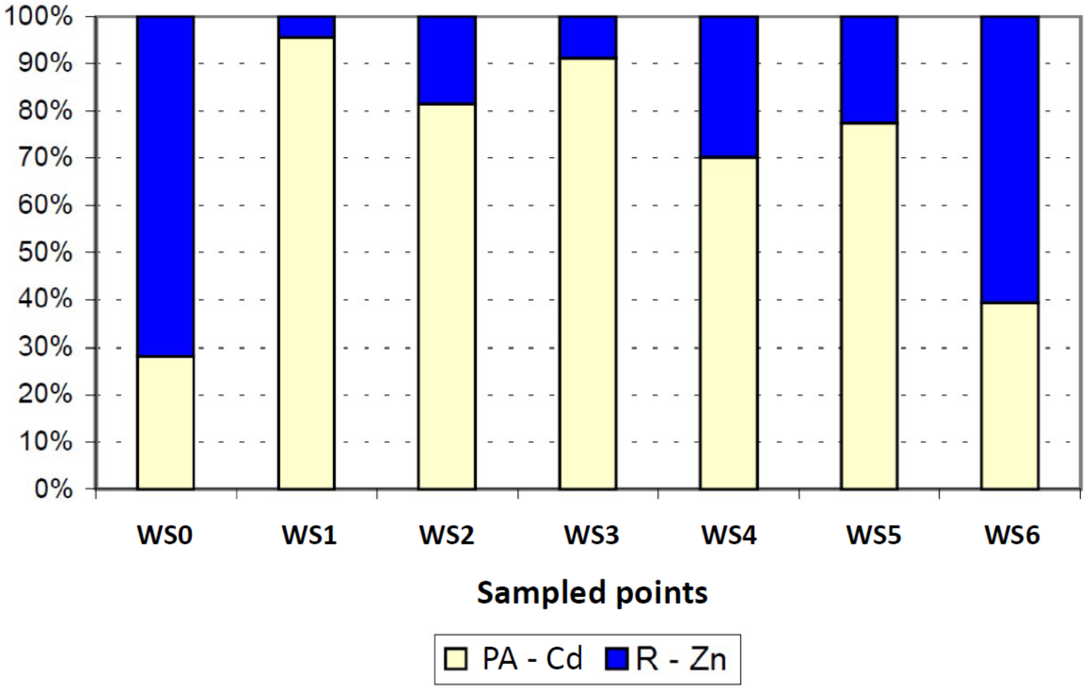


Figure 8.34 – Potentially available zinc

Sediment values range from 840 to 8,995 µg/g, while the reference value for the industrial area, according to CETEB (2001) is 1,500 mg/kg (Figure 8.35). Both at the sampled points of the WS1 sediment and WS6 soil, the PA values are lower than the concentrations for the residual phase.

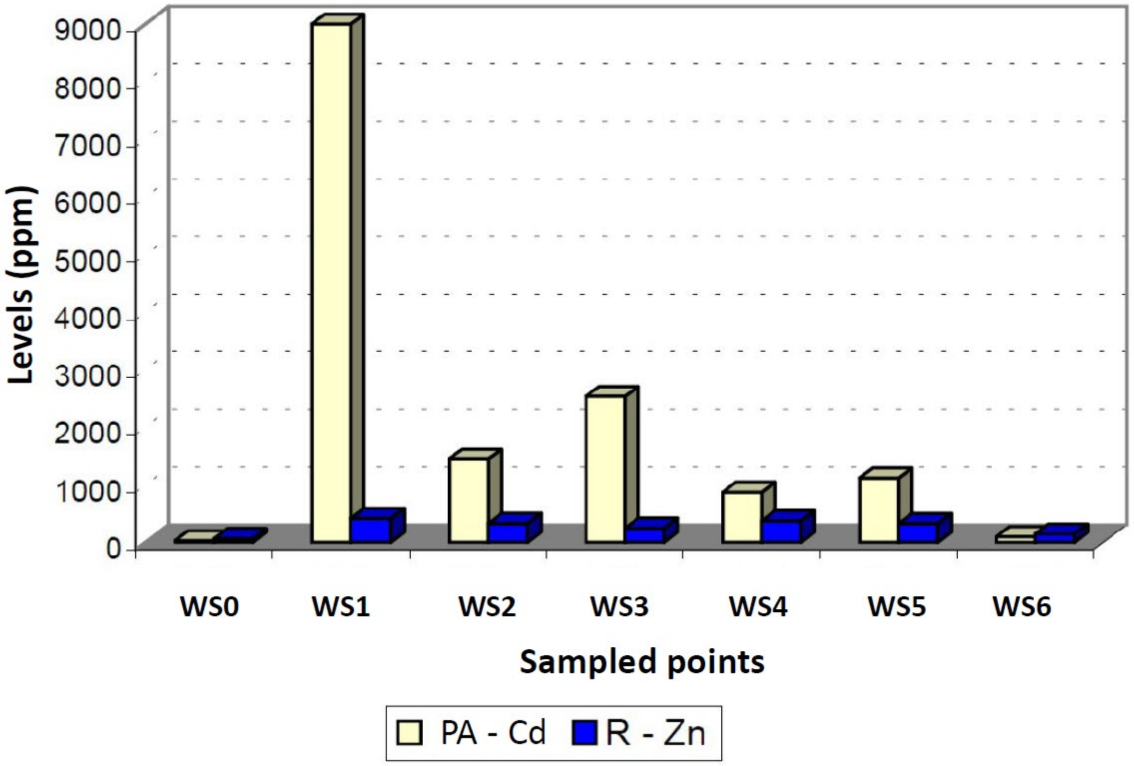


Figure 8.35 – Potentially available zinc concentration

8.2 - Second stage - During the coating of the slag

8.2.1 - Analysis and discussion on slag coating

The slag coating project presented by the Plumbum Co. was developed and executed by MORSA ENGENHARIA Ltda. This project did not comply with CRA's Technical Proposition No. 55/95 – SFA/CRA, Public Civil Action No. 302/97 and the Expert Report, which establish the implementation of "surface encapsulation of the slag valley or hydraulic encapsulation" as a remediation technique for the area.

The project prepared and executed by MORSA comes with the following flaws:

1) regarding the Technical Project, Plumbum should present a project according to procedures established by NBRs standards – 1183 Storage of hazardous waste (current NBR 12235) and 1264 Storage of non-inert waste. NBR 1

With the characterization of slag as hazardous waste (SANTOS 1995 and ANJOS and SÁNCHEZ 1997), the norm to be applied in the area is NBR 12235/92.

> NBR 12235/92 – Storage of hazardous solid waste aims to establish the conditions required for the storage of solid waste in order to protect public health and the environment. The application of the standard is recommended for Class I – Hazardous waste.
>
> Waste storage, specified in NBR 12235/92, must be carried out as temporary containment of waste, in an area authorized by the environmental agency, awaiting recycling, recovery, treatment or adequate final disposal, provided that it meets the basic safety conditions.
>
> This standard establishes that for packaging hazardous waste, such as slag, it must be carried out in bulk storage "in duly waterproofed buildings". Still according to the norm, "storage in heaps on the ground, in large quantities, is acceptable, provided that it is duly authorized by the environmental agency".
>
> This premise is provided in CRA's technical propositions, which determines as minimum prerequisites for the storage of slag the "control of soil and water pollution, such as: providing a waterproofing system for the base of the storage location and providing a retention system of solids".
>
> According to NBR 12235/92, the storage of bulk waste must have a containment and/or waterproofing system designed, built and installed in order to prevent any migration of waste components to the atmosphere, to the adjacent sub-surface soil or for surface and groundwater during on-site operation and the closure period.
>
> As complementary documentation in the application of NBR 12235/92 at the Plumbum site, it is necessary to consult the norms

NBR 10004 – Solid waste – Classification and NBR 10157 – Hazardous waste landfills – Criteria for projects, constructions and operation – Procedures.

2) Plumbum partially complied with CRA's determination to collect all the slag dispersed in the metallurgy site and dispose of it in the valley, where there was already a large amount of slag (Photos 8.1);

3) Plumbum's project did not qualify or quantify the contaminated soil, including that which was immediately below the slag and which had been removed, mixed and placed as a 30 cm layer (Photo 8.2) and which later, due to the erosion process , would expose the dross (Photo 8.3). Contaminated soil must be treated as waste, which is why there are dozens of remediation technologies for containment, control or soil washing, in addition to the guiding values for intervention established by CETESB (2000);

Photo 8.1 - Slag deposited around the Plumbum site should have been removed.

Photo 8.2 – Shows contaminated soil (reddish feature with slag residue) and **Photo 8.3** (below) showing an erosion process rediscovering the slag in the dam.

4) A dike was built around the valleys in order to prevent the slag from being carried out of Plumbum's premises. This proposition is technically unfounded for the area, as the flow of surface water from

the valley is directed into a pipe that passes below the built dike (Photo 8.4).

5) the project did not include all the slag deposited in front of the built dike, leaving out the slag located between the railroad and the road and on the banks of the Subaé River;
6) the company did not comment on the groundwater, no mention was made about a monitoring project for the area, and no safety and identification signs were installed for the waste stored there.

Photo 8.4 - Water coming from both the pipe passing under the railroad and from rainfall accumulated upstream of the slag dam.

8.2.2 - Analysis of metals and support parameters

The pH and precipitation measured in the second stage of the investigation, compared with the pH and precipitation measured in the first one, showed a significant increase in the volume of weekly rainfall, causing the leaching of the surface soil and its erosion, while the pH remained in the range of alkaline.

As for the metals evaluated at the exit of the wetland, we can see that cadmium (Figure 8.37) has its highest concentrations in the month of July. Correlating these data with the values of weekly rainfall in the second stage (Figure 8.36) it is possible that the availability of cadmium in the wetland system is related to the high volume of rain verified in this stage, due to the soil being removed and easily eroded and carried to the flooded zone.

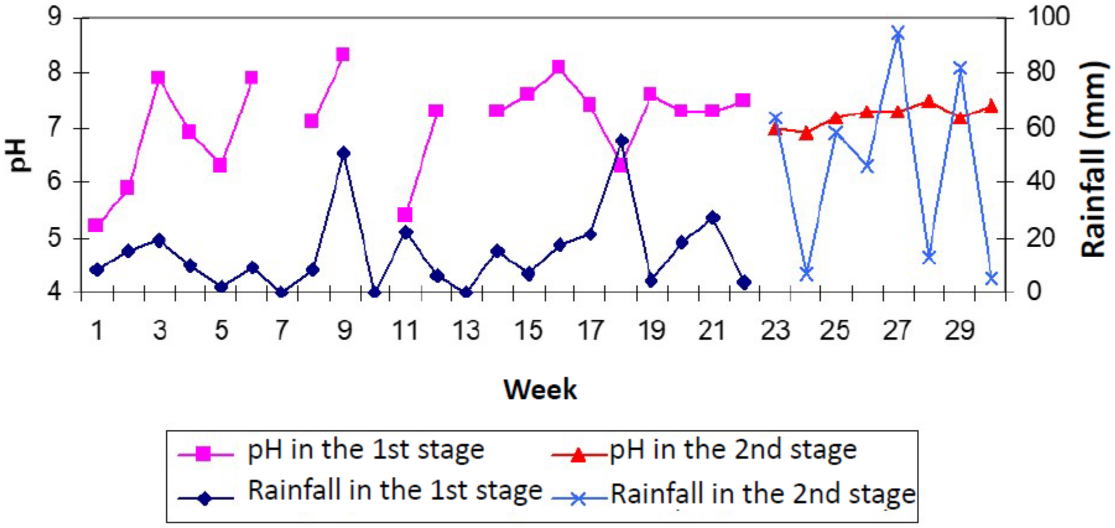


Figure 8.36 - pH and rainfall in the first and second stages

As for lead levels at point 02 of the second stage, it can be seen that it (Figure 8.38) continues to present concentrations below the analytical detection limit at the exit of the wetland, and even with a large volume of rain verified in this stage the flooded system maintained the total removal of lead, copper and zinc. This condition places the wetland as an excellent retention system for these metals, even with high rainfall volumes.

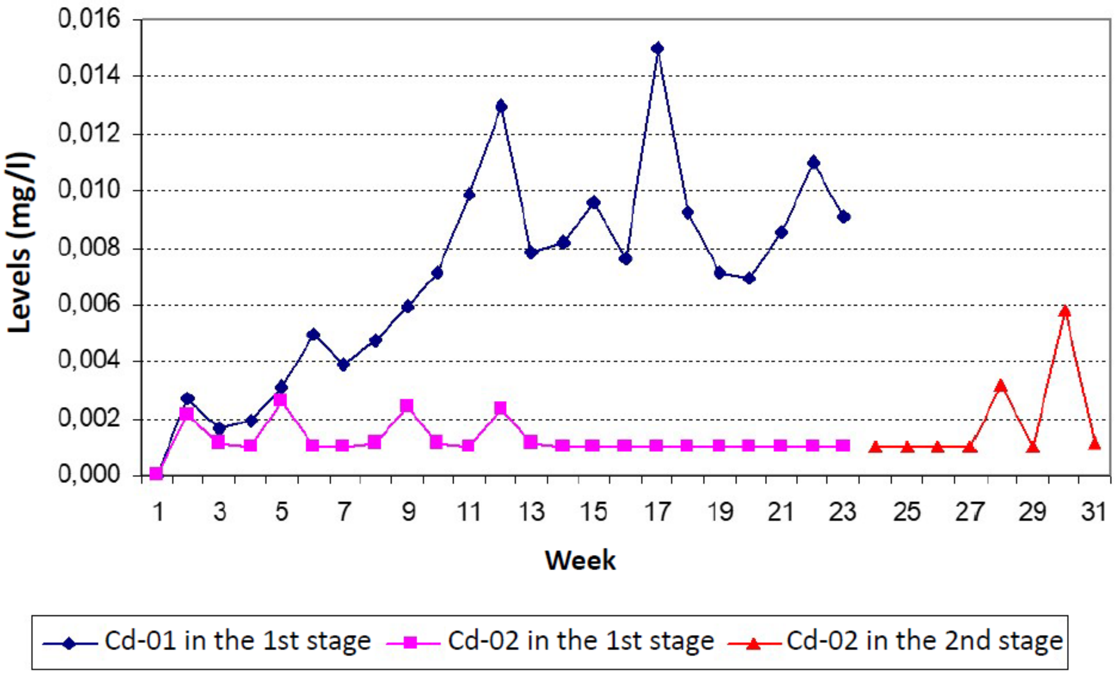


Figure 8.37 – Cadmium levels in the first and second phase

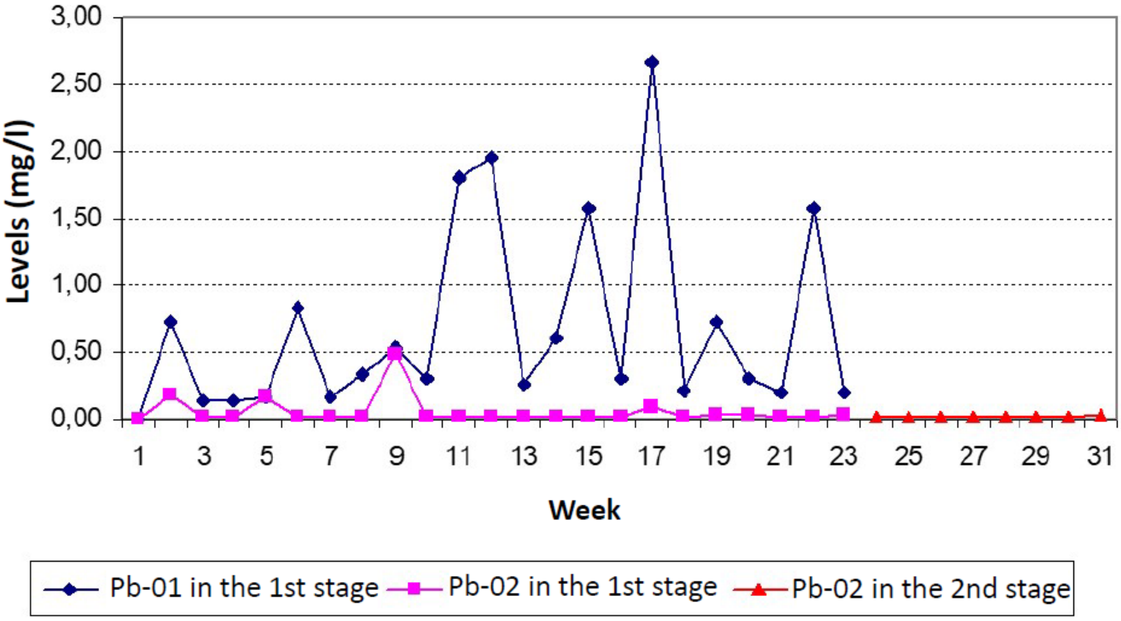


Figure 8.38 - Lead levels in point 02 of the second stage

8.3 – Third stage – After coating

8.3.1 - Erosive process and migration of metals after surface coating

Given the high levels of rainfall that occurred in the months of June to October (Figure 8.39) and the soil being removed and decompressed, the erosion process most probably took place since the beginning of this stage.

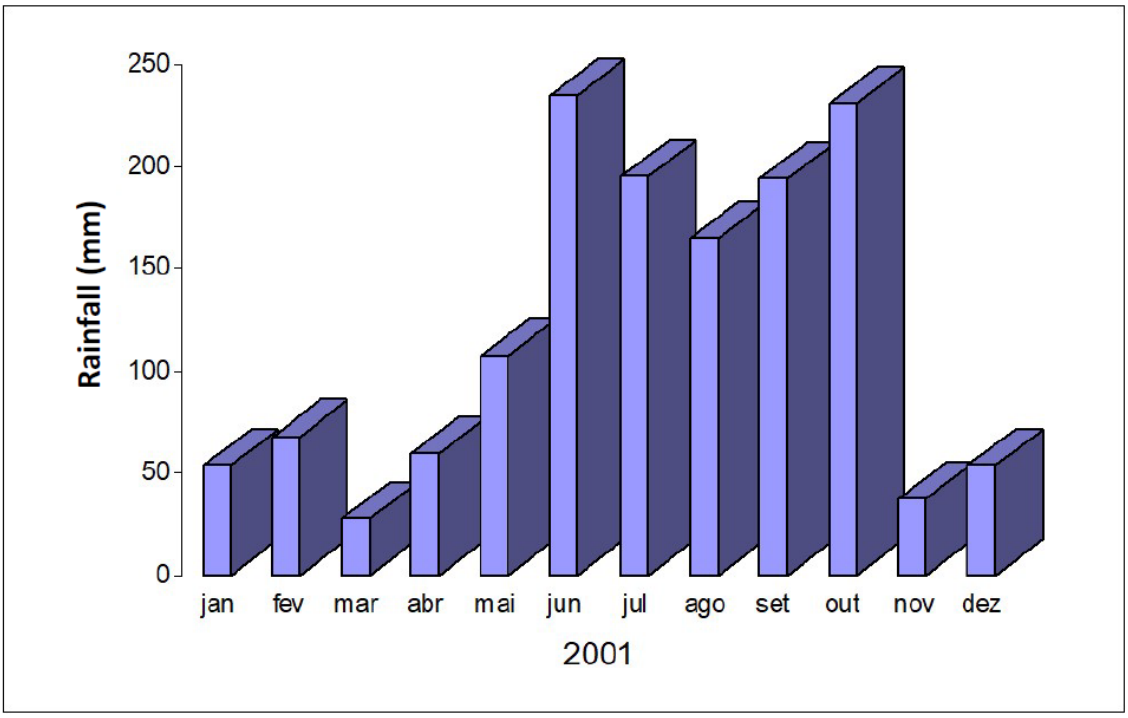


Figure 8.39 – Average monthly rainfall for the year 2001

Once the surface covering process was completed, the water continued to migrate to the wetland. This fact is due to two factors: although the slag was covered, there was no confinement or encapsulation; and after the work was concluded, heavy rainfall continued, leaching the surface sediments and infiltrating the now covered slag dam.

The rains caused erosion in the entire area covered with loose soil, this process was accentuated, as vertisols are "problematic" soils (TINER 1999) and need special conditions to be compacted, mainly with the steep slope found in the valley areas.

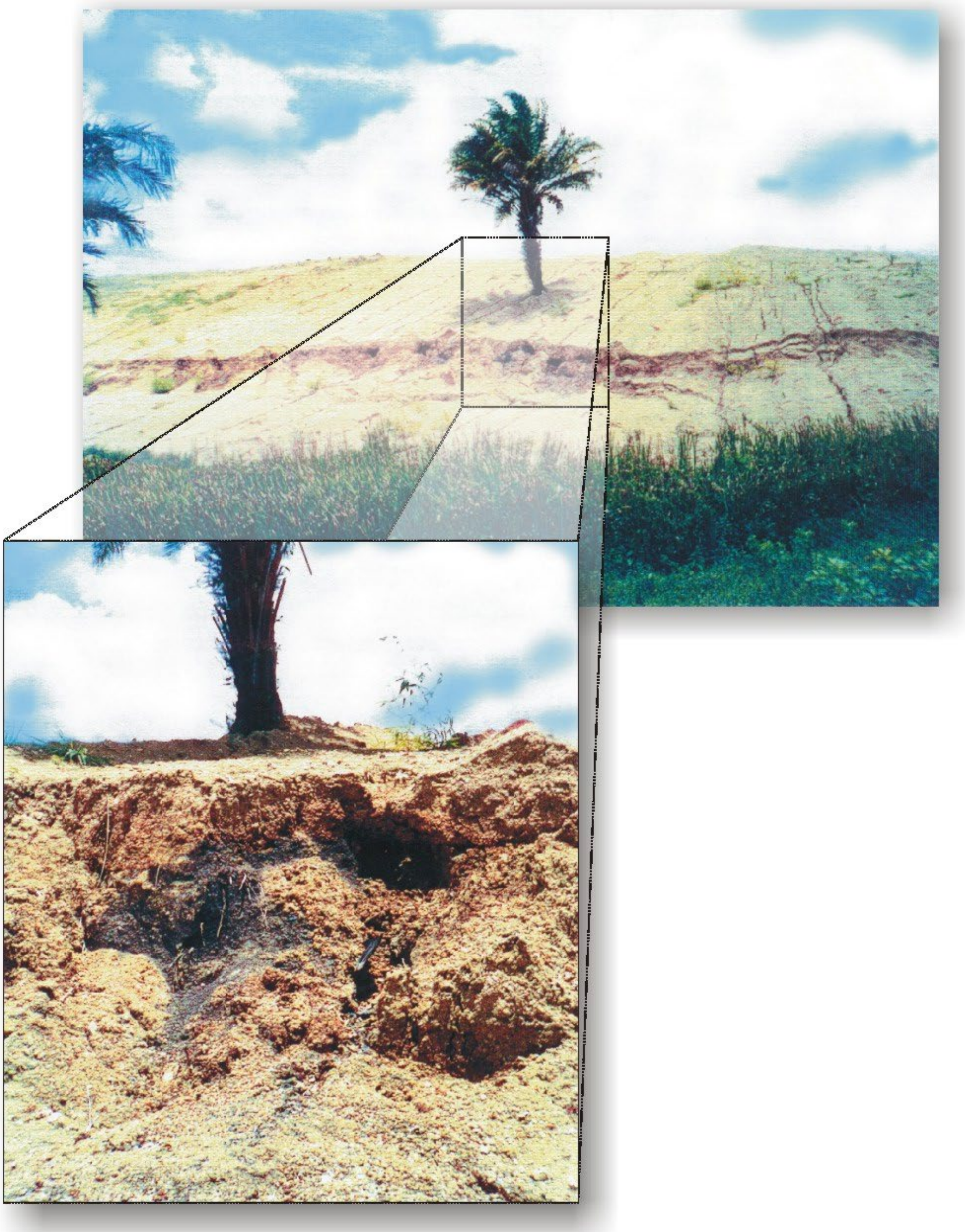
The process of superficial erosion was also accelerated, due to the superficial covering project not having established technical procedures for adequate revegetation of the soil, such as “for example”, the lack of superficial organic layer for the development of the planted species.

However, the biggest geotechnical problem found in the area was the rupture of the slope of the hill in the wetland area that forms a watershed with the valley of the tailings basin. This rupture occupies a large longitudinal extension of the slope and exposed the slag removed to the lower parts of the slope (Photos 8.5 and 8.6). Before the collapse, the hill was covered by a small layer of slag. Erosive processes - collapse of slopes and ravines - collaborated with the leaching and migration of metals from the contaminated soil and slag to the wetland.

This step was characterized by the high availability of cadmium (Figure 8.40) at the exit of the wetland (Cd-2 3rd step) after surface coating. This migration of metals was due to the exposure of the contaminated soil that was found stratigraphically below the slag or on the surface of the industry ground, and which was remobilized in the process of covering the slag. This entire metal migration process was conditioned by high rainfall rates, carrying cadmium to the wetland, solubilized and made available from the Plumbum wetland.

As for lead (Figure 8.41), only in the first weeks there were lower levels at the exit of the wetland, while after the coating, even with the great transport of particulates to the wetland, there was predominantly no migration of lead from the system into the flooded system. As for copper and zinc, levels above the values established by the Conama resolution do not occur at the exit points of the wetland zone.

However, from point 02 at the exit of the wetland, to point 03 of the drainage system, after the pipeline, all metals available from the wetland were retained, demonstrating that the biogeochemical processes of metal removal continue in the drainage that flows into the Subaé River .



Photos 8.5 and 8.6 – The rupture of the slope near the wetland reached a large area and (in detail) exposed the slag that should have been covered by the soil.

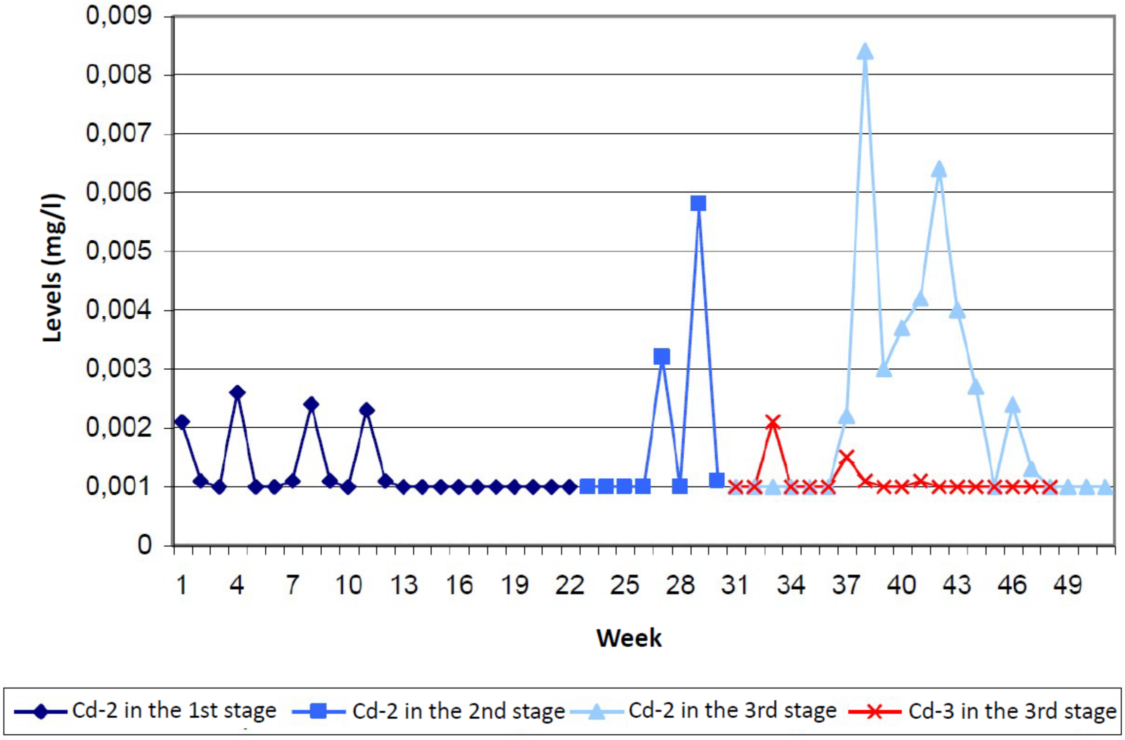


Figure 8.40 – Cd-2 levels in the first, second and third steps.

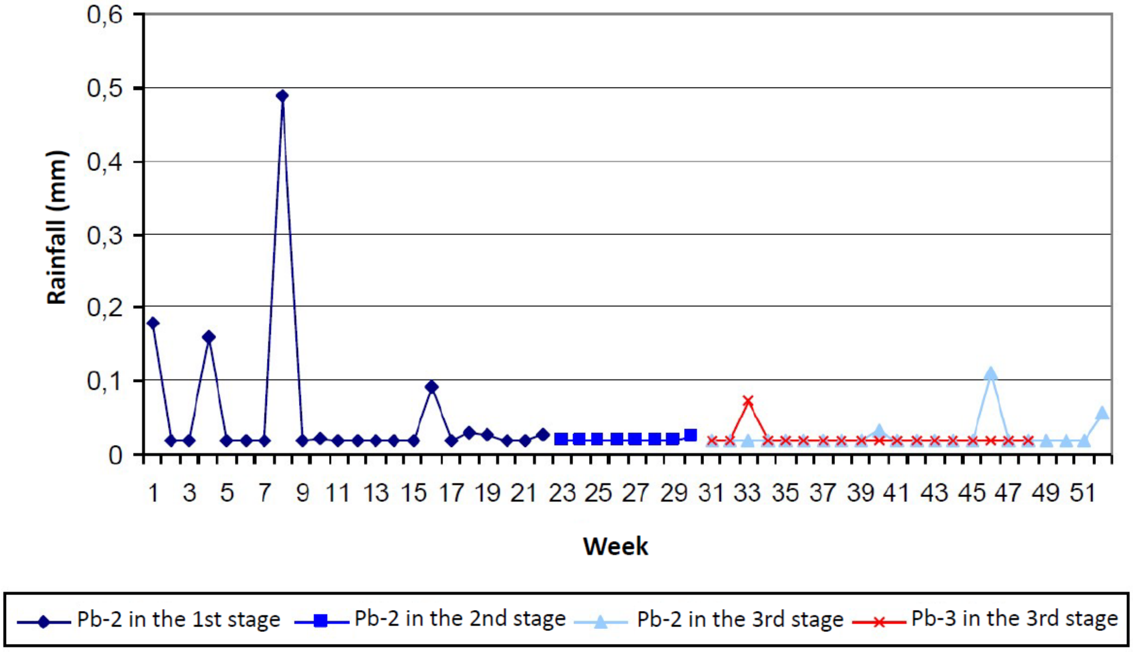


Figure 8.41 – Pb-2 levels in the first, second and third stages

CHAPTER 9: PROPOSALS FOR REMEDIATION

The strategy for recovering the area affected by the Plumbum Co. must cover the entire contaminated area in actions that include immediate, mid- and long-term interventions. The planning and sequenced actions for the recovery of the site should include intervention measures extending from Plumbum's industrial facilities to the contaminated area of the Todos os Santos Bay (TSB) (Figure 9.1).

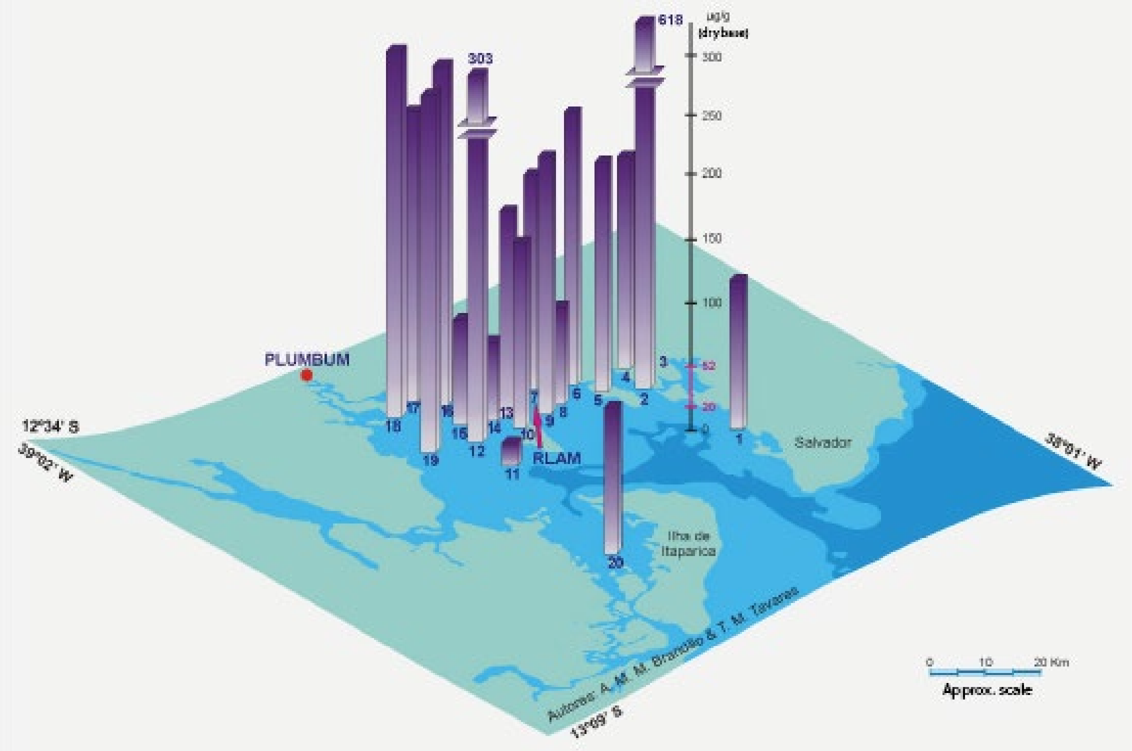


Figure 9.1 – Extent of lead contamination in the Todos os Santos Bay area, indicated by lead level bars in the bay's sediments. Source: TAVARES (1996).

As an initial strategy, the extent of contamination was carried out by analyzing all available data on the area. In this investigation, three distinct areas for intervention were delimited: the first represented by the metallurgy headquarters and its immediate surroundings; the second comprising the areas of slag landfills (sub-base paving the streets of Santo Amaro and landfills on public roads in the urban and rural areas of the municipality) and; the third uniting the Subaé River, its estuary and Todos os Santos Bay.

However, the implementation of remediation measures for the Plumbum site depends on the desired degree of recovery in the area, which is related to its future use. This condition is subordinated to soil intervention values established by CETESB (2001), and to the contribution of resources to be made available for the Environmental Recovery Plan, which directly involves the costs for the implementation of control technologies and, especially, the remediation of the ground.

According to these assumptions, the main steps proposed for the formulation of the Environmental Recovery Plan at the Plumbum site include the following:

1) Delimitation of the areas covered by the contamination: the following areas were delimited (Figure 9.2):
    - the area of direct influence and the main source of contamination is delimited by Plumbum's facilities and its immediate surroundings (ANJOS 1998);
    - the area of indirect influence, comprising the secondary sources of contamination located in the urban area of the town, which occurred through inadequate deposition, in the form of landfills, of slag, in streets without pavement and disposal of slag in the sub-base of paved roads, in addition to contaminants carried into the sediments of the Subaé River (ANJOS 1998 and COSTA 2001), and
    - the area of influence here called regional is made up of the surroundings of the town of Santo Amaro, the estuary of the Subaé river and Todos os Santos Bay (TAVARES 1990 and 1996) and SANTOS (2002).

2) Delimitation of the emergency intervention area: as it is the main source of contamination, Plumbum's industrial area and its surroundings must undergo interventions, in the short term, through an Environmental Recovery Plan for the industrial site;

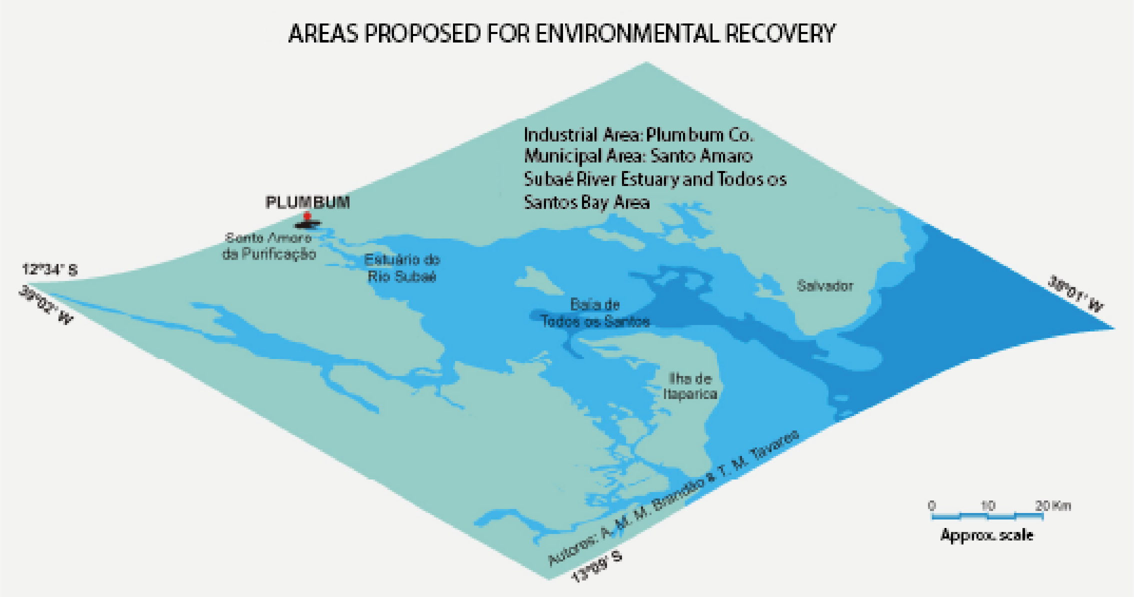


Figure 9.2 – Areas proposed for environmental recovery

3) Evaluation of the source of soil and groundwater contamination in the industrial area: developed by ANJOS (1998) and COSTA (2001), which aimed to determine the extent and degree of compromise of the source of contamination, of the surface soil, subsurface and groundwater;
4) Assessment of contamination of the aquatic environment in the industrial area: researched by ANJOS (1998), it aims to evaluate surface waters, sediments to determine the extent and degree of impairment resulting from the input of pollutants to the aquatic environment;
5) Environmental risk assessment: it was not carried out in the studies carried out by TAVAVES (1990 and 1996), ANJOS (1998), COSTA (2001) and SANTOS (2002) that established the degree of contamination of the physical environment and the population surrounding the metallurgy and the Subaé estuary, as well as shellfish and vegetables consumed by the population. It should be noted that Plumbum was chosen by the National Health Foundation (FUNASA) as one of the six model areas in Brazil for the development of health risk assessment according to the Agency for Toxic Substances and Disease Registry (ATSDR) methodology; and
6) Degraded Area Recovery Plan (DARP): as proposed below.

Steps 1 to 5 were developed in previous studies in this thesis.

9.1 - Premises for the DARP of the Plumbum site

The first effective proposals for the recovery of the Plumbum site were carried out by the Santo Amaro Urban Development Master Plan (BAHIA 1999). In this work, lead levels measurements were carried out in the soil of several streets and in the sediment of the Subaé River, and immediate intervention measures were proposed. However, the project was not accepted by the City Council of Santo Amaro, rejecting the proposal for environmental recovery.

The area defined for the DARP includes Plumbum's facilities and their immediate surroundings. A few initiatives to recover the area were implemented by Plumbum and its tenant, the Boka Loka Paper Co.. In sum, moving the slag donated by Boka Loka to the sub-base of the road that connects the Ruy Barbosa Street to the Bacraft factory increased the area of influence of contamination, in addition to randomly start to cover the slag with contaminated soil from works on the streets of Santo Amaro for the Blue Bahia State Government project.

The actions for environmental recovery developed by Plumbum were discussed above, in Chapter 8. The interventions did not not comply with the technical procedures specified by the relevant ABNT Standards, contributing to the increase of the background of contaminants in the area and their carry-over to the drainages that converge to the Subaé River.

The proposals for the DARP in the Plumbum's industrial area include the following activities:

- Definition of the recovery strategy;
- Proposal for removal and disposal of waste;
- Proposal for controlling contamination routes;
- Proposition for surface dynamics processes;
- Proposal for recovery and occupation of buildings, and
- Environmental Monitoring Plan.

9.1.1 - Area recovery strategy

The strategy for defining the Recovery Plan proposed for the area was based on the following criteria:

- the definition of the area of direct influence comprised by Plumbum's facilities and its immediate surroundings;
- determination of slag and fine residues found in industrial installations as the main active sources of soil and surface water contamination;
- the assessment of the risk to human health constitutes the main parameter for the decision to remediate the area;
- the finding that this route of contamination from the slag dam currently does not pose a risk of contamination to human health, as the metals are retained in the sediments of the wetland within Plumbum's facilities and because no plume of contamination is found contaminating wells, waterholes, and the Subaé River;
- the strategy for recovery of the area involves real knowledge of the toxic metals contained in the source of contamination and the processes of removal and disposal that occur on the surface of the soil and sediments;
- the routes of arsenic, bismuth and mercury introduced in the sinter-reduction process for the production of lead alloys must be evaluated to establish their risk to human health;
- the slag found on Plumbum's premises does not represent an immediate risk to health, due to its leachate and/or solubilization with metals being retained in the existing flooded areas in the drainage that percolates to the Subaé River;
- contaminated soil, after being turned over and mixed with slag, represents the main route of contamination;
- propose technologically efficient and economically viable alternatives for controlling the migration of heavy metals to the Subaé River and its estuary;
- the environmental recovery project should be financed, prepared and executed by the companies holding the environmental liability, namely, the Plumbum Mining and Metallurgy Co., as was carried out for the DARPs of the mines and metallurgy operations found in the states of Paraná and São Paulo, whose licenses are now under analysis by the respective state agencies;

- reduce the risk of human and natural resource exposure to pollutants and make surface contamination levels compatible with reference values (CETESB 2001) for future use;
- apply the Recovery Plan for Degraded Areas in accordance with the new conditions imposed by the slag coating project developed by the Plumbum Co., and
- apply remediation technologies that are efficient in removal and economically viable for cleaning the slag and the contaminated soil.

According to these premises, the industrial area of the Plumbum Co. and its surroundings was further divided in four compartments for a better understanding of the propositions presented here (Figure 9.3): the first one includes the main building outside the two valleys (Area I); the second comprises valley-01 which represents, respectively, the area where the old reduction furnaces, wet scrubbers, gas exhausters are located; decantation tanks, refinery pots and the tailings basin (Area II); the third compartment comprises valley-02 where the covered slag dam and the wetland are located (Area III); and the fourth compartment comprising the area between the railway and the Subaé River (Area IV).

Among the immediate actions established for the area with the objective of controlling direct contact with the source of contamination, it includes not using the slag for landfills and sub-base of streets and roads, in addition to fencing the entire area to prevent access by animals and people (SANTOS 1995 and ANJOS 1998). These procedures were implemented when complying with Public Civil Action 302/97.

9.2 – Proposal developed by the Purifica Project

As a measure for the removal and disposal of waste from the Plumbum site, MACHADO (2001) presented an alternative for passive containment called encapsulation. This project had as a purpose guiding the courts in the execution of the slag coating. The slag confinement project consists of five stages that would allow the containment of heavy metals leached from the slag, as they are found inside the Plumbum buildings, described as follows (Figure 9.4):

First stage – Isolation of the area – It is characterized by the construction of a fence throughout Plumbum's domain, which aims to prevent access by people and animals to the contaminated area.

Second stage – Displacement and grounding of the slag – This phase corresponds to the earthwork service for the displacement of the slag that is found around the factory and its disposal in the valley where a large amount of slag is already found in the form of a dam. The purpose of carrying out this stage is to dispose of the 57,160 m^3 of slag in a proper way up to elevation 115m and a displacement of up to 53m towards the studied wetland area.

Third stage – Waterproofing system – This stage aims to implement the waterproofing system of the top and sides of the slag dam, in order to avoid leaching of the slag. The waterproofing system at the top of the dam is composed of superimposed layers of topsoil, draining material and a hydraulic barrier composed of compacted clay (minimum thickness of 0.6, degree of compaction greater than 95%, moisture content within the range of ±2% and permeability lower than 10-7 cm/s) intercalated by a polyethylene geomembrane with a thickness of 1mm. Complementing the system, waterproofing of the bottom of the lagoon was planned with layers of compacted clay of 0.3 m and a geomembrane of 1 mm thick and a stone masonry with a foundation located 2 m deep from the surface and top at elevation 108.

Fourth stage – Drainage system – In this stage, the surface drainage elements composed of channels and berms were dimensioned to intercept and divert the flow of rainwater out of the dam area and avoid the appearance of erosion, in addition to suggesting a gallery for the removal and conduction of water accumulated upstream of the slag damming.

Fifth stage – Containment system – Refers to the construction of a gravity wall with a total height of approximately 4m, including the height of the base (2m), to prevent the percolation of water from the lagoon.

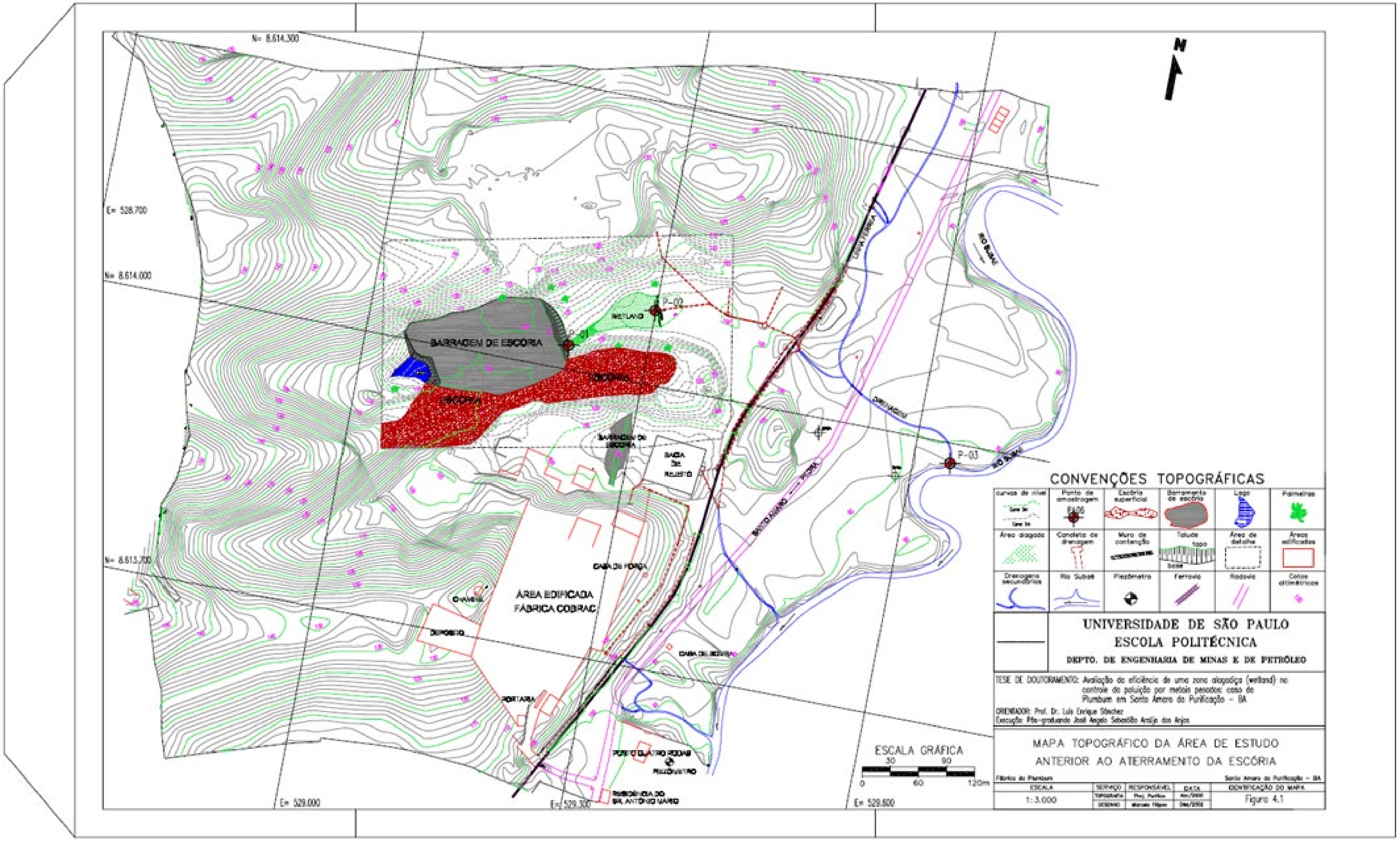


Figure 9.3 – Map of the area, including the industrial facilities and its surroundings.

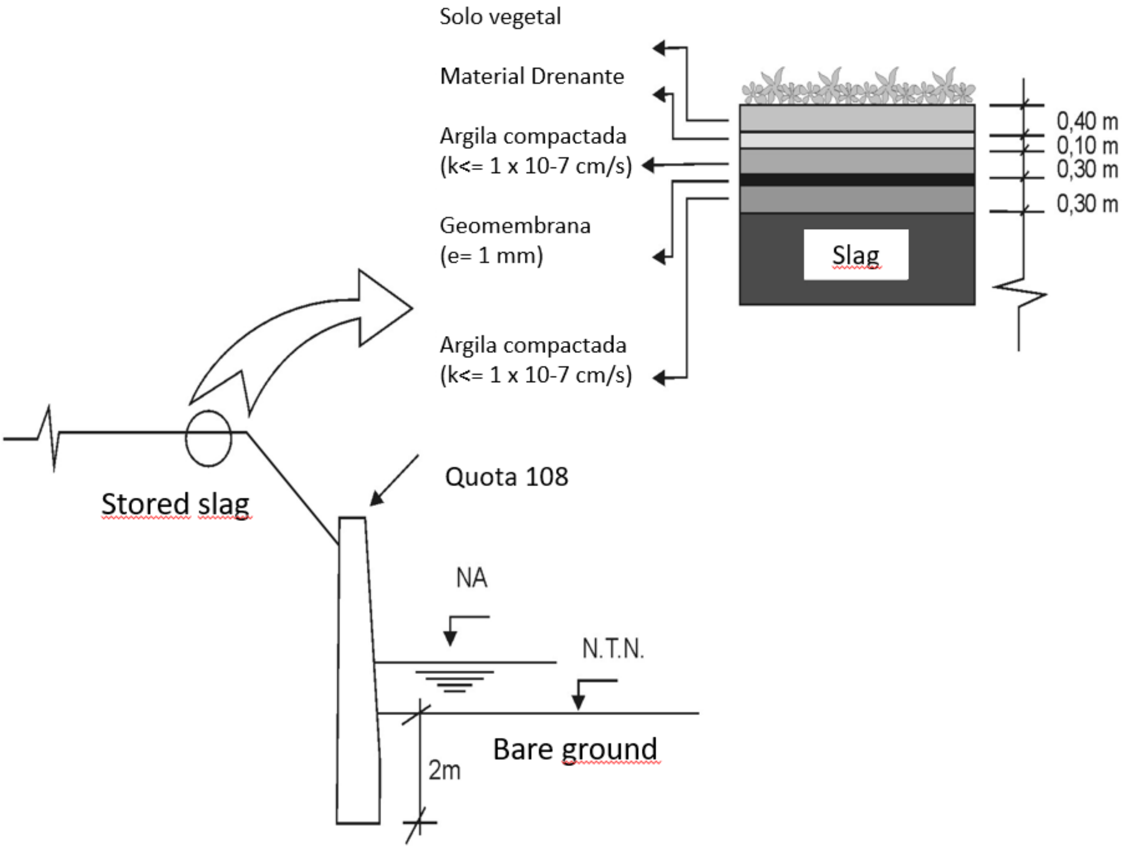


Figure 9.4 - Scheme of the waterproofing system. Source: MACHADO (2001).

The tradeoffs of the encapsulation system for the Plumbum site are summarized in Table 9.1.

Table 9.1 – BENEFITS AND DOWNSIDES OF SLAG ENCAPSULATION.

BENEFITS	• Prevents leaching and/or solubilization of metals from the slag. • Decreases the visual impact of the area. • Controls erosion if done well
DOWNSIDES	• The project only considers slag as a source of contamination. • High cost for implementation • Projects for the reuse of slag would have the additional cost of demobilizing the encapsulation. • Does not include a monitoring and maintenance program. • Destroys the existing wetland, which would certainly provide the availability and transport of high concentrations of metals retained in this system. • Increases the risk of health contamination. • Does not propose an alternative for remediation of contaminated soil.

9.3 - Proposals for the PRAD of the industrial area and its immediate surroundings

Based on the strategies proposed for Plumbum's industrial area, proposals were developed for the area's environmental recovery. The proposed alternatives for the DARP had as their focus the assessment of health risk as the main decision-making point for proposing the remediation of the site. Within this context, procedures are proposed for the removal and destination of contaminated waste (slag and soil), control of contaminant migration routes, reuse of Plumbum facilities and their immediate surroundings and monitoring plan, through the following actions:

1) Stabilize the contaminated soil through revegetation and slope containment;
2) Delimit all areas where slag was deposited in the form of a landfill and remove all existing contaminated soil, transporting it to Plumbum's facilities;
3) Recover existing buildings and reuse them as an industrial undertaking. Evaluate the levels of metals on the walls of buildings and define their use as an industrial undertaking. This alternative tries to recover jobs for the region, as the reference levels are easier to comply with (CETESB 2001);
4) Assess the actual contamination of valley-01, where old furnaces, exhaust fans and the lead refinery are located, including the soil and walls of buildings, in addition to the slag mixed with the contaminated soil and currently covered;
5) As a control measure for surface water, we propose the installation of a new wetland in the old tailings basin, to be built with soil from the lateral slope and revegetated with Typha sp found in valley-02. An alternative would be the removal of all soil contaminated and mixed with slag, in addition to the rubble of buildings eventually demolished, to valley-02;
6) Convert valley-02 into another controlled industrial landfill area, a place to receive slag and contaminated soil from streets and existing landfills in the Santo Amaro region and from Plumbum's own industrial area. The proposed change stems from the efficient control system for heavy metals carried out by the existing wetland (Figure 9.3);
7) The valley would work as a combination of containment techniques (through controlled disposal of slag and contaminated soil) and control through wetland to remove metals that migrate from the soil and toxic waste (Figures 9.5 and 9.6);
8) In these valleys, wells should be installed to monitor groundwater and the two built wetlands should be monitored, analyzing the inflow and outflow of each cell, metals in the water entering and exiting the system, pH of rainwater and pluviometry.
9) In the area between the railroad and the Subaé river, vegetables and fruits produced in the small garden installed in front of the factory

must be evaluated. The living fence used by the owner can be applied by Plumbum as an alternative to reducing the visual impact; and

10) All the slag, pure or mixed with the soil, must be disposed in valley-02.

The tradeoffs for developing the mixed wetland disposal and control system in Vale-02 at the Plumbum site are summarized in Table 9.2.

Table 9.2. – BENEFITS AND DOWNSIDES FOR THE CONTROLLED DISPOSAL AND USE OF THE FLOOD ZONE.

BENEFITS	• The project includes the control of slag leachate and contaminated soil. • In case the slag can be reused, it will be in a single location and arrangement, easy to be removed. • The project has an adequate surface and groundwater monitoring program. • The project includes all slag and contaminated soil disposed of in the streets and landfills possibly found in the area. • The effective costs for its adaptation are low.
DOWNSIDES	• Does not prevent leaching/solubilization of slag and contaminated soil. • Does not control erosion of contaminated soil.

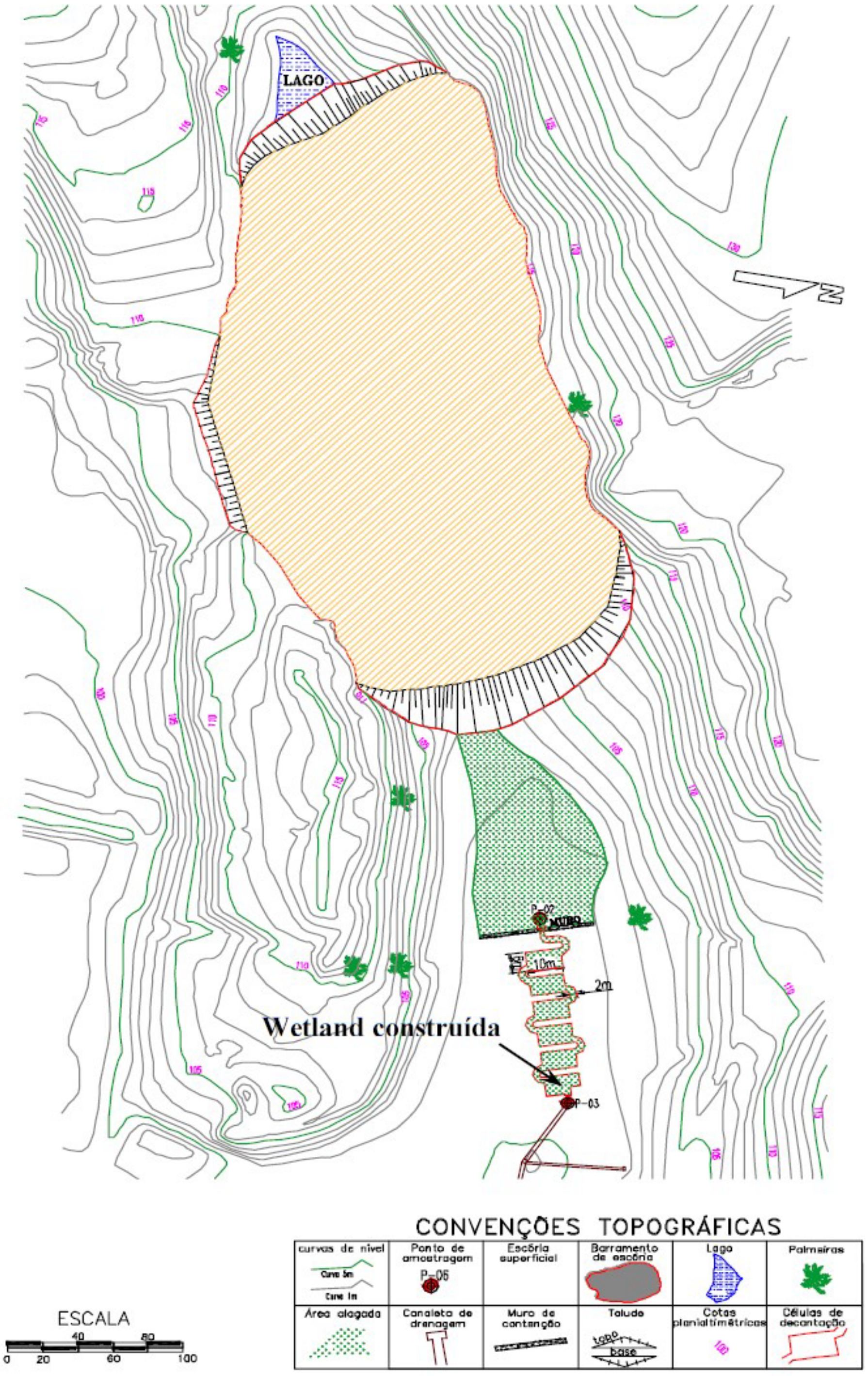


Figure 9.5 – Wetland built in the landfill zone of valley 2.

The choice of landfill zone for the location of the constructed wetland zone was based on the following aspects: proximity to the current wetland zone; the constitution of the same type of soil with high physical attenuation capacity (soil hydraulic conductivity equal to 10^{-9} cm/s) (MACHADO, 2001) and chemical attenuation given by the high cation exchange capacity of montimorilonite and organic matter; for being a flat land easily adapted to wetland works; and for being within the Plumbum's facilities and control.

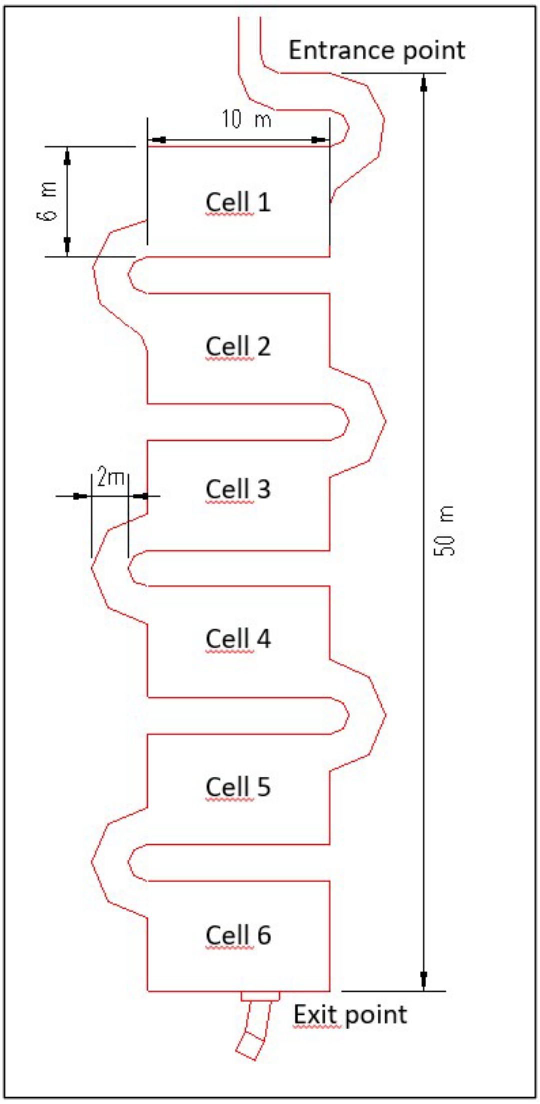


Figure 9.6 - Detail of proposed wetland cells

The investigation on wetlands built to control heavy metals is incipient and has not yet established criteria for cell standardization. Given this fact, the current project for the new Plumbum wetland is based on the geochemical properties raised in this study.

The choice of six alternating cells can provide a longer residence time for surface water in the flooded system compared to the current wetland and thus increase the metal removal capacity. Cells must have the same hydraulic gradient as the existing pipeline in the area, which currently controls surface water from the current wetland

CHAPTER 10 - CONCLUSIONS

The Plumbum wetland probably did not exist prior to the installation of the industrial plant. It arose due to engineering works in the area and without the intention of becoming a pollution control system, hence it is not a natural wetland, nor was it built or adapted. This conclusion is based on the following findings:

a) the topography of the area is represented by an elevation where most of Plumbum's facilities were built and by two small parallel valleys, with intermittent drainage, perpendicular to the Subaé River;
b) before the installation of the metallurgical plant, there was already a road along the Subaé river and, between the buildings of Plumbum and this road, a railroad was built to transport the lead ore mined in Boquira;
c) buildings were installed in the first valley, such as ovens, extractors, tanks and lead refining, in addition to a decantation basin. This area also contained most of the slag in the form of small piles until 1993, when the enterprise was abandoned;
d) in the second valley, a small embankment was built, with submerged pipes, for the drainage of water from rainfall in the valley, with the objective of directing the water passing through pipes under the railway and roadways, later flowing into the Subaé River;
e) in 1995, at the request of CRA agency, the slag, which was scattered throughout Plumbum's premises, was largely deposited, without any standard procedure, in the second valley, close to the landfill area where slag could already be found in significant quantity, in the form of a dam. The environmental agency's intention was to dispose of the slag in a single location, in view of the largely negative visual impact of the slag piles;
f) between the slag dam and the landfill zone, a wetland was installed, topographically lower than the landfill zone, now fed not only by

rainwater directly affecting the entire valley, but also by rainwater that accumulated upstream the dam, and migrated slowly, feeding the wetland with the leached and/or solubilized residue of the contaminated slag; and

g) in this swampy area, a hydromorphic sediment accumulated, rich in montmorillonite clay, from the vertisol, and in organic matter, originating from the decomposition of macrophyte vegetation adapted to the area. This flooded system presents surface flow and provides the development of physical-chemical and biological processes causing the removal of chemical elements introduced into the system.

This understanding of the evolution of the flooded system, together with surveys carried out by ANJOS (1998), helped to characterize this flooded zone as a natural biogeochemical and physical barrier controlling the contamination of surface and underground waters. However, the elucidation of a few other issues was necessary for the evaluation of the wetland as an effective pollution control system. These considerations guided the development of this investigation.

The main questions raised were: what is the relationship between rainwater and the leaching and/or solubilization of toxic waste towards the Subaé River? What physical-chemical parameters can influence the removal and availability of contaminants? What is the current metal removal capacity of the flooded system?

Faced with these issues, a strategy was developed to evaluate the behavior of physical-chemical parameters and their interactions and interference with the migration and retention of metals in surface waters and hydromorphic sediment.

An adaptation of the investigation strategy was necessary, due to the implementation of certain measures, by court order. In view of the new strategy for researching the area, the main conclusions obtained during the three stages of the survey were as follows.

For the data evaluated before the slag coating, we can conclude that:

1) there is no correlation between the volume of rainwater and the concentrations of metals measured weekly in the Plumbum wetland, however, even at neutral to alkaline pH, leaching processes and/or solubilization of metals contained in the slag dam can occur;
2) heavy metals like cadmium, lead, copper and zinc have been retained by the wetland and the system was 100% efficient in removing copper and zinc, 82% for lead and 73% for cadmium;
3) the lower removal of cadmium is due to its high solubility, however the loads released by the flooded system, with a maximum concentration of 0.003 mg/L Cd, are small in relation to the maximum values established by Conama for Class 2 (0.001 mg/L Cd);
4) lead retention showed 82% efficiency, but this value becomes extremely relevant if we consider the small size of the wetland zone and the high concentrations of metals contained in the slag and, mainly, retained in the hydromorphic sediment of the wetland zone;
5) the conditions of neutral to alkaline pH and predominantly oxidizing Eh favor the precipitation and removal of metals in the surface sediments of the wetland, actually behaving as controlling parameters of the metal removal processes;
6) the metal concentration levels surveyed showed a strong correlation between the lead, copper and zinc, and a low correlation for cadmium, as it presents high solubility;
7) support metals are of great importance in processes involving the removal of heavy metals, in particular the capacity for cation exchange with montmorillonite, retaining heavy metals and releasing aluminum;
8) the pH of the rainwater showed slightly acidic values in January, what is particularly unsettling, as the acidity of the pH provides the solubilization of metals and facilitates their entry into the food chain;
9) the BoxPlot graphs clearly showed the different concentrations of heavy metals at the entrance and exit of the wetland, in addition to the discrepant points occurring for lead at point 02 and for zinc at point 01;
10) the smoothing graphs for heavy metals showed trends that were not always very clear, especially when performed at the exit points of the wetland;

11) Pearson's correlation matrix clearly demonstrated the correlation between zinc concentrations with lead and copper and, to a lesser extent, with cadmium at the entry point of the wetland;
12) causality analyses for time series demonstrated that the analysis for 22 weekly samples is not possible to obtain significant results, and for 52 weeks, few results showed any correlation, and when they did, it was not possible to establish a cause-and-effect relationship among the analyzed parameters;
13) chemical analyses for heavy metals in soil and sediments have shown that hydromorphic sediments retain very high concentrations mainly of lead, cadmium, and zinc;
14) analyses by sequential extraction in soil and sediments showed that lead, cadmium, and zinc are strongly linked in all phases, especially in the exchangeable, carbonate and reducing phases, while copper is linked to the oxidizable and residual phases;
15) the acids used in the sequential extraction demonstrated that all metals can be removed from the contaminated soil and sediment, and can serve as examples in the proposition of soil cleaning techniques;
16) the sediment at the entry point of the wetland has the highest concentration levels of lead, zinc, and copper, while cadmium is high at the point located in the middle of the wetland; and
17) cadmium is the heavy metal with the highest availability potential, followed by lead, zinc and copper.

The second stage of the survey, carried out during the covering of the slag dam, presented the following conclusions:

1) the MORSA Co. did not carry out the encapsulation of the slag provided for by the CRA agency and the Public Civil Action, in addition to not collecting the slag disposed around the Plumbum Co.;
2) recommendations by the experts hired by the courts in Santo Amaro da Purificação presents inaccuracies and lack of knowledge of the procedures and analyses of the parameters related to the physical environment, especially surface water and soil;

3) the covering procedure did not take into consideration that the contaminated soil is also considered hazardous waste and, therefore, could not be unpacked and disposed over the slag;
4) the covering project did not present a proposal for monitoring the area, essential to assess the effects produced by the area recovery project;
5) the project to cover the area landfilled the entry point of the wetland, interrupting the process of evaluation of the efficiency of the system as a measure of control the leached and/or solubilized water from the slag, this procedure radically modified the evaluation process of the area ceasing to be carried out an annual survey that would serve as "background" parameters for understanding the migration of metals throughout the year and, for proposals for new evaluations and monitoring; and
6) the analyses carried out at the exit point of the wetland zone showed that only a small amount of cadmium was available at this stage, while the other heavy metals were retained in the sediments of the wetland zone.

The third and final stage of the survey was carried out after the slag had been covered and presented the following conclusions:

1) the high rainfall levels recorded in this stage were responsible for the leaching of metals retained in the soil and contaminated sediment that were improperly disposed on the slag;
2) the coating carried out outside the procedures recommended by the ABNT technical standards caused an intense erosion process in the area and the rupture of the slope, causing the appearance and erosion of slag;
3) the surface covering process carried out by Plumbum, without adequate vegetation covering, accelerated the breakdown of soil particles and their transport by surface runoff, causing laminar erosion on the surface, creeping from the rupture between the surface soil and the slag deposited in sub-surface, in addition to landslide disposed on the slope of the slag dam;

4) this coating caused the availability of cadmium in the wetland for more than ten weeks, demonstrating the potential risk to health when intervening in a contaminated area without specific knowledge;
5) in order to control erosive processes, a project is necessary that contemplates the diversion of surface water by storm drains, the regularization and protection of slopes and greater revegetation of the exposed soil by species adapted to the area;
6) the cadmium available from the wetland was retained by the sediments from the drainage flowing into the Subaé River, demonstrating a high efficiency of the processes supporting the surface water and sediment system;
7) the thickness of the hydromorphic sediment layer, above 30cm, and the compact vegetation of the Typha sp. species, are indicators that the Plumbum wetland is a surface flow system that is in a mature stage in the evolution of wetlands;
8) possibly, the erosion process is responsible for the rapid sedimentation of the small Plumbum wetland, modifying its dynamics and existing balance between the support parameters of surface water and the processes of removal and availability of metals. Hence, as a measure to control the availability of metals not retained in the Plumbum wetland, the installation of a constructed wetland is recommended, as an effective measure to control the metals migrating to the Subaé River;
9) the current contamination levels found in the fine sediments of the Subaé River, its estuary and in the Todos os Santos Bay came mostly from effluents released directly into the Subaé River before the metallurgical plant was abandoned;
10) according to the data collected, the slag deposited inside the metallurgical facilities does not present a risk to health, given the small "input" of contaminants in the Subaé River, as demonstrated in the weekly survey, when no large outflows of metals from the wetland was found, with the exception of cadmium during and after slag coating;
11) a large monitoring system is needed for the entire Plumbum site, among which a rainfall base should be installed to measure the volume of rainfall and support parameters, while for surface water the survey

carried out in this investigation should be extended to the wetlands of the Plumbum Co.;

12) for the two proposed wetlands, one in each valley, monitoring of metals (lead, cadmium, zinc, copper, arsenic and bismuth) and main support parameters (pH and Eh) should be carried out;

13) for groundwater, monitoring for heavy metals should be carried out using the wells installed by the Purifica Project. The survey should be carried out every six months in order to verify evidence of trace elements in the groundwater; and

14) it is suggested the installation of a controlled industrial landfill in valley-01, to receive all the contaminated soil and slag existing in the municipality of Santo Amaro da Purificação.

The results contained in this study demonstrate that the wetlands behave as geochemical, physical and biological barriers in controlling the existing contamination in the area.

This survey carried out in 2001, despite all the changes, represented the first major assessment of surface water, the main route of contamination from the slag deposited at Plumbum's facilities. These results will effectively contribute to the development of propositions and strategies for the environmental recovery of the entire Plumbum contaminated site.

The modifications caused by the coating of the slag showed that the contaminated soil represents the main risk to health, due to the easy transport caused by rainwater, this fact deserves special attention, due to the large amount of landfills carried out in unpaved streets in urban areas. and rural areas of Santo Amaro da Purificação and its districts.

The slag deposited in the streets, after a few years, contaminates the soil, and possibly maintains high levels of metals in the environment and in human receptors, especially in children who play in these areas and maintain direct contact with the soil.

The procedure for covering the slag can make it difficult to remove both the contaminated soil or soil mixed with the slag, as well as the slag itself for future treatment, as the slag in valley-01 is already mixed with the soil and receives the contaminated soil from the slope for its covering, and in valley-02 the slag has been thrown into the wetland, mixed and covered with the contaminated soil itself .

Before coating, it would have been possible to remove the slag deposited on the soil and subsequently the contaminated soil for separate treatment. Now it is a mixture of soil contaminated with slag, what makes the application of decontamination techniques more difficult and expensive. Any project meant to reduce the toxicity of slag cannot be dissociated from cleaning the soil.

It is important to point out that no assessment of contamination by arsenic, antimony, bismuth and mercury (metals introduced during the production of lead metal alloys) has not yet been developed by any of the universities that carry out research in the area. These surveys are highly expensive and hampered due to sampling being extremely selective, and analytical methods not always allowing detection levels that can assess their existing concentration levels in water and soil samples.

It is concluded that the Plumbum wetland constitutes, even involuntarily, a barrier to control contaminants from the slag. This technique should be monitored for greater knowledge of its efficiency and serve as a model for immediate control of large, contaminated areas, such as those degraded by mining.

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SUPPLEMENT 1 – Rainfall and pH levels

	pH	Rainfall (mm)
JANUARY		
WEEKLY SAMPLE		
RAIN - WS-01	**5,2**	**08**
RAIN - WS-02	**5,9**	**15**
RAIN - WS-03	**7,9**	**19**
RAIN - WS-04	**6,9**	**10**
RAIN - WS-05	**6,3**	**02**
FEBRUARY		
WEEKLY SAMPLE		
RAIN - WS-06	**7,9**	**09**
RAIN - WS-07	N/M	0
RAIN - WS-08	7,1	08
RAIN - WS-09	8,3	51
MARCH		
WEEKLY SAMPLE		
RAIN - WS-10	N/M	O
RAIN - WS-11	5,4	22
RAIN - WS-12	7,3	06
RAIN - WS-13	N/M	0
APRIL		
WEEKLY SAMPLE		
RAIN - WS-14	7,3	15
RAIN - WS-15	7,6	6,5
RAIN - WS-16	8,1	17,5
RAIN - WS-17	7,4	21

MAY		
WEEKLY SAMPLE		
RAIN - WS-18	6,3	55
RAIN - WS-19	7,6	4,5
RAIN - WS-20	7,3	18
RAIN - WS-21	7,3	27
RAIN - WS-22	7,5	3,5
JUNE		
WEEKLY SAMPLE		
RAIN - WS-23	7	64
RAIN - WS-24	6,9	67
RAIN - WS-25	7,2	58
RAIN - WS-26	7,3	46

	pH	**Rainfall (mm)**
JULY		
WEEKLY SAMPLE		
RAIN - WS-27	**7,3**	**95**
RAIN - WS-28	**7,5**	**13**
RAIN - WS-29	**7,2**	**82**
RAIN - WS-30	**7,4**	**05**
AUGUST		
WEEKLY SAMPLE		
RAIN - WS-31	**8,5**	**16**
RAIN - WS-32	8,0	29
RAIN - WS-33	7,7	22
RAIN - WS-34	8,2	85
RAIN - WS-35	8,1	13
SEPTEMBER		
WEEKLY SAMPLE		

RAIN - WS-36	8,4	55
RAIN - WS-37	8,4	03
RAIN - WS-38	7,4	131
RAIN - WS-39	7,1	05
OCTOBER		
WEEKLY SAMPLE		
RAIN - WS-40	7,0	10
RAIN - WS-41	8,1	50
RAIN - WS-42	8,1	142
RAIN - WS-43	N/M	00
RAIN - WS-44	8,6	29
NOVEMBER		
WEEKLY SAMPLE		
RAIN - WS-45	N/M	00
RAIN - WS-46	8,9	15
RAIN - WS-47	8,4	04
RAIN - WS-48	7,5	09
DECEMBER		
WEEKLY SAMPLE		
RAIN - WS-49	7,5	50
RAIN - WS-50	8,6	05
RAIN - WS-51	N/M	00
RAIN - WS-52	N/M	00

N/M (Not Measured)

SUPPLEMENT 2 – Wetland water quality parameters before slag coating performed by the Plumbum Co.

Surveyed parameters

JANUARY

	pH	Eh	Cond.	O D	T
WEEKLY SAMPLE		MV	µS/cm	mg/L	°C
WS-01	**8,5**	**189**	**683**	**0,4**	**27,8**
WS-01.1	**6,9**	**54**	**745**	**0,4**	**26,9**
WS-02	**8,2**	**160**	**720**	**2,2**	**29,3**
WS-02.1	**6,6**	**140**	**784**	**1,2**	**27,1**
WS-03	**7,6**	**177**	**833**	**1,0**	**27,8**
WS-03.1	**6,6**	**110**	**931**	**1,4**	**26,2**
WS-04	**7,6**	**133**	**972**	**0,2**	**29,2**
WS-04.1	**6,5**	**110**	**1068**	**0,1**	**28,7**
WS-05	**7,2**	**167**	**755**	**0,1**	**29,9**
WS-05.1	**6,2**	**81**	**927**	**0,1**	**29,1**

FEBRUARY

	pH	Eh	Cond.	O D	Temp ° C
WEEKLY SAMPLE		MV	µS/cm	mg/L	°C
WS-06	**7,5**	**175**	**788**	**0,5**	**29,0**
WS-06.1	6,3	130	962	0,5	28,8
WS-07	7,1	N/M	817	0,6	28,7
WS-07.1	6,2	N/M	1093	0,4	27,7
WS-08	7,1	N/M	714	0,2	27,7
WS-08.1	6,6	N/M	571	0,2	26,3
WS-09	7,1	248	851	2,3	29,0
WS-09.1	6,3	160	940	1,9	28,1

	pH	Eh	Cond.	O D	Temp ° C
MARCH					
WEEKLY SAMPLE		MV	µS/cm	mg/L	ºC
WS-10	6,8	193	923	0,4	28,3
WS-10.1	6,3	144	1050	0,4	28,2
WS-11	6,6	165	913	0,8	28,7
WS-11.1	5,8	110	1034	0,1	27,6
WS-12	7,1	240	841	0,1	29,4
WS-12.1	6,3	119	987	0,1	27,7
WS-13	7,1	289	808	0,1	28,6
WS-13.1	6,3	165	1088	0,1	27,7

	pH	Eh	Cond.	O D	Temp ° C
APRIL					
WEEKLY SAMPLE		MV	µS/cm	mg/L	ºC
WS-14	7,1	305	734	0,2	28,0
WS-14.1	6,4	271	1030	0,3	26,9
WS-15	6,8	330	785	0,1	27,3
WS-15.1	6,3	125	1033	0,2	25
WS-16	7,1	346	800	0,3	28
WS-16.1	6,4	56	945	0,3	26,5
WS-17	6,8	322	803	0,1	27,6
WS-17.1	6,5	71	971	0,2	26

MAY	pH	Eh	Cond.	O D	Temp ° C
WEEKLY SAMPLE		MV	µS/cm	mg/L	ºC
WS-18	7,1	206	736	0,1	27,6
WS-18.1	6,6	54	739	0,1	27
WS-19	6,9	346	798	0,7	27,3
WS-19.1	6,6	48	951	0,8	26,5
WS-20	6,9	331	805	0,3	28,2
WS-20.1	6,7	40	942	0,8	26,5
WS-21	6,9	278	770	0,3	27,5
WS-21.1	6,7	-25	850	0,1	24,6
WS-22	6,5	245	1121	0,8	27,5
WS-22.1	6,5	-4	1273	0,1	25,4

SUPPLEMENT 2 – Wetland water quality parameters during slag coating

JUNE

WEEKLY SAMPLE	pH	Eh	Temperature
		MV	ºC
WS-23.1	6,7	88	24,7
WS-24.1	6,9	152	23,4
WS-25.1	6,9	148	24,5
WS-26.1	7,1	128	24,9

JULY

WEEKLY SAMPLE	pH	Eh	Temperature
		MV	ºC
WS-27.1	7,3	278	25,1
WS-28.1	7,4	344	25,3
WS-29.1	7,5	149	24,9
WS-30.1	7,6	231	26

SUPPLEMENT 2 – Wetland water quality parameters after slag coating

AUGUST

	pH	Eh	Temperature
WEEKLY SAMPLE		MV	°C
WS-31.1	7,8	238	26,3
WS-31.2	8,1	257	26
WS-32.1	7,9	180	24,6
WS-32.2	8,2	229	24,4
WS-33.1	7,9	182	24,7
WS-33.2	8,4	218,5	24,4
WS-34.1	7,6	245,5	27
WS-34.2	8,1	258	26,1
WS-35.1	8,1	171	25,6
WS-36.2	8,7	153	25,3

SEPTEMBER

	pH	Eh	Temperature
WEEKLY SAMPLE		MV	°C
WS-36.1	7,9	218,7	25,6
WS-36.2	8,4	216,3	25,1
WS-37.1	7,8	204	26,7
WS-37.2	8,6	298,5	26,2
WS-38.1	8,1	228,3	25,1
WS-38.2	8,2	270	24,4
WS-39.1	8,2	221,5	27,2
WS-39.2	8,7	257	26,6

OCTOBER

	pH	Eh	Temperature
WEEKLY SAMPLE		MV	°C
WS-40.1	7,8	213,7	26
WS-40.2	8,6	247,2	26,2
WS-41.1	8,2	158,6	24,2
WS-41.2	8,7	223,3	24,6
WS-42.1	8,1	192,6	27
WS-42.2	8,6	275,1	27
WS-43.1	8,1	174,5	27
WS-43.2	8,9	200,6	27
WS-44.1	7,8	243,2	27,9
WS-44.2	8,8	254,4	27,3

NOVEMBER

	pH	Eh	Temperature
WEEKLY SAMPLE		MV	°C
WS-45.1	7,8	215,6	26,1
WS-45.2	8,8	282,9	26,3
WS-46.1	8,1	225,6	26,1
WS-46.2	8,9	283,4	26
WS-47.1	7,9	190,4	26,3
WS-47.2	8,8	283,4	26,5
WS-48.1	8,3	315,3	27
WS-48.2	7,9	374,3	27,4

DECEMBER	ph	Eh	Temperature
WEEKLY SAMPLE		MV	°C
WS-49.1	7,9	454,1	28
WS-49.2	N/M	N/M	N/M
WS-50.1	8,3	373,1	28,1
WS-50.2	N/M	N/M	N/M
WS-51.1	7,7	125,5	27,3
WS-51.2	N/M	N/M	N/M
WS-52.1	7,8	258,9	27,1
WS-52.2	N/M	N/M	N/M

N/M (Not Measured)

SUPPLEMENT 3 – Analyses of metals in surface water in January

Chemical analyses

	Al	Ca	Cd	Pb	Cu	Fe
JANUARY						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-01	**0,52**	**136**	**0,0027**	**0,73**	**0,14**	**1,02**
WS-01.1	**1,36**	**126**	**0,0021**	**0,18**	**<0,02**	**1,77**
WS-02	**<0,1**	**131**	**0,0016**	**0,14**	**<0,02**	**<0,1**
WS-02.1	**0,16**	**156**	**0,0011**	**<0,02**	**<0,02**	**0,29**
WS-03	**<0,1**	**126**	**0,0019**	**0,14**	**<0,02**	**<0,1**
WS-03.1	**0,11**	**146**	**<0,001**	**<0,02**	**<0,02**	**0,34**
WS-04	**<0,1**	**186**	**0,0030**	**0,16**	**<0,02**	**0,15**
WS-04.1	**1,21**	**211**	**0,0026**	**0,16**	**<0,02**	**3,32**
WS-05	**0,72**	**236**	**0,0049**	**0,84**	**0,18**	**1,41**
WS-05.1	**0,11**	**243**	**<0,001**	**<0,02**	**<0,02**	**1,38**

	Mg	Zn	Mn	Co	Cr	Ni
JANUARY						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-01	**4,11**	**0,99**	**0,052**	**<0,05**	**<0,02**	**<0,02**
WS-01.1	**6,36**	**0,096**	**0,97**	**<0,05**	**<0,02**	**<0,02**
WS-02	**4,46**	**0,13**	**<0,05**	**<0,05**	**<0,02**	**<0,02**
WS-02.1	**6,31**	**0,066**	**1,14**	**<0,05**	**<0,02**	**<0,02**
WS-03	**5,33**	**0,14**	**<0,05**	**<0,05**	**<0,02**	**<0,02**
WS-03.1	**6,38**	**0,056**	**0,72**	**<0,05**	**<0,02**	**<0,02**

WS-04	6,35	0,28	<0,05	<0,05	<0,02	<0,02
WS-04.1	7,63	0,10	3,26	<0,05	<0,02	<0,02
WS-05	7,57	1,45	0,061	<0,05	<0,02	<0,02
WS-05.1	9,19	0,054	1,18	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in February

Chemical analyses

FEBRUARY

	Al	**Ca**	**Cd**	**Pb**	**Cu**	**Fe**
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-06	<0,1	253	0,0039	0,16	<0,02	<0,1
WS-06.1	0,14	283	<0,001	<0,02	<0,02	0,52
WS-07	0,16	216	0,0047	0,34	0,042	0,27
WS-07.1	<0,1	382	0,0010	<0,02	<0,02	0,37
WS-08	0,24	216	0,0059	0,53	0,13	0,59
WS-08.1	0,16	134	0,0024	0,49	<0,02	0,26
WS-09	0,13	191	0,0071	0,31	0,045	0,20
WS-09.1	0,11	266	0,0011	<0,02	<0,02	0,35

	Mg	Zn	Mn	Co	Cr	Ni
FEBRUARY						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-06	7,62	0,42	<0,05	<0,05	<0,02	<0,02
WS-06.1	9,28	0,056	0,66	<0,05	<0,02	<0,02
WS-07	8,50	0,77	<0,05	<0,05	<0,02	<0,02
WS-07.1	10,1	0,071	1,04	<0,05	<0,02	<0,02
WS-08	6,77	1,3	0,066	<0,05	<0,02	<0,02
WS-08.1	4,37	0,14	0,23	<0,05	<0,02	<0,02
WS-09	8,03	1,18	0,052	<0,05	<0,02	<0,02
WS-09.1	12,1	0,092	3,09	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in March

Chemical analyses

	Al	Ca	Cd	Pb	Cu	Fe
MARCH						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-10	1,64	248	0,0099	1,80	0,44	4,85
WS-10.1	0,14	286	<0,001	0,021	<0,02	0,64
WS-11	2,04	209	0,013	1,96	0,51	4,18
WS-11.1	<0,1	232	0,0023	<0,02	<0,02	0,41
WS-12	0,12	215	0,0078	0,26	0,033	0,20

WS-12.1	**0,13**	**228**	**0,0010**	**<0,02**	**<0,02**	**1,22**
WS-13	**0,56**	**204**	**0,0082**	**0,61**	**0,13**	**1,07**
WS-13.1	**<0,1**	**255**	**<0,001**	**<0,02**	**<0,02**	**0,37**

	Mg	**Zn**	**Mn**	**Co**	**Cr**	**Ni**
MARCH						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-10	**8,92**	**4,81**	**0,19**	**<0,05**	**<0,02**	**<0,02**
WS-10.1	**8,38**	**0,050**	**5,37**	**<0,05**	**<0,02**	**<0,02**
WS-11	**9,25**	**5,17**	**0,20**	**<0,05**	**<0,02**	**<0,02**
WS-11.1	**9,65**	**0,14**	**1,80**	**<0,05**	**<0,02**	**<0,02**
WS-12	**9,57**	**0,85**	**<0,05**	**<0,05**	**<0,02**	**<0,02**
WS-12.1	**9,29**	**0,090**	**2,90**	**<0,05**	**<0,02**	**<0,02**
WS-13	**8,45**	**1,48**	**0,068**	**<0,05**	**<0,02**	**<0,02**
WS-13.1	**10,9**	**0,050**	**3,63**	**<0,05**	**<0,02**	**<0,02**

SUPPLEMENT 3 – Analyses of metals in surface water in April

Chemical analyses

APRIL	Al	Ca	Cd	Pb	Cu	Fe
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-14	1,59	185	0,0096	1,57	0,36	3,86
WS-14.1	0,12	240	<0.001	<0,02	<0,02	0,55
WS-15	0,19	185	0.0076	0,30	0,54	0,34
WS-15.1	<0,1	240	<0.001	<0,02	<0,02	1,10
WS-16	2,40	200	0,015	2,67	0,62	5,78
WS-16.1	0,45	216	<0.001	0,091	<0,02	6,44
WS-17	<0,1	207	0,0092	0,21	0,027	<0,1
WS-17.1	<0,1	222	<0.001	<0,02	<0,02	3,10

APRIL	Mg	Zn	Mn	Co	Cr	Ni
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-14	8,01	3,97	0,17	<0,05	<0,02	<0,02
WS-14.1	10,2	<0,05	4,90	<0,05	<0,02	<0,02
WS-15	7,45	1,22	0,051	<0,05	<0,02	<0,02
WS-15.1	9,84	<0,05	5,04	<0,05	<0,02	<0,02

WS-16	8,81	5,95	0,24	<0,05	<0,02	<0,02
WS-16.1	9,49	<0,05	6,97	<0,05	<0,02	<0,02
WS-17	8,14	1,47	0,072	<0,05	<0,02	<0,02
WS-17.1	8,96	<0,05	4,41	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in May

Chemical analyses

MAY

WEEKLY SAMPLE	**Al**	**Ca**	**Cd**	**Pb**	**Cu**	**Fe**
	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-18	0,66	215	0,0070	0,73	0,13	1,23
WS-18.1	0,17	178	<0,001	0,030	<0,02	3,13
WS-19	0,26	185	0,0069	0,31	0,054	0,41
WS-19.1	0,18	226	<0,001	0,027	<0,02	5,44
WS-20	<0,1	230	0.0085	0,19	0,024	<0,1
WS-20.1	<0,1	204	<0,001	<0,02	<0,02	5,10
WS-21	2,02	189	0,010	1,58	0,40	15,4
WS-21.1	0,16	185	<0,001	<0,02	<0,02	5,31
WS-22	<0,1	177	0,0090	0,20	0,027	<0,1
WS-22.1	0,18	213	<0,001	0,026	<0,02	4,62

MAY

	Mg	Zn	Mn	Co	Cr	Ni
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-18	10,1	1,24	0,071	<0,05	<0,02	<0,02
WS-18.1	7,41	<0,05	2,41	<0,05	<0,02	<0,02
WS-19	8,47	1,25	0,068	<0,05	<0,02	<0,02
WS-19.1	8,97	<0,05	4,35	<0,05	<0,02	<0,02
WS-20	9,79	1,16	<0,05	<0,05	<0,02	<0,02
WS-20.1	9,04	<0,05	6,23	<0,05	<0,02	<0,02
WS-21	10,6	15,2	0,38	<0,05	<0,02	<0,02
WS-21.1	8,97	<0,05	5,70	<0,05	<0,02	<0,02
WS-22	8,65	1,28	0,05	<0,05	<0,02	<0,02
WS-22.1	9,11	<0,05	4,70	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in June

Chemical analyses

JUNE

	Al	Ca	Cd	Pb	Cu	Fe
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-23.1	0,16	208	<0,001	<0,02	<0,02	3,28
WS-24.1	<0,1	256	<0,001	<0,02	<0,02	1,23
WS-25.1	<0,1	303	<0,001	<0,02	<0,02	0,82
WS-26.1	0,22	296	<0,001	<0,02	<0,02	0,97

JUNE

	Mg	Zn	Mn	Co	Cr	Ni
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-23.1	**9,16**	**<0,05**	**2,82**	**<0,05**	**<0,02**	**<0,02**
WS-24.1	**15,4**	**<0,05**	**1,45**	**<0,05**	**<0,02**	**<0,02**
WS-25.1	**16,7**	**<0,05**	**0,40**	**<0,05**	**<0,02**	**<0,02**
WS-26.1	**23,1**	**<0,05**	**0,57**	**<0,05**	**<0,02**	**<0,02**

SUPPLEMENT 3 – Analyses of metals in surface water in July

JULY

	Al	Ca	Cd	Pb	Cu	Fe
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-27.1	**<0,1**	**353**	**0,0032**	**<0,02**	**<0,02**	**0,55**
WS-28.1	**<0,1**	**276**	**<0,001**	**<0,02**	**<0,02**	**0,25**
WS-29.1	**<0,1**	**225**	**0,0058**	**<0,02**	**<0,02**	**0,24**
WS-30.1	**0,14**	**219**	**0,0010**	**<0,024**	**<0,02**	**0,69**

JULY

	Mg	Zn	Mn	Co	Cr	Ni
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-27.1	26,5	<0,05	0,32	<0,05	<0,02	<0,02
WS-28.1	29	<0,05	0,19	<0,05	<0,02	<0,02
WS-29.1	32,5	<0,05	0,19	<0,05	<0,02	<0,02
WS-30.1	26,6	<0,05	0,22	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in August

AUGUST

	Al	Ca	Cd	Pb	Cu	Fe
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-31.1	<0,1	310	<0,001	<0,02	<0,02	0,16
WS-31.2	1,22	13,3	<0,001	<0,02	<0,02	2,38
WS-32.1	<0,1	343	<0,001	<0,02	<0,02	0,12
WS-32.2	1,58	10,2	<0,001	<0,02	<0,02	3,04
WS-33.1	<0,1	297	<0,001	<0,02	<0,02	0,10
WS-33.2	0,42	310	0,0020	<0,072	<0,02	3,08
WS-34.1	<0,1	347	<0,001	<0,02	<0,02	0,16
WS-34.2	0,11	118	<0,001	<0,02	<0,02	0,40
WS-35.1	<0,1	357	<0,001	<0,02	<0,02	0,13
WS-35.2	0,15	131	<0,001	<0,02	<0,02	0,15

AUGUST

	Mg	Zn	Mn	Co	Cr	Ni
WS-31.1	23,9	<0,05	0,14	<0,05	<0,02	<0,02
WS-31.2	7,16	<0,05	0,091	<0,05	<0,02	<0,02
WS-32.1	22,6	<0,05	0,13	<0,05	<0,02	<0,02
WS-32.2	7,92	<0,05	0,097	<0,05	<0,02	<0,02
WS-33.1	22,5	<0,05	0,075	<0,05	<0,02	<0,02
WS-33.2	27	<0,05	0,78	<0,05	<0,02	<0,02
WS-34.1	21,1	<0,05	0,10	<0,05	<0,02	<0,02
WS-34.2	30	<0,05	0,12	<0,05	<0,02	<0,02
WS-35.1	20,3	<0,05	0,060	<0,05	<0,02	<0,02
WS-35.2	31,8	<0,05	<0,05	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in September

	Al	Ca	Cd	Pb	Cu	Fe
SEPTEMBER						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-36.1	0,12	384	<0,001	<0,02	<0,02	0,13
WS-36.2	0,12	145	<0,001	<0,02	<0,02	<0,1
WS-37.1	0,18	214	0,0022	<0,02	<0,02	0,24
WS-37.2	2,66	57,4	0,0015	<0,02	<0,02	2,38
WS-38.1	0,14	270	0,0084	<0,02	<0,02	0,24
WS-38.2	0,14	151	0,0010	<0,02	<0,02	0,17
WS-39.1	0,14	306	0,003	<0,02	<0,02	0,15
WS-39.2	0,15	125	<0,001	<0,02	<0,02	0,12

	Mg	Zn	Mn	Co	Cr	Ni
SEPTEMBER						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-36.1	18	<0,05	0,077	<0,05	<0,02	<0,02
WS-36.2	36,8	<0,05	<0,05	<0,05	<0,02	<0,02
WS-37.1	22,5	0,11	0,071	<0,05	<0,02	<0,02
WS-37.2	13,3	<0,05	<0,05	<0,05	<0,02	<0,02
WS-38.1	22,8	0,088	<0,05	<0,05	<0,02	<0,02
WS-38.2	33,9	0,088	<0,05	<0,05	<0,02	<0,02
WS-39.1	14,6	0,061	<0,05	<0,05	<0,02	<0,02
WS-39.2	36,3	<0,05	<0,05	<0,05	<0,02	<0,02

SUPPLEMENT 3– Analyses of metals in surface water in October

	Al	Ca	Cd	Pb	Cu	Fe
OCTOBER						
WEEKLY SAMPLE	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-40.1	1,18	200	0,0037	0,032	<0,02	1,16
WS-40.2	0,55	109	<0,001	<0,02	<0,02	0,48
WS-41.1	0,55	214	0,0042	<0,02	<0,02	0,54
WS-41.2	0,16	99	0,0011	<0,02	<0,02	0,14
WS-42.1	0,32	296	0,0064	<0,02	<0,02	0,36
WS-42.2	0,14	131	<0,001	<0,02	<0,02	0,10

WS-43.1	0,13	163	0,004	<0,02	<0,02	0,33
WS-43.2	0,10	105	<0,001	<0,02	<0,02	<0,1
WS-44.1	0,16	173	0,0027	<0,02	<0,02	0,26
WS-44.2	0,14	123	<0,001	<0,02	<0,02	<0,1

OCTOBER

WEEKLY SAMPLE	Mg	Zn	Mn	Co	Cr	Ni
WS-40.1	21,6	0,056	0,31	<0,05	<0,02	<0,02
WS-40.2	30,6	<0,05	<0,05	<0,05	<0,02	<0,02
WS-41.1	14,4	0,057	0,13	<0,05	<0,02	<0,02
WS-41.2	24,2	<0,05	<0,05	<0,05	<0,02	<0,02
WS-42.1	16,4	0,062	0,14	<0,05	<0,02	<0,02
WS-42.2	36	<0,05	<0,05	<0,05	<0,02	<0,02
WS-43.1	15,2	<0,05	0,14	<0,05	<0,02	<0,02
WS-43.1	37,4	<0,05	<0,05	<0,05	<0,02	<0,02
WS-44.1	13,6	<0,05	0,10)	<0,05	<0,02	<0,02
WS-44.2	37	<0,05	<0,05	<0,05	<0,02	<0,02

SUPPLEMENT 3 – Analyses of metals in surface water in November

NOVEMBER

WEEKLY SAMPLE	Al	Ca	Cd	Pb	Cu	Fe
	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-45.1	0,12	200	<0,001	<0,02	<0,02	<0,1
WS-45.2	0,10	117	<0,001	<0,02	<0,02	0,11
WS-46.1	0,92	208	0,0024	0,11	<0,02	1,84
WS-46.2	0,14	103	<0,001	<0,02	<0,02	0,13
WS-47.1	0,35	176	0,0013	0,020	<0,02	0,58
WS-47.2	0,19	94,8	<0,001	<0,02	<0,02	0,15
WS-48.1	<0,1	200	0,0010	<0,02	<0,02	0,42
WS-48.2	0,11	98,4	<0,001	<0,02	<0,02	<0,1

NOVEMBER

WEEKLY SAMPLE	Mg	Zn	Mn	Co	Cr	Ni
WS-45.1	39,2	<0,05	<0,05	<0,05	<0,02	<0,02
WS-45.2	37,4	<0,05	<0,05	<0,05	<0,02	<0,02
WS-46.1	16,5	<0,05	0,18	<0,05	<0,02	<0,02
WS-46.2	39,6	<0,05	<0,05	<0,05	<0,02	<0,02
WS-47.1	20,5	<0,05	0,32	<0,05	<0,02	<0,02
WS-47.2	37,4	<0,05	<0,05	<0,05	<0,02	<0,02
WS-48.1	17,1	<0,05	0,25	<0,05	<0,02	<0,02
WS-48.2	38,5	<0,05	<0,05	<0,05	<0,02	<0,02

SUPPLEMENT 3– Analyses of metals in surface water in December

DECEMBER

WEEKLY SAMPLE	Al	Ca	Cd	Pb	Cu	Fe
	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l
WS-49.1	<0,1	208	<0,001	<0,02	<0,02	0,38
WS-49.2	N/M	N/M	N/M	N/M	N/M	N/M
WS-50.1	0,11	212	<0,001	<0,02	<0,02	0,35
WS-50.2	N/M	N/M	N/M	N/M	N/M	N/M
WS-51.1	0,27	230	<0,001	<0,02	<0,02	0,53
WS-51.2	N/M	N/M	N/M	N/M	N/M	N/M
WS-52.1	0,45	246	0,0012	<0,057	<0,02	2,09
WS-52.2	N/M	N/M	N/M	N/M	N/M	N/M

DECEMBER

WEEKLY SAMPLE	Mg	Zn	Mn	Co	Cr	Ni
WS-49.1	18,3	<0,05	0,30	<0,05	<0,02	<0,02
WS-49.2	N/M	N/M	N/M	N/M	N/M	N/M
WS-50.1	17,5	<0,05	0,30	<0,05	<0,02	<0,02
WS-50.2	N/M	N/M	N/M	N/M	N/M	N/M
WS-51.1	19,4	<0,05	0,53	<0,05	<0,02	<0,02
WS-51.2	N/M	N/M	N/M	N/M	N/M	N/M
WS-52.1	14,2	<0,05	0,52	<0,05	<0,02	<0,02
WS-52.2	N/M	N/M	N/M	N/M	N/M	N/M

SUPPLEMENT 4 – Sample Results

Lead samples WS0 and WS1 (sediment)

SAMPLE	WS0		WS1	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	0	0	4.368	35,33
II – Carbonatic	0	0	4.053	32,78
III – Reducible	8	100	1.649	13,34
IV – Oxidable	0	0	954	7,72
V – Residual	0	0	1.339	10,83
Σ (Fractions I-V)	8	100	12.363	100,00

Lead samples WS2 and WS3 (sediment)

SAMPLE	WS2		WS3	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	1.240	16,50	1.338	15,50
II – Carbonatic	3.209	42,71	3.818	44,24
III – Reducible	1.756	23,37	1.377	15,95
IV – Oxidable	807	10,74	953	11,04
V – Residual	502	6,68	1.145	13,27
Σ (Fractions I-V)	7.514	100,00	8.631	100,00

Lead samples WS4 and WS5 (sediment)

SAMPLE	WS4		WS5	
Analyzed Fraction	μg/g	%	μg/g	%
I – Exchangeable	518	12,77	3.481	40,32
II – Carbonatic	1.514	37,32	2.969	33,54
III – Reducible	1.061	26,15	818	9,24
IV – Oxidable	655	16,15	824	9,31
V – Residual	309	7,62	761	8,59
Σ (Fractions I-V)	4.057	100,00	8.853	100,00

Lead samples WS6 (Soil)

SAMPLE	WS6	
Analyzed Fraction	μg/g	%
I – Exchangeable	21	1,15
II – Carbonatic	620	33,84
III – Reducible	789	43,07
IV – Oxidable	279	15,23
V – Residual	123	6,71
Σ (Fractions I-V)	1.832	100,00

Cadmium samples WS0 and WS1 (sediment)

SAMPLE	WS0		WS1	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	0	0	142	64,84
II – Carbonatic	0	0	54	24,66
III – Reducible	0	0	15	6,85
IV – Oxidable	0	0	7	3,20
V – Residual	0	0	1	0,46
Σ (Fractions I-V)	0	0	219	100,00

Cadmium samples WS2 and WS3 (sediment)

SAMPLE	WS2		WS3	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	41	49,40	23	12,78
II – Carbonatic	30	36,14	96	53,33
III – Reducible	9	10,84	44	24,44
IV – Oxidable	2	2,41	14	7,78
V – Residual	1	1,20	3	1,67
Σ (Fractions I-V)	83	99,99	180	100,00

Cadmium samples WS4 and WS5 (sediment)

SAMPLE	WS4		WS5	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	25	26,88	28	65,12
II – Carbonatic	42	45,16	10	23,26
III – Reducible	21	22,58	2	4,65
IV – Oxidable	4	4,30	2	4,65
V – Residual	1	1,08	1	2,33
Σ (Fractions I-V)	93	100,00	43	100,00

Cadmium samples WS6 (Soil)

SAMPLE	WS6	
Analyzed Fraction	µg/g	%
I – Exchangeable	4	19,05
II – Carbonatic	9	42,86
III – Reducible	5	23,81
IV – Oxidable	2	9,52
V – Residual	1	4,76
Σ (Fractions I-V)	21	100,00

Copper samples WS0 and WS1 (sediment)

SAMPLE	WS0		WS1	
Analyzed Fraction	μg/g	%	μg/g	%
I – Exchangeable	0	0	7	0,63
II – Carbonatic	0	0	58	5,25
III – Reducible	0	0	7	0,63
IV – Oxidable	0	0	670	60,63
V – Residual	31	100	363	32,85
Σ (Fractions I-V)	31	100	1.105	99,99

Copper samples WS2 and WS3 (sediment)

SAMPLE	WS2		WS3	
Analyzed Fraction	μg/g	%	μg/g	%
I – Exchangeable	0	0	0	0
II – Carbonatic	0	0	0	0
III – Reducible	0	0	0	0
IV – Oxidable	47	35,61	121	55,25
V – Residual	85	64,39	98	44,75
Σ (Fractions I-V)	132	100,00	219	100,00

Copper samples WS4 and WS5 (sediment)

SAMPLE	WS4		WS5	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	0	0	0	0
II – Carbonatic	0	0	5	2,72
III – Reducible	0	0	0	0
IV – Oxidable	0	0	83	45,11
V – Residual	68	100	96	52,17
Σ (Fractions I-V)	68	100	184	100,00

Copper samples WS6 (Soil)

SAMPLE	WS6	
Analyzed Fraction	µg/g	%
I – Exchangeable	0	0
II – Carbonatic	0	0
III – Reducible	0	0
IV – Oxidable	2	3,13
V – Residual	62	96,87
Σ (Fractions I-V)	64	100,00

Zinc samples WS0 and WS1 (sediment)

SAMPLE	WS0		WS1	
Analyzed Fraction	μg/g	%	μg/g	%
I – Exchangeable	0	0	3.900	41,47
II – Carbonatic	6	7,32	2.454	26,09
III – Reducible	13	15,85	1.474	15,67
IV – Oxidable	4	4,88	1.167	12,41
V – Residual	59	71,95	410	4,36
Σ (Fractions I-V)	82	100,00		100,00

Zinc samples WS2 and WS3 (sediment)

SAMPLE	WS2		WS3	
Analyzed Fraction	μg/g	%	μg/g	%
I – Exchangeable	201	11,29	154	5,55
II – Carbonatic	450	25,28	941	33,89
III – Reducible	586	32,91	826	29,74
IV – Oxidable	213	11,97	614	22,11
V – Residual	330	18,64	242	8,71
Σ (Fractions I-V)	1.780	99,99	2.777	100,00

Zinc samples WS4 and WS5 (sediment)

SAMPLE	WS4		WS5	
Analyzed Fraction	µg/g	%	µg/g	%
I – Exchangeable	49	3,95	249	17,27
II – Carbonatic	318	25,65	381	26,42
III – Reducible	318	25,65	234	16,23
IV – Oxidable	185	14,92	254	17,61
V – Residual	370	29,84	324	22,47
Σ (Fractions I-V)	1.240	100,01	1.442	100,00

Zinc samples WS6 (Soil)

SAMPLE	WS6	
Analyzed Fraction	µg/g	%
I – Exchangeable	0	0
II – Carbonatic	12	5,08
III – Reducible	56	23,73
IV – Oxidable	25	10,59
V – Residual	143	60,59
Σ (Fractions I-V)	236	99,99

SUPPLEMENT 5 - Autocorrelation and Partial Autocorrelation Function Charts

Figure A5-1. Rainfall volume autocorrelation and partial autocorrelation (mm), n = 52 weeks

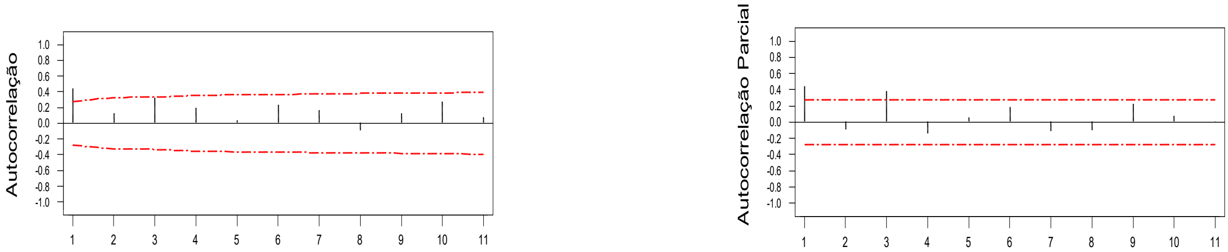

Figure A5-2. Rainfall pH autocorrelation and partial autocorrelation, n = 52 weeks

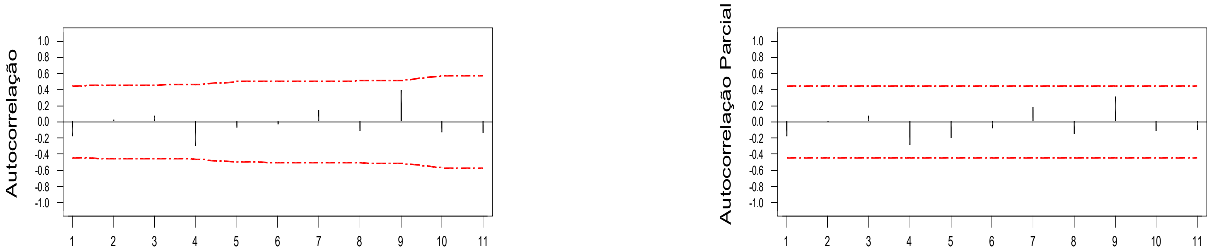

Figure A5-3. Rainfall volume autocorrelation and partial autocorrelation (mm), n = 22 weeks

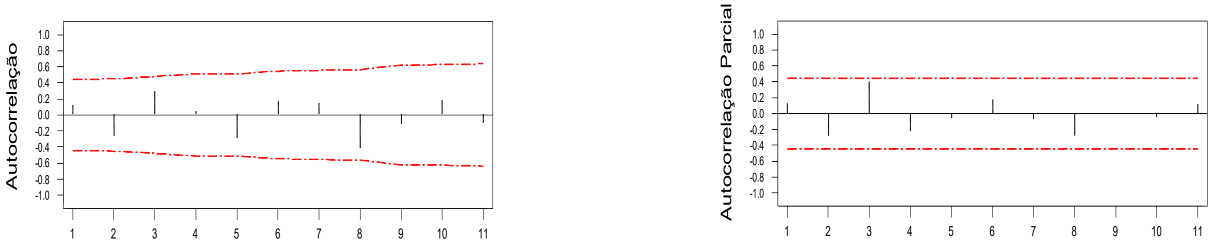

Figure A5-4. Rainfall pH autocorrelation and partial autocorrelation, n = 22 weeks

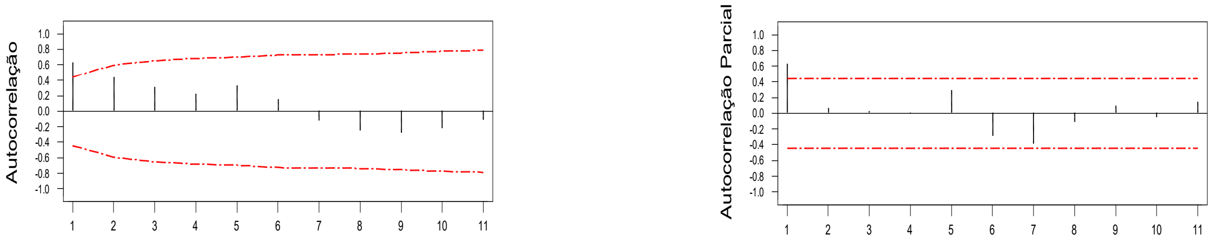

Figure A5-5. Autocorrelation and partial autocorrelation of

Cadmium levels (mg/l) at Point 1

Figure A5-6. Autocorrelation and partial autocorrelation of

Cadmium levels (mg/l) at Point 2

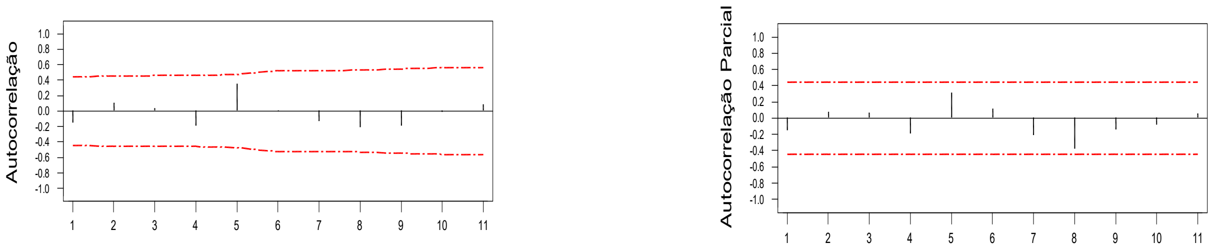

Figure A5-7. Autocorrelation and partial autocorrelation of

lead levels (mg/l) at Point 1

Figure A5-8. Autocorrelation and partial autocorrelation of

lead levels (mg/l) at Point 2

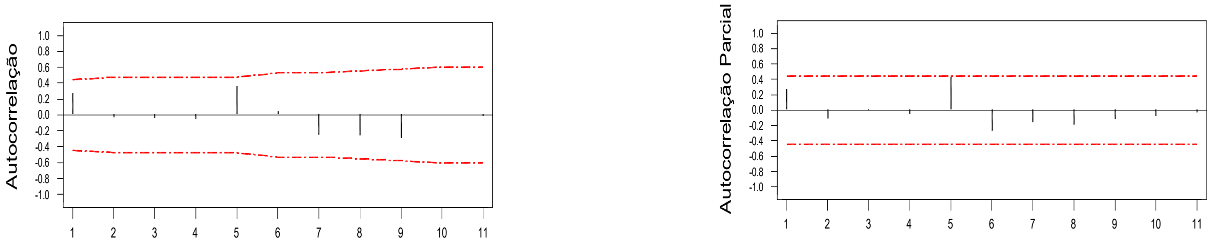

Figure A5-9. Autocorrelation and partial autocorrelation of Copper levels (mg/l) at Point 1

Figure A5-10. Autocorrelation and partial autocorrelation of Copper levels (mg/l) at Point 2

Figure A5-11. Autocorrelation and partial autocorrelation of Zinc levels (mg/l) at Point 1

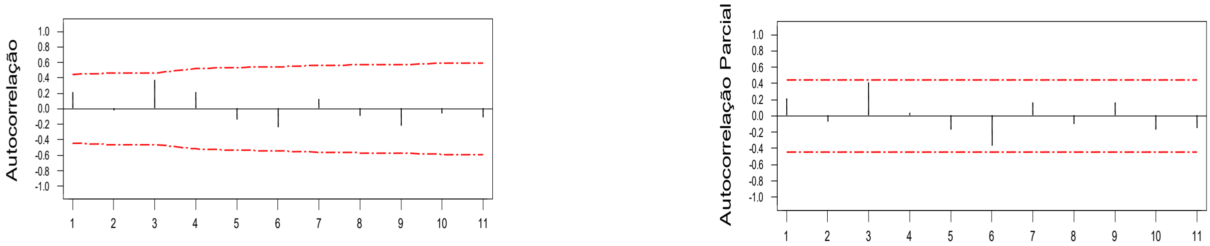

Figure E1A5-12. Autocorrelation and partial autocorrelation of Zinc levels (mg/l) at Point 2

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