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FACULDADE DE CIÊNCIAS E TECNOLOGIA

UNIVERSITY OF ALGARVE

HEAVY METALS IN A LATIN AMERICAN COASTAL LAGOON
- SEDIMENTS, WATER AND MACROPHYTES

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Master Thesis

Master of Science in Ecohydrology

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2015

Declaração de autoria de trabalho

Declaro ser a autora deste trabalho, que é original e inédito. Autores e trabalhos consultados estão devidamente citados no texto e constam da listagem de referências incluída.

“I may have failed to do the best, but I fought so that the best could be done. I'm not what I should be, but thank God, I am not what it was before”.

(Martin Luther King)

Acknowledgments

To the God first, for making this achievement possible and giving me the strength to get here.

To my parents and my uncle for all the love and support in my life, who always understood my absence while being dedicated to my work.

To Felipe for companionship, dedication, priceless help and every moment of joy.

To my supervisor Prof. Dr. Manuela Moreira da Silva for her confidence in my work and devotion.

To my co-supervisor Prof. Dr. Fabian Sá for help in conducting chemical analyses and all dedicated time and patience.

To Dr. Eduardo Schettini Costa for the big support and constant presence.

Thank to my friends Ricardo and Elisa for help in granulometry analyses and preparation of maps.

To the Department of Oceonography and Oceonography Base of Federal University of Espirito Santo, especially Prof.Dr. Gilberto Barosso who made this work happen.

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Abstract

Coastal lagoons are considered to be some of the most productive ecosystems on Earth, providing a wide range of ecosystem services and resources. Jacunem lagoon, ES, Brazil, was studied to evaluate the impact of anthropogenic activities on heavy metal concentrations in sediments, water and macrophytes (*Eichhornia crassipes* and *Typha domingensis*). In order to verify the presence of heavy metals in lagoon and define an ecohydrological strategy for improvement of ecological status, eight sampling points were defined among the ecosystem. Concentrations of Al, V, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in water, sediments, and *Eichhornia crassipes* and *Typha domingensis* were quantified and results were compared with Brazilian legal references and Enrichment Factors and Translocation Factors were calculated. High concentrations of Zn and V were found in sediments. The spatial distribution of the highest concentrations of heavy metals in sediments, in general, was according the proximity to anthropogenic sources of pollution. Concentrations of all studied heavy metals in dissolved fraction of water, were below reference values, however, in suspended matter were found high concentrations of metals, mainly of Ni and Pb. Both *E. crassipes* and *T. domingensis* showed capacity to absorb and accumulate heavy metals from human activities around the Jacunem Lagoon. The distribution of metals among the organs of these macrophytes presented some distinct patterns, according species and depending of metals. Metals were mainly accumulated in roots of both species, however, higher concentrations of Cd, Zn were quantified in leaves and stems. To develop an ecohydrological approach to the sustainable management of this lagoon this study showed that is possible to use the abilities of *E. crassipes* and *T. domingensis* to remove the studied heavy metals from ecosystem. Both species showed high ability to remove V from aquatic environment and accumulate this metal in the roots. In the case of Zn (which can cause environmental damages), both macrophytes phytoremediated this metals and distributed it among roots, stems and leaves. EF of *T. domingensis* were promising for Cu, Zn and Cd revealing ability of this plant to phytoremediate these metals. However, this study should be continued in order to obtain more information about hydrodynamics of the lagoon, the biogeochemistry of the sediments and more water quality parameters.

Key words: Heavy Metals, Coastal Lagoons, Macrophytes, Phytoremediation, Ecohydrology

Resumo

Os sistema lagunares costeiros são considerados como dos mais produtivos do planeta, assegurando um grande número de ecosserviços às populações locais. Neste trabalho estudou-se o impacto que as actividades humanas têm no sistema da Lagoa de Jacunem, Espírito Santo, Brasil, em termos de metais peasados, tendo em conta sedimentos, água e macrófitas (*Eichhornia crassipes* and *Typha domingensis*). O objectivo geral deste estudo foi quantificar os metais pesados nos diversos componentes deste ecossistema aquático e definiri uma estratégia ecohidrológica que permita melhorar o seu estado ecológico. Determinaram-se as concentrações de Al, V, As, Cd, Cu, Fe, Mn, Ni, Pb and Zn em oito pontos de amostragem, incluindo a água (fracção dissolvida e matéria em suspensão), sedimentos e plantas, e nestas foram separadas raízes, caules e folhas. Os resultados foram comparados com os valores de referência da legislação Brasileira. Calcularam-se os Fatores de Enriquecimento (FE), e os Fatores de Translocação (FT) para as duas macrófitas. Constataram-se elevadas concentrações de Zn e de V nos sedimentos. As concentrações mais elevadas de metais pesados foram encontradas nos locais mais próximos das fontes poluidoras. Embora as concentrações dos metais dissolvidos na água tenham sido inferiores aos máximos referidos na legislação Brasileira, a matéria particulada apresentou elevadas concentrações, nomeadamente de Ni e de Pb. Ambas as espécies de macrófitas revelaram capacidade para absorver e acumular metais pesados oriundos das atividades humanas na envolvente da lagoa. A distribuição de metais pelos diversos órgãos das plantas dependeu da espécie e do metal. Embora de um modo geral, os metais se tenham acumulado mais nas raízes, foram quantificadas elevadas concentrações de Cd and Zn nas folhas e nos caules. Assim é possível definir umja estratégia ecohidrológica para fitorremediação de metais nesta lagoa utilizando-se a *Eichhornia crassipes* e a *Typha domingensis.* Ambas revelaram grande capacidade de remoção de V do meio e da sua acumulação nas raízes. No caso do Zn, presente na lagoa em concentrações susceptíveis de causarem danos ambientais, ambas as macrófitas o removem, acumulam nas raízes mas também translocam para os órgão aéreos. O FE da *T. domingensis* revela que esta espécie tem habilidade para fitoremediar Cu, Zn e Cd dos sedimentos. Futuramente para se avançar com uma intervenção ecohidrológica para melhoria do estado ecológico deste ecossistema, será necessária a recolha de mais informação, nomeadamente sobre: a hidrodinâmica dentro da lagoa, a biogeoquímica dos sedimentos para se perceber a biodisponibilidade dos metais que lá se encontram e a monitorização de mais parâmetros da qualidade da água.

Palavras Chave: Metais Pesados, Lagoas Costeiras, Macrófitas, Fitorremediação, Ecohidrologia.

Contents

1. INTRODUCTION

1.1. Scope of the Work

In recent centuries, the growing urbanization and agricultural practices have increased the input of heavy metals in shallow coastal lakes worldwide, causing changes in the biological structure and dynamics of these environments (Jeppesen *et al.*, 2005). Elevated concentrations of heavy metals have been recorded in coastal lake sediments and biota all over the world, which often reflects the long-term pollution caused by human activities (Lacerda *et al.*, 1992; Perdomo *et al.*, 1998; Harris and Santos, 2000; Tam and Wong, 2000). In fact, one of the most serious environmental issues concerning trace elements, which distinguish them from other toxic pollutants, is that they are resistant to biodegradation and have potential to bio-accumulate and become biomagnified, increasing the exposure of aquatic communities and human populations through the trophic chain (Gao and Chen, 2012; Subida *et al*., 2013).

Coastal and estuarine areas are among the most important places for human inhabitants (McKinley *et al.,* 2011). Consequently, with rapid urbanization and industrialization, heavy metals are continuously carried to the estuarine and coastal lake sediments from upstream of tributaries (Morton *et al*., 2001). Heavy metal contamination in sediment could affect the water quality and bioaccumulation of metals in aquatic organisms could result in potential long-term implication for human health and ecosystems. Since heavy metals cannot be degraded biologically, they get easily transferred and concentrated into plant tissues from soils, posing the long-term damaging effects on plants.

Over the last few decades the studies of the aquatic sediments and plant tissue have shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on study environments (Harikumar and Nasir, 2010). Sediments as a matrix constitutes one of the most important source of water contamination by trace elements, as well as, an important carrier of these hazardous substances within the rivers, reservoirs and other waters (Sekabira *et al*., 2010; Yaun *et al*., 2014). Sediment analyses provide the basic information for identifying the possible sources of contamination and delineation of the areas where its concentration exceeds the threshold values and the strategies of site remediation, including the phytoremediation using the very native plants (Sollitto *et al.,* 2010). Therefore, understanding the mechanisms of accumulation, chemical deposition and spatial distribution of heavy metals in sediments, water and biota is crucial for the sustainable management of coastal lakes.

On the other hand, a detailed knowledge of coastal lagoons was overlooked by the scientific community until the last twenty years when an increasing interest towards these ecosystems was highlighted. Despite the great number of coastal lagoons worldwide, not all world's area have been well documented by a recent literature. Lagoon ecosystem science is in general relatively young and still today coastal lagoons in the tropical world have been poorly studied so far (Esteves *et al.*, 2008). Nevertheless "Coastal Lagoons: Critical Habitats of Environmental Change ", by Kennish *et al*. (2010), thoroughly examines the function and structure of coastal lagoonal ecosystems and the natural and anthropogenic drivers of change that affect them. Consequently, in the last years an increasing number of studies have been carried out in coastal lagoons with the purpose to understand the role of halophyte vegetation on retention, bioavailability and remediation of the pollutants that reach colonized coastal areas.

Similarly, The State of Espirito Santo (ES, Brazil), has a substantial number of lagoons distributed along the shoreline, but only a few have been studied limnologically and consequently there is a low information on a trace metals presence and distribution within these lakes. The explanation for this is mainly related to local, political, economic and social troubles and lack of resources to perform ecological studies. Studies include those of Huszar *et al.* (1990), Bozelli *et al*. (1992), Dias Jr. *et al.* (1998) and few others. For instance, Duarte *et al*. (2012) discovered concentrations of Al and Cd in the water samples of the lake Jacunem to be above the maximum concentrations allowed (according to CONAMA 357/2005 – established standards for classification of Brazilian water bodies). Similarly, some studies from Sanchez-Galan *et al.* (1999) and Ayllon & Garcia-Vazquez (2000) reported the high cadmium presence in tilapia (*Tilapia rendalli*) tissue and DNA present in Jacunem. Taking into consideration that the Jacunem lagoon has undergone a very few studies on a quantification of trace metals, the purpose of this work was to quantify the presence of heavy metal contaminants in aquatic sediments, water and two macrophyte species of the Jacunem coastal lake, determining the spatial distribution of these metals in three mentioned matrices together with the establishment of the possible relationship between the pollutant distribution among them.

Hypothesis being tested in this work were:

1. The environment (sediments, water and mycrophytes) is enriched with heavy metals from anthropogenic sources, potentially threatening the lake's Jacunem equilibrium.

2. Both species, Typha domingensis and Eichhornia crassipes, have capacity to remediate the heavy metals in studied environment.

3. We can improve the ecological status of the lagoon using an phytotechnological approach.

1.2. State-of-Art

1.2.1. Coastal Lagoons

Phleger (1969,1981), Kjerfve (1986, 1994), Gonenc and Wolflin (2004) defined the coastal lagoons as a shallow inland marine waters, usually oriented parallel to the coast, separated from the ocean by a barrier, and connected to the ocean by one or more restricted inlets. Coastal lagoon ecosystems are a particular type of estuarine systems where sea water mixes with fresh water from their continental catchments. These ecosystems occupy 13% of coastal areas worldwide (Figure 1.1), and are often impacted by both natural and anthropogenic influences (Mee, 1978; Sikora and Kjerfve, 1985). Depending on local climatic conditions, rainfall exposure to wave action and tides, lagoons exhibit salinities which range from completely fresh to hypersaline (Moore and Slinn, 1984; Kjerfve, 1986; Knoppers *et al*., 1991; Starczak *et al*. 2011). In tropical humid areas precipitation exceeds evaporation. During the rainy season the water level rises and creates natural openings that discharge high suspended sediment loads. During the dry season, however, seawater invades lagoons and salinity can vary from 0-30 PSU.

Coastal lagoons such is Jacunem in Serra, ES are specific ecosystems which are common in some parts of the Brazilian coast and can be considered as the Brazilian coastal lagoons most representative of the country. They are ecosystems whose size range from small depressions filled with rainwater, river water, groundwater and marine water to the large coastal systems as the Patos Lagoon (Esteves, 1988). According Bozelli *et al.* (1992), ecological studies of these ecosystems are of a great importance since many of them are highly environmentally altered.

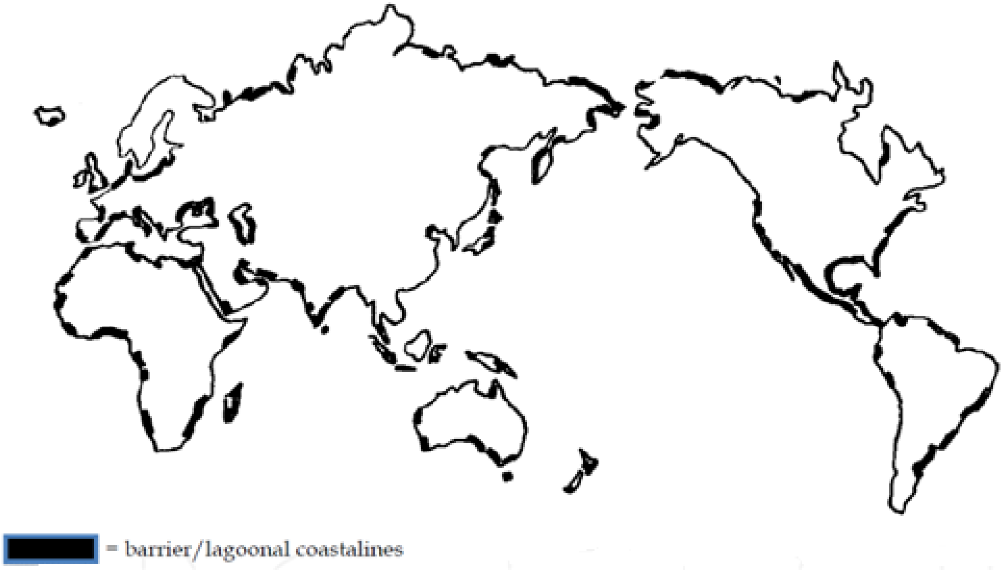

Figure 1.1. World distribution of lagoon coastlines (Reproduced from Barnes (1980), Coastal Lagoons)

Adding the potential sea level rise, storm frequency and river flood changes which could occur in the future, coastal lagoons are among the most threatened aquatic ecosystems under global change pressure (Troussellier, 2007).

1.2.1.1. Ecology and Ecosystem Services of Coastal Lagoons

Coastal lagoons are highly productive ecosystems. They contribute to the overall productivity of coastal waters by supporting a variety of habitats, including salt marshes, sea grasses and mangroves. These specific habitats support a range of natural services that are highly valued by society (Gönenç and Wolflin, 2005), including fisheries, storm protection, tourism and others. Kjerfve (1986) explains that coastal lagoons are valuable as traps of inorganic sediments and organic matter and like such represent an important material sink. Although there is considerable literature on the physical and ecological dimensions of lagoons, there is much less literature focused on their economic and social values.

Coastal lagoons have exceptional ecological, recreational, and commercial values. They provide diverse habitats (e.g. open waters, submerged aquatic vegetation, unvegetated bottom sediments, tidal flats and creeks, and fringing wetlands) that serve as nurseries, feeding, and refuge areas for numerous estuarine, marine, and terrestrial organisms. Many marine species of recreational and commercial importance spend at least a portion of their life cycles in lagoonal and adjoining coastal wetland habitats. Aside from the value of their fisheries, coastal lagoons are used by humans for aquaculture, electric power generation, biotechnology, transportation and shipping. Coastal lagoons also protect coastal watershed areas, buffering the infrastructure from the damaging effects of storms, floods, and erosion.

According to the diagnosis of Aquaculture Chains of the Espirito Santo state, given by SEBRAE (2006) in 2004, of the 78 municipalities in the state, at least 56 commercially develop aquaculture in the Jacaraipe basin. The opening of new enterprises, motivated by good acceptance of aquatic products in state and highly developed national market, has brought for ES an income of around £ 20 million a year. According to Andrade (2000), the aquaculture potential of the ES allows a sustainable expansion to a level of 20,000 tonnes and may in the future generate a revenue of R$ 80 million per year, considering products commercialized and processed frozen. The Juara lagoon (major lagoon of Jacaraipe basin) has been used since 2001 for the intensive tilapia growth, and today has a total of 150 fish cages producing yearly 95 tons of tilapia, providing employment and income for 30 families in a community of fishermen in Jacaraipe (De Oliveira, 2010.) Jacunem lagoon on the other hand, has no such an extensive aquaculture development, but still has significant number of local fisherman taking adventage of the food source despite the potential risk of contamination.

1.2.1.2. Management and Conservation of Coastal Lagoons

Historically, coastal regions have been areas prone to human habitation. They provide excellent opportunities for agriculture and tourism sectors on the one hand and for fishery and aquatic products sectors on the other hand. Exponential increase in human population and the corresponding demand for food and energy resources as well as for space and transport, have in the last century stimulated the promotion of economic growth of these areas. Most of natural lagoons located close to the urbanized settlements have been seen until recently as “wastelands” and are being extensively replaced by intensive crop farms, tree plantations, commercial fish culture, harbors, and industrial complexes (Vadineanu, 2005).

In the case of costal lagoons, limnology in the tropics has only recently past the stage of exploration (Melack 1996; Talling & Lemoalle 1998), but the need for application of limnological knowledge is as pressing at tropical latitudes as it is in the temperate zones. However, the extent to which the limnology of temperate latitudes can be applied in the tropics is not always clear. General limnological principles are often transferable across latitude. For example, the growth of algae in a lake at any latitude is likely to be limited by the availability of one or more key nutrients; an increase in the supply of these nutrients by humans is likely to change many of the characteristics of the lake. On the other hand, some limnological principles are not so easily applicable across latitude. For example, it is familiar that temperate lakes have a growing season that coincides with the warm months, but taking into consideration the tropical lake the question which arises is whether these lakes have a growing season at all.

There are approximately 10 million lakes on the earth (Wetzel 1992), very few of which are large. Protection and management of the world's largest lakes present a difficult and exceedingly important problem to which limnologists working at tropical latitudes must make a contribution. However, many regions and even entire nations are remote from any of the largest lakes. In such cases, lakes of small to moderate size are of paramount importance. Therefore, many practical questions in applied limnology relate to the abundance, distribution, and typology of lakes that are of small to moderate size. These lakes do not make a significant contribution to the global surface area but are of critical importance to human populations throughout the tropics. On the other hand it is considerable to notice that human perception of social and economic values deriving from lagoon protection strategies is a function which varies depending on geographic and economic situation of the country taking into consideration different market values of commercial products and local population's needs (Costanza *et al.,* 1997.)

During monitoring studies, a critical and preliminary consideration on factors affecting these ecosystems could allow researchers and politicians to evaluate the relative weight of single variables and perform well-sized sampling campaigns, monitoring and management programs.

1.2.2. Heavy Metals

Heavy metal term is used by different authors in different ways. Macedo (2002) cites some definitions similarly like Garcia *et al*. (1990) relating the term "heavy metal" with a substance of a minimum density of 4.5 g / cm^3; Coker & Matthews (1983) stipulate a density of 5 and Ferguson (1993) of 6.5 g / cm^3. According to Malavolta (1994), heavy metals are defined as elements that have specific weight greater than 5 g / cm3 or having an atomic number greater than 20. This term encompasses metals, semi-metals and even non-metals. Alloway (1994) also includes arsenic to the term. An alternative term for this group of elements is trace metals, but is not widely used. This relationship is due to the occurrence of these elements in the environment in very low levels from parts per million or even less (Manahan, 1993).

Some of these trace elements are among the most harmful pollutant elements in nature. They are known as toxic metals and the best known from this group are lead, cadmium and mercury. The most important toxicity mechanism is certainly the inactivation of enzymes. All divalent transition metal reacts readily with the amino group and the sulfhydryl group of proteins. Some of them can compete with essential elements and replace them in enzymatic metabolism, such as zinc. Some metals can also damage cells, by acting as an anti-metabolic or forming precipitates or chelates with essential metabolic agents (Forstner, 1989). Trace elements may also precipitate phosphates or catalyze its decomposition (Manahan, 1993). Some authors, like Alloway & Ayres (1994) refer to these elements as non-essential, as it is not known yet some of their essential biochemical functions. They include, in addition to the aforementioned, the elements such are arsenic, antimony, uranium, plutonium and thallium. The toxicity occurs when the concentrations of these elements exceed the tolerance limit of the bodies, but at low concentrations they will not cause any functional disorders. On the other hand, other elements of the same group are considered as essential (in small concentrations) for many living organisms and are necessary for a healthy growth and development, nevertheless, these too in excessive concentrations can cause toxicity (Alloway; Ayres, 1994). Grossi (1993) cited in Venezuela (2001) classifies the trace elements in relation to toxicity into three groups: the first group are those considered slightly toxic, which are mostly taken as micronutrients, but in high concentrations, are toxic. They are aluminum, cobalt, copper, manganese, molybdenum, selenium, vanadium, zinc and tin. The second group consists of trace elements that have a risk of cancer occurrence: arsenic, beryllium, chromium and nickel and the third group are the metals that have a significant toxic character and are not included in the foregoing groups: lead, cadmium, mercury and thallium.

1.2.2.1. Sources of Heavy Metals in Coastal Lagoons

In coastal lagoons, the natural processes such as weathering of rocks, leaching of soils, eruptions of volcanoes and emissions of hydrothermal vents are the source of a significant amount of trace metals. On the other hand, anthropogenic inputs augment to a great extent the natural loads and, finally, in some industrialized and urbanized coastal systems, can exceed natural concentrations. Such diverse sources could be municipal and industrial wastewater discharges, leaching of ship paints, deposition of dredged material, combustion of fossil fuels, mining, manufacture of dyes, paints and textiles (Reboreda & Caçador, 2007). Water feeding sources of coastal lagoons such are rivers and canals which at the same time represent the connection to a coast line through the tidal fluctuations also can provide large quantities of these pollutants to coastal lagoons.

Like any other anthropological source of heavy metals in the environment, their dispersion through the sewage output into the water bodies, is of a considerable concern. The heavy metals present in raw sewage arise from a number of sources. Many industrial effluents contain considerable concentrations of metals and together with domestic sewage, they comprise an important contributor of heavy metal polluters. In addition, when storm water enters the waste water treatment plant, this contributes a number of metals, most commonly Cd, Cu, Pb, Ni, Cr, and Zn (K.R. Reddy *et al*., 2014.) Methods of heavy metals removal from industrial effluents exist, but they are economically viable and therefore a little used even today, therefore these wastewaters are frequently discharged to surface waters either directly or trough sewage treatment plants.

The main heavy metals of concern in sewage are Cd, Zn, Cu, Pb, Se, Mo, Hg, Cr, As and Ni and their concentration depend mainly on a type and amount of discharges into the sewage treatment system. Metals highly soluble in the sewage matrix, either as free ions or as a complex, are expected to pass through the treatment plant and be discharged as a final effluent at the concentrations similar to the once present in raw sewage. This could lead to a substantial metallic pollution of the receiving waters (Bradl H., 2005).

1.2.2.2. Bioavailability of Heavy Metals in Sediments

In the water cycle, about 0.1% of the pollutants are dissolved in the water, while the remaining 99.9% is stored in sediments and soils. However, the dissolved fraction is more mobile and more bioavailable. The bioavailability of sediment-bound trace metals is dependant not only on the total metal concentration, but also on the strength of the connection between the metal and sediment compounds. Besides the determination of concentrations of trace elements in water is necessary to evaluate the concentrations of these metals in the sediment matrix, correlate their concentrations and especially know the way these elements occur in the environment, which represents its' chemical speciation. The chemical speciation describes the different forms (species) in which there is an element of a system. The species of trace elements in aquatic systems or forms of associations with sediments are: adsorption on the particle surface (such as clays, humic acids and metal oxy-hydroxides); connection to carbonates; occlusion in iron oxy-hydroxides and / or manganese; linkage with the organic matter; connection to sulfides and linkage with matrix commonly made of aluminum silicates (Salomons; Forstner 1980. cited Birth, 2003).

Jenne & Luoma (1997) showed that metals bound to different substrates of a given sediment are incorporated at different rates by benthic organisms. Metals bound to biogenic carbonates and organic matter are much more available than metals strongly bound to other sediment compounds such are iron oxides (Jenne & Luoma, 1997) and sulfides (Lacerda *et al.*, 1988.) The proportion of exchangeable metals in a given sediment is dependent on numerous environmental variables other than the sediment composition itself. Among them the physical and chemical characteristics of pore and overlying waters are important.

Sediments are part of the geochemical cycle in which particular material is transported from the continents to the rivers, lakes and oceans. The end attachment sites of the trace elements in the nature are the soils and sediments. The fixing ability of trace elements in the sediment depends, among other factors, on the mineralogical nature, particle size, physical and chemical characteristics of sediments (Boaventura, 1989). Several interactions determine the concentration of dissolved elements in the fraction, such as pH, temperature, oxidation state, salinity, etc. Despite the fact that most trace metals are vital for the metabolism of organisms at low concentrations, at higher once they may be toxic. There is a significant difference between the soil pollution by metals from air or from water, because the persistence of trace metals in soil is much higher than in other compartments of the biosphere (Padmavathiamma & Li, 2007). Moreover, metals tend to be retained more strongly in watered soils compared with upland soils

(Gambrell, 1994). These metals tend easily to be sorbed to particulate matter and accumulated in fine-grained sediments of coastal environments, and since they are not biodegradable, they persist for long periods of time in benthic habitats. Therefore, sediments represent a major storage for trace metals and a source for their later remobilisation within the water column. As Kennish (2001) emphasizes, the concentrations of trace metals are three to five orders of magnitude greater in the bottom sediments of coastal lagoons than in the overlying waters. According to the National Environmental Council (CONAMA), referring to the Conditions and Water Quality Standards (Resolution No. 357, 2011 Cap. III, Section 1, Art. 9, paragraph 2) "In cases where the available analytical methodology is insufficient to quantify the concentrations of trace elements in water, sediment and/or aquatic biota will be investigated for the possible presence of these substances."

The total content of heavy metals in sediment does not reflect the amount of elements that can be transferred to the roots, since only a fraction is available to plants (Figure 1.2).

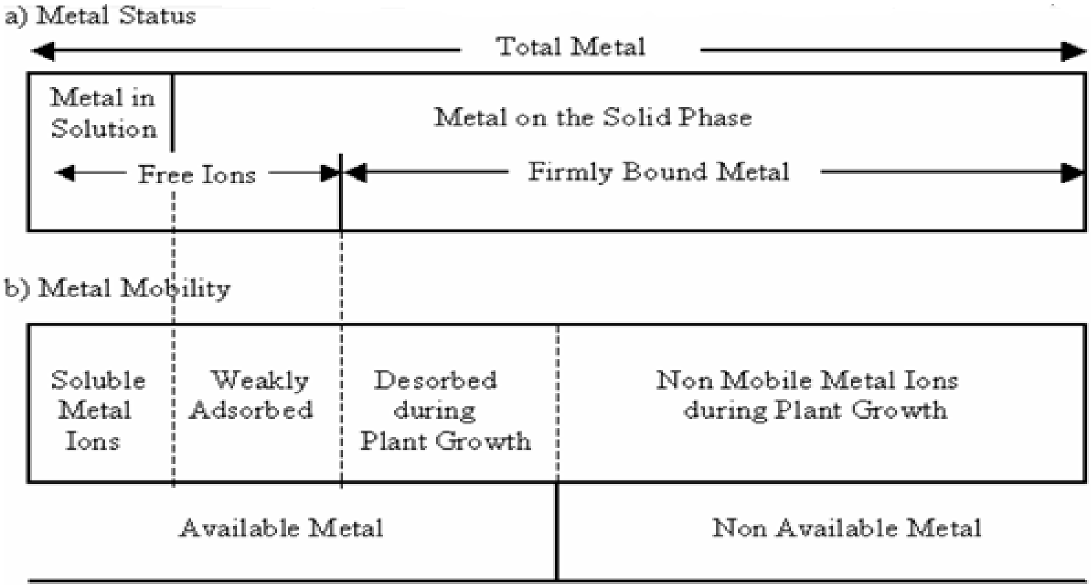

Figure 1.2. Model for available trace elements in sediments (Found in Moreira da Silva, 2008)

On the other hand, the quantity of trace elements in the sediment solution is much lower than the quantity eventually taken up by a seasonal growing. Therefore, a large proportion of the bioavailable fraction is located in the solid phase, either as a component of sediment minerals or as part of the sediment organic matter (Fitter and Hay, 1993). According to their mobility, trace elements in sediments can be schematically fractioned in four compartments or pools (Figure 5). The first two compartments are immediately available ions, i.e., ions in solution, and ions weakly adsorbed to the solid phase. The third pool represents the ions bound to the solid phase, but able to pass into solution, and become available during plant growth. In fourth pool are trace elements unavailable during the growth period, being firmly bound to sediment particles or integrated in minerals and/or organic compounds. Bioavailable trace elements in sediment are present in the first three compartments and their level depends closely on sediment properties and plant ability to absorb elements and modify the substratum environment (Morel, 1997).

Macrophytes contribute significantly to the primary production of water bodies in the littoral zone, forming a fundamental part of the trophic structure of aquatic ecosystems. During the recirculation of nutrients, aquatic plants can uptake large amounts of metals from the environment (Jackson, 1998). Their absorption capacity of metals through roots and leaves (Cardwell *et al.*, 2002.) combined with their sedentary nature, makes these plants suitable for detecting changes or alterations in the aquatic environment (Sawidis *et al.,* 1995). High concentrations of metals in aquatic plants can be accumulated from the water column and/or from sediments demonstrating the usefulness of macrophytes as biomonitors for aquatic systems. Moreover, measuring the accumulation of persistent pollutants in aquatic plants can provide time-integrated information about the presence of toxic compounds in the aquatic ecosystems and plants ability of participating in self-purification of the water bodies. The bioavailability, toxicity and mobility of trace element ions are directly linked to speciation. It is essential to understand that the degree of toxicity of a chemical element in relation to living beings is also a function of speciation of these elements. Uptake and accumulation of trace elements by plants are affected by several sediment factors, including pH, temperature, redox potential, clay content, organic matter content, nutrient balance and, concentration of other trace elements in sediments. The pH is one of the most important factors controlling plant uptake of trace elements. In general, availability of essential as well as nonessential elements is low at high pH values, as precipitation and adsorption on the soil solid phase increases. Conversely, a decrease in soil pH improves, in general, solubility of toxic elements and their transfer to root surfaces and subsequent absorption. However, an increase in sediment pH may not necessarily result in a decrease in metal availability, for example, molybdenum is more soluble when the pH increases and cadmium uptake or even toxicity has been observed at high-pH soils than in low-pH soils

(Morel, 1997). As redox potential decreases, trace elements become less available. Although estuarine sediments are generally considered as a sink for metals (Caçador *et al.,* 1996; Doyle and Otte, 1997; Almeida *et al*., 2004; Reboreda and Caçador, 2007a; Reboreda and Caçador, 2007b; Reboreda and Caçador, 2008) their mobility and biovailability is a function of their speciation that is determined by various physico-chemical and biological parameters (Weis *et al*., 2002; Almeida *et al*., 2004; Caetano *et al.,* 2007; Reboreda and Caçador, 2007a; Reboreda and Caçador, 2007b; Suntornvongsagul *et al*., 2007). Under waterlogged conditions, such as in shallow coastal lakes, iron and manganese are particularly soluble and precipitates may appear on the root surface through the oxidation of metals supplied by the mass flow. Large amount of metals (e.g. Zn and Cu) can be adsorbed to those iron oxides, leading to an increase in the metal uptake by roots. De Souza *et al*. (1999) studied the phytoaccumulation of heavy metals Cd(II), Cr(VI), Cu (II), Ni (II), Se (VI) with the specie (*E. crassipes*) under hydroponic conditions and concentrations ranging from 0.1 to 10 mg/L in a period of 14 days. For a concentration level of 0.10 mg/L the bioaccumulation capabilities were: 1.85 mg Cd/kg dry mass.; 1.15 mg Cu/kg dry mass.; 0.53 mg Cr/kg dry mass.; 0.58 mg Se/kg dry mass and 1.04 mg Ni/kg dry mass. Absorption of trace elements by roots is controlled by the concentration of other elements, and interactions have often been observed. Macronutrients interfere antagonistically with uptake of trace elements (Morel, 1997). Phosphate ions reduce the uptake and translocation of cadmium and zinc in plants. Calcium controls the absorption of metals, e.g., cadmium, as a result of competition for available absorption sites on the root surface.

Antagonism between micronutrients is quite frequent. An excess of metals such as zinc, nickel and copper, which depress iron uptake by plant roots, can induce leaf chlorosis, a symptom due to iron deficiency. Conversely, iron affects cadmium absorption, acting as a strong antagonist to the toxic metal. Cadmium and zinc, two metals chemically close i.e., with similarity in electronic configuration and reactivity with organic ligands, interact in the soil – plant system, causing Cd/Zn antagonism (Costa and Morel, 1993). Various synergistic interactions have been reported for metals with several species, where the addition of cadmium, copper, manganese, or zinc to a nickel-supplemented solution culture was shown to produce higher nickel-related inhibition of root growth. These interactions make it difficult to draw absolute toxicity limits for trace elements without considering the biovailability of other major or trace elements, which is a complex task since, most often, multiple interactions occur in soils (Morel, 1997).

Plant Uptake of Trace Metals (Rhizosphere, Root, Transport to Aboveground Organs and Partitioning Within the Plant)

The activity of free ions in solution at the root surface reflects trough the availability of trace elements to plants. Elements in solution are transferred from the soil pores to the root surface by two main processes - ***diffusion and mass flow.*** Diffusion occurs against the gradient normal to the root axis created by uptake of elements and subsequent depletion of the soil solution concentration at the soil-root interface. Mass flow is due to the movement of the soil solution to the root surface as a result of leaf transpiration. Both processes take place simultaneously but at different rates according to the soil solution concentration. Except in highly polluted soils where the soil solution may contain high concentrations of toxic elements, diffusion accounts for most of the transfer (Morel, 1997). Plant roots exert a strong influence on their close environment, i.e., the rhizosphere, as they release organic as well as inorganic compounds into the surrounding soil. In this context, it is important to use a broad definition of the rhizosphere to include the volume of soil adjacent to and influenced by the root, the root surface, and the root itself, which includes the cells of the root cortex where invasion and colonization by endophytic microorganisms has occurred. Metals are exposed to the rhizosphere conditions before reaching to the root surface. Their flow towards the root surface by diffusion or mass flow is subjected to mobilization-immobilization processes in the soil-root interface (Jeffries *et al*., 2003). Exudates exhibit weak acidic properties and may bind metals, thus modifying mobility of metals in soil. In rhizosphere root exudates serve as a source of carbon and energy to bacteria and fungi that occur in much higher numbers than in the bulk sediment (Morel, 1997). These microorganisms may positively interact with plants by producing growth-promoting substances and modify the status of elements around the root, thus increasing or decreasing their solubility and subsequent uptake by root cells. Microbial activity may alter metal solubility around the roots. Biodegradation of organic matter releases metal ions in the soil solution as well as soluble organic compounds that may maintain metals in solution.

Metal ions have the tendency to accumulate in the root free space, some being firmly bound to the cell walls. Studies with *Halimione portulacoides* showed that zinc, lead, cobalt, cadmium, nickel and copper were mostly retained in the cell wall compounds, in roots, stems and leaves (Sousa *et al*., 2008). This binding contributes largely to the total content of metal in roots, and increases the subsequent uptake of metals by root cells. In general, dicotyledons, which exhibit a higher root cation exchange capacity than monocotyledons, hold higher amounts of metals in free space and show higher uptake than monocotyledons (Carneiro *et al.*, 2001). Metals can be transported radially in the root free space via the apoplasmic route (Figure 3) limited by the Casparian band of the endodermis, which constitutes a barrier for the entry of toxic metals (e.g., cadmium) in the stele, thus cortex cells contain more metal than cells of the stele (Morel, 1997). The ultimate barrier between soil solution and cell is a tiny membrane, the plasma membrane where elements are transported from the external solution into the cytoplasm, through the symplasmic route (Figure 1.3). Radial transport in symplasm plays the key role and requires bridges, the plasmodesmata, across the cell walls that connect the cytoplasm of neighboring cells (Marschner, 1995).

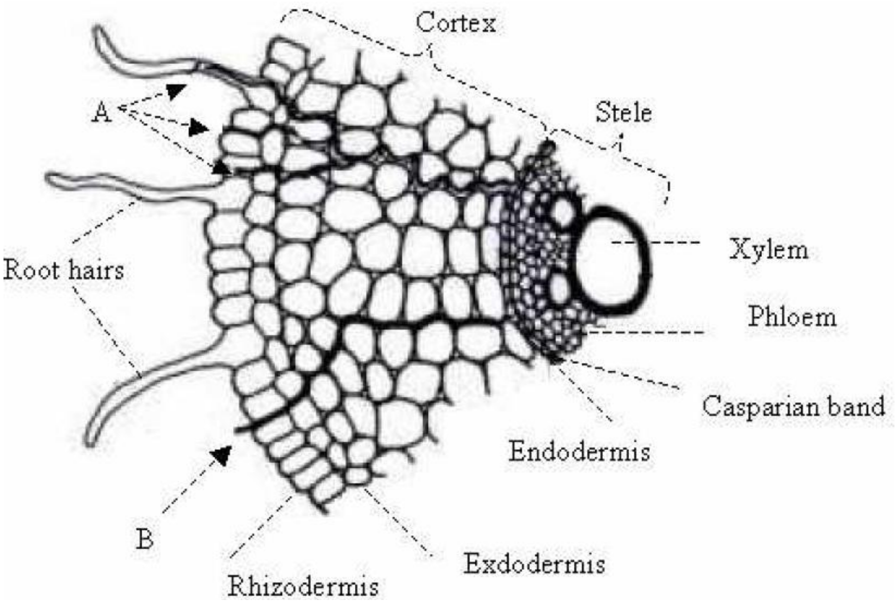

Figure 1.3 A root section showing the symplasmic (A) and the apoplasmic (B) pathways of ions transport across the root (adapted from Marschner, 1995; found in Moreira da Silva, 2008).

Once metals' ions have entered the roots, they can either be stored or exported to the shoot, this transport primarily takes place through the xylem although metals can also be translocated via the apoplast and in phloem (Fritioff and Greger, 2006). Metals in the cytoplasm may be transported radially from cell to cell through the symplasmic pathway, transferred to the stele, loaded into the non-living xylem vessels, and transported to the shoots. In the xylem the flux is driven by the water potential gradient created through the plant during transpiration (Collins *et al.*, 2006). Free cations may interact with the negatively charged groups of the cell walls of the xylem, which restricts their transport along the vessels to a slow exchange process. However, in the fluid sap, complexation of free metal ions with organic acids, such as citrate, malate or malonate, and with amino acids prevents their immobilization in the xylem and allows their transfer to the shoots. Theoretical studies have predicted that the majority of Fe(II), Zn(II) and Ni(II) should be chelated by citrate, whereas Cu(II) should be chelated by various amino acids including histidine and asparagine (Salt *et al*., 1998).

Metal translocation and storage capacity is rather heterogeneous and controlled by genetic, environmental and toxicological factors (Sheppard *et al*., 1992 in Morel, 1997; Stoltz and Greger, 2002). Previous studies showed that roots are the main pool of metals within shallow coastal lakes plants (Caçador *et al*., 2000; Wang *et al*., 2002; Weis *et al.*, 2002; Fritioff and Greger, 2006; Caetano *et al*., 2007; Duman *et al*., 2007; Reboreda *et al*., 2007a; Caetano *et al*., 2008; Sousa *et al*., 2008; Zhang *et al*., 2008, H. B. Soni and S. Thomas, 2015). Immobilization of metals in roots i.e., binding to cell wall and cell membrane, complexation and precipitation in cytoplasm and vacuole, contributes to a large percentage of plant metal recovery in roots, 80 to 98 % of the total absorbed metal (Morel, 1997). Most of the metals in plant roots are located in the free space, and are associated with the pectin and protein compounds of the cell wall (Conrad, 2008). However, some species may accumulate the major part of the absorbed metal in their upper parts, e.g., tobacco with more than 80 % of Cd in the leaves. In aboveground parts, metals are present preferentially in vegetative organs and scarcely transferred to the storage or reproductive organs, although metals that have low phloem mobility, such as iron, zinc, manganese and cadmium, may be stored in the seeds as the plant matures. Several mechanisms, not well studied yet, seem to control the distribution of metal in the plant, and this suggests the existence of successive physiological boundaries and/or changes in the chemical status of metal (Morel, 1997). Metal-tolerant plants absorb metals through their roots and translocate them in aerial parts, stems and leaves. So called hyper-accumulating plants can thus contain up to several thousands of mg/kg of a given metal in their shoots and leaves. Those plants develop efficient root absorption mechanisms that allow them to specifically accumulate metals from soils, even in cases where metals biovailability is too low to affect other non-accumulating plant species (Montargès-Pelletier *et al.*, 2008). There is a requirement for a balance between the uptake of essential metal ions and the ability of plants to protect sensitive cellular structures and activities from excessive levels of metals. To promote the homeostasis of metal ions in the cytoplasm, which is essential to avoid the inhibition of a number of cytoplasmic enzymes, tolerant species developed several internal mechanisms.

Beside root absorption, plants may also accumulate metals from the atmosphere by their aboveground parts after wet or dry deposition of polluted material, i.e., soil, ash, and metal particles. Foliar uptake of trace elements occurs in a similar manner for nutrients and toxic elements. Metals enter the leaf through the cuticle, a hydrophobic surface layer protecting the leaf from excessive water loss from transpiration, where cavities, i.e., ectodesmata, allow direct penetration of solutes into leaf tissue. Foliar absorption of metals is much more efficient than root absorption since the soil does not interact as an adsorbing competitor (Morel, 1997).

1.2.2.3. Harmful Effects of Heavy Metals on Ecosystems

Approximately 60% of the world's population is concentrated in settlements within the coastal zones, i.e. areas that extend 50 km inland from the coastline (Crossland *et al*., 2005). However, coastal areas have been neglected, poorly understood and exploited and are under increasing pressure from rapid human population growth and over-exploitation of resources. Humans are affecting these systems with great pressure (Aliaume *et al*., 2007). As a result of recent human activities many lagoons along the Brazilian coast are evidently negatively affected. In the area of Patos lagoon and estuary (located at the very south of Brazil), the dispersal of nonindigenous marine species and heavy metal deposition at the lake and estuary is largely a result of increasing navigation (ship incrustation and ballast water) and aquaculture activities effecting the lagoon ecology (Ferreira *et al.*, 2009). Land-use change, freshwater withdrawal of ground and surface water sources, sedimentation, point and nonpoint pollution sources, shoreline hardening and overfishing are examples of anthropogenic stressors that can have profound and sudden impacts on coastal lagoon ecosystems (U.S. Environmental Protection Agency 2007, Khan 2007, Rodriguez *et al.* 2007, Bilkovic and Roggero 2008, Hollister *et al.* 2008).

The intensive anthropogenic input of heavy metals into the coastal lagoons present a significant threat to organisms because, as it was mentioned before, once they are present above the threshold they act as enzyme inhibitors. Organisms exposed to heightened heavy metal concentration often experience serious physiological, reproductive and developmental changes (Kennish, 2001). Intensive anthropogenic contribution to the release of trace elements into the water bodies makes them bioavailable - able to be incorporated by organisms (including man) that are directly or indirectly in contact with polluted water sources (Forstner & Wittmann, 1981).

The heavy metal elements differ from the toxic organic compounds to be totally non-degradable, so that they can accumulate in environment components expressing their toxicity (Baird, 2002). Many aquatic organisms, may bioconcentrate trace elements; for example, oysters and mussels, which may contain mercury and cadmium levels 100,000 times greater than the areas in which they live. Most trace elements can undergo bioaccumulation in the food chain, from aquatic plants, invertebrates up to the fishes and mammals and, as a rule, the higher the trophic level of the organism is the greater the metal bioaccumulation occurs (Azevedo *et al.*, 2003). The toxicity of many trace elements depends largely on the chemical form of the element. This is due to the fact that very few of them insoluble can pass through organisms without being harmful, while soluble forms can pass through biological membranes of the protective bodies causing a great damage.

In plants, many of the heavy metals affect and damage various developmental and biochemical processes causing reduction in growth, inhibition of photosynthesis and respiration and degeneration of main cell organelles. In a higher plants, phytotoxic amounts of metals can cause inhibition of several enzymes through two mechanisms, binding of the metal to sulphydryl groups involved in catalytic action or structure of enzyme, and the lack or substitution of essential metals in metal-protein complexes (Morel, 1997). When concentration of heavy metals reaches the critical toxicity values, plant growth reduces and eventually death occurs. Toxicity symptoms are difficult to interpret, therefore complementary plant tissues analysis as well as soil analysis must be done.

1.3. Case Study: Jacunem, Serra, ES, Brazil

Hydrographic basin of river Jacaraipe (Serra, ES) is comprised out of two main sub-basins – basin of the lagoon Jacunem and lagoon Juara (Figure 1.4), located in a set of contiguous basins called Hydrographic Unit of the North-Central coast of Espirito Santo – UHLCN (Zamboni *et al.*, 2009).

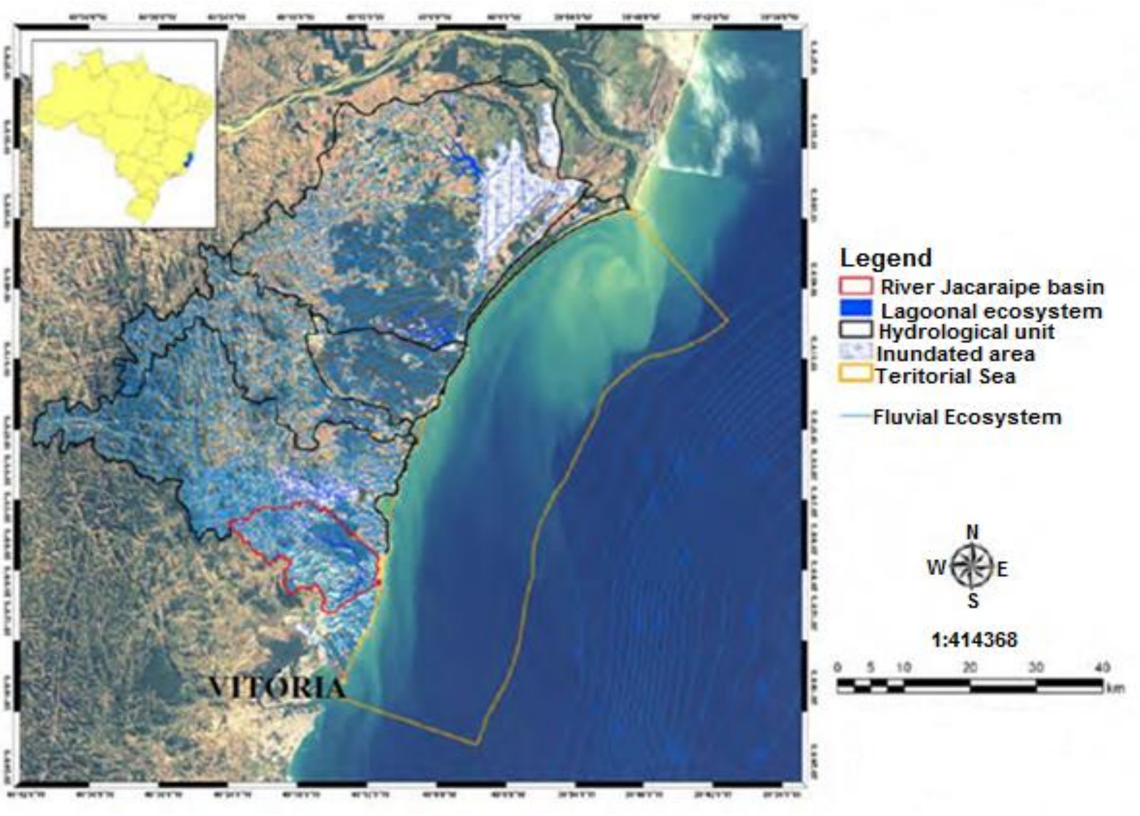

Figure 1.4. Location of the river Jacaraipe basin within the Hydrographic Unit of the North-Central coast of Espirito Santo – UHLCN (Lellis and Barroso, 2007.)

The basin of the Jacaraipe river is found in the city of Serra in the metropolitan region of the city of Vitoria, Espirito Santo state. The area around the Jacunem lagoonand corresponding catchment in year 2000 (IBGE 2000) had a population of 145.272 inhabitants. Between 2000 and 2010 the city population grew by 27% (IBGE - census 2010) resulting in 184000 inhabitants. Under this major basin, sub-basin of the lagoon Jacunem consists out of 3 minor river sub-basins - Venner, Barro Branco and Jacunem with the total catchment area of 35 km^2 (Figure 1.5).

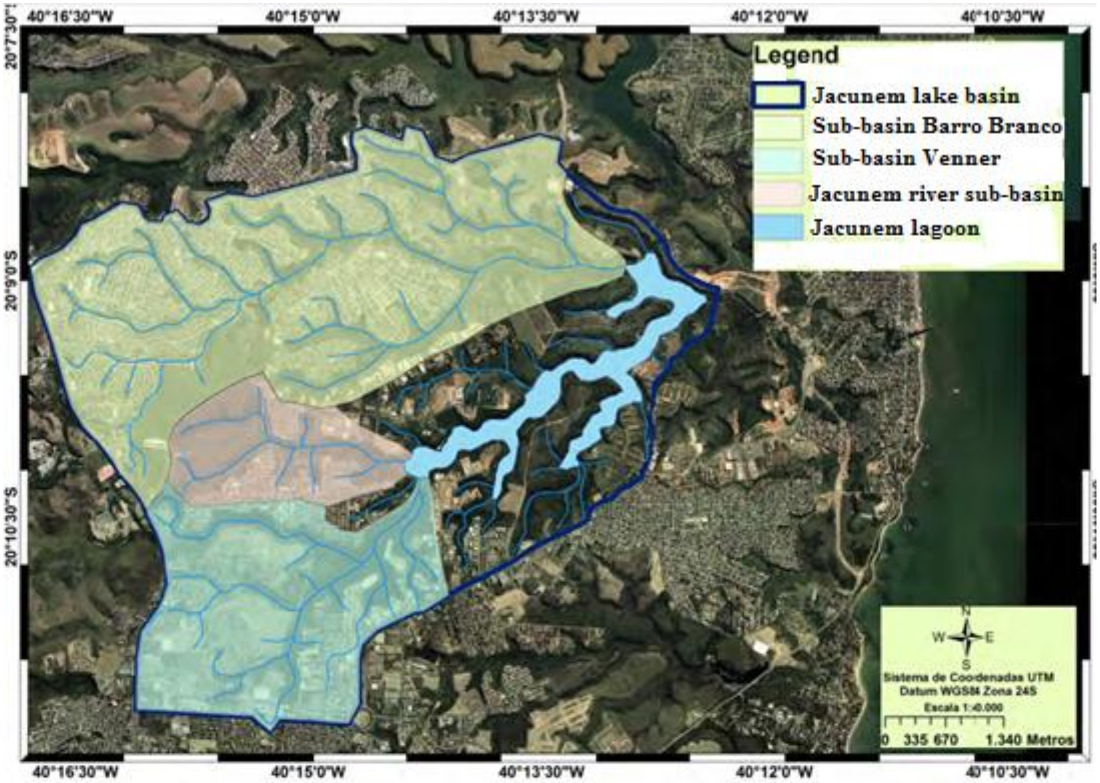

Figure 1.5. Sub-basins of the Jacunem lagoon, Serra (ES), (Lellis, 2010)

The lake Jacunem, whose sediments and macrophytes are targeted by this research, located in the central-eastern portion of the city of Serra, has a surface area of 1.4 km^2 and is considered to be a freshwater coastal lagoon. The average depth of the lake is 1.8 m (max. 3 m) thus the average volume of the lake is estimated to be 2.550.000 m^3 (Lellis, 2010).

1.3.1. Climatology

The predominant type of climate of the region is tropical humid, with the rainy season during the summer (December - February) and a dry season during the winter time (June - August). Average monthly temperatures referred as medium, maximum and minimum are 23,3 °C, 26,9 °C, 19,4 °C respectively. Relative air humidity varies between 75 and 87 % and average annual precipitation is 1400 mm (Feitoza *et al*., 2001). Lake discharge during the rainy season amounts 1, 15 m^3/s and during the dry season 0.143 m^3/s. Residence time of the lagoon is observed to be 29 days (Lellis, 2010). Wind regime is characterized by the frequency of two major winds, the NE-ENE (northeast – east-north-east) and SW (south-west). The first one is associated with the trade winds blowing during the most of the year and the second one is connected to the cold front gusts periodically reaching the cost of the Espirito Santo (Albino *et al*., 2001; Albino, 1999).

1.3.2. Contamination of Sediments and Water of the Jacunem Lagoon and Land Uses in the Surrounding Area

The accelerated industrial growth, which hit the metropolitan region of Grand Vitoria in '70's and '80's followed by the improper land use plan, resulted in the degradation of natural resources of the region causing serious pollution problems (Jacaraipe basin Committee, 2006). This information gives an indication of environmental condition which ruled roughly some twenty years ago where the water body still was at the high quality level. Even though Jacunem lagoon has been a part of Environmental Protected Areas, it has undergone serious environmental impact through industrial waste water and municipal sewage discharge compromising drastically the water quality of the lake. Due to the basin features favorable for the touristic, recreational, economic and urban expansion, lagoon Jacunem is facing multiple land use. Today, the Jacunem basin represents a mosaic of different anthropogenic uses and occupations (Figure 1.6) such are big residential areas, chemical industries of fertilizers, cleaning products, textile and paint industries and a sewage treatment station with obvious improper solid waste disposal (Dassie, 2001). Majority of chemical industries is located within, so called, CIVIT area (Industrial Center of Vitoria city) in a very vicinity of Jacunem lagoon (Leal, 2006).

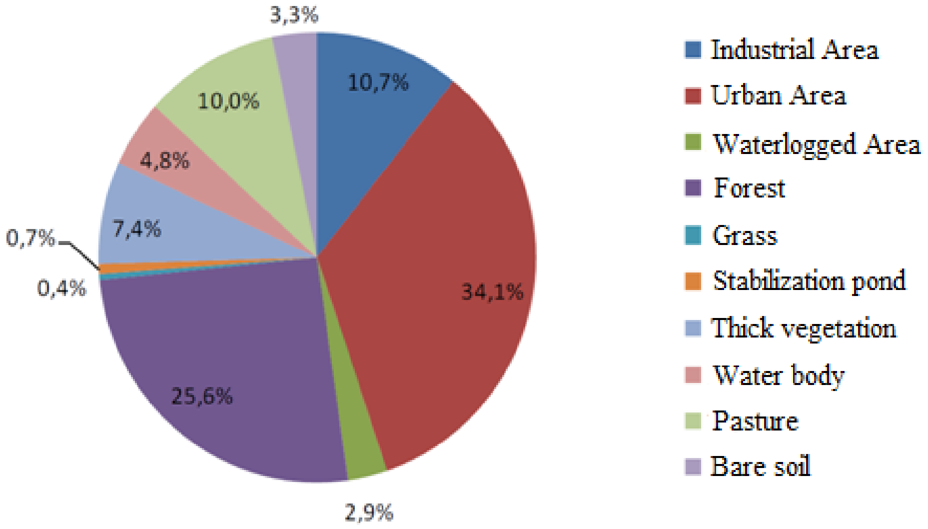

Figure 1.6. Mosaic of land use in the Jacunem basin, Serra (ES). (Adopted and modified from Lellis, 2010.)

According to Duarte *et al.,* (2012), the main pollution sources of heavy metals inside the Jacunem lagoon are the chemical industries of textile and paint. In addition, the river Jacaraipe basin is located in the Atlantic forest biome area, and its rural areas are formed in lowlands surrounded by hillside forests that were, over time, deforested and disfigured in order to establish arable land for many different cultures, such are the pineapple and sugar cane (Figure 1.7). Currently, these rural areas are predominantly covered with pastures, coffee plantations and eucalyptus (De Oliveira, 2010) and the lagoon has much of its water mirror covered with macrophytes like *Pistia stratiotes*, *Echhornia crassipes* and *Motrichardia linifera* probably due to the high content of nutrients and organic matter in the water body. The presence of anthropogenic contaminants in this environment, such are trace elements, pesticide residue, fertilizer leached from the arable land in the vicinity causing eutrophication (characterized through the occasional increased presence of cyanobacteria *Mycrocistis aeruginosa*), domestic and industrial sewage, can compromise a wellbeing of the biota and residents of the area. From the Figure 6, which represents a land use map of the Jacaraipe river basin, could be understood how a different land occupations influence the quality of the lakes explaining the potential high level of heavy metals concentration in sediments and aquatic plants of Jacunem lagoon coming from anthropogenic sources (sewage water discharge at the first place).

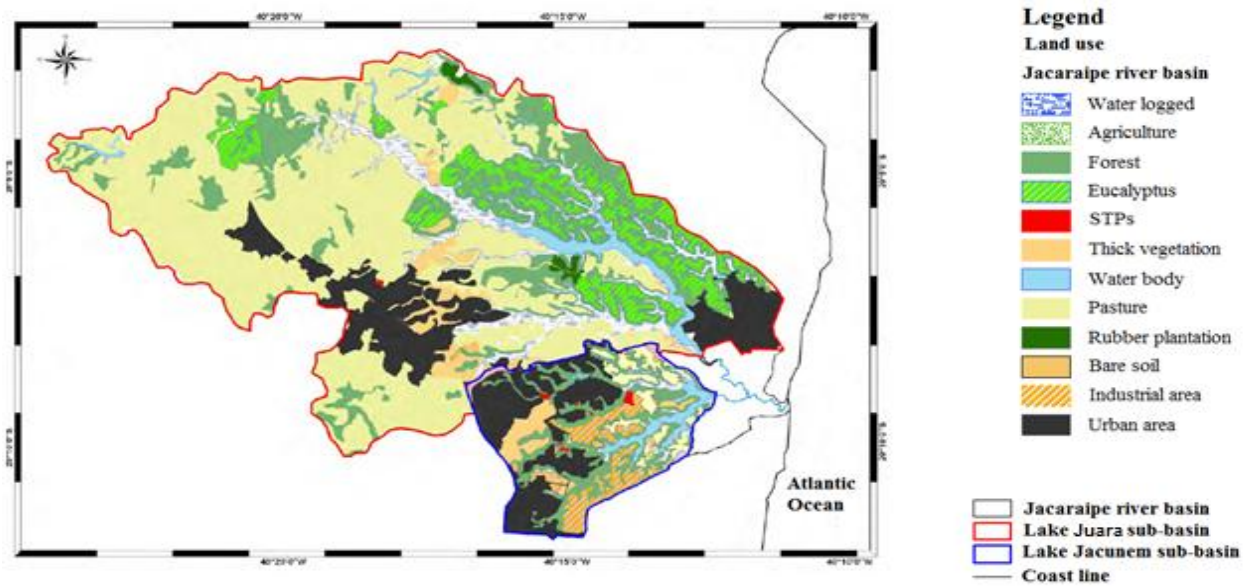

Figure 1.7. Land use of the Jacaraipe river basin (Adapted from Lellis, 2010).

1.3.2. Sewage Disposal in the Area

According to the IBGE census (2000), only 62.7% of the population living in mountainous regions of the Jacaraipe river basin are connected to a sewage network. 28% of the population are connected to the sewage tanks while 9.3% is not connected to any type of sewage network disposal. Therefore, it is clear that both the surface and the underground water are under great pressure from the domestic sewage discharge.

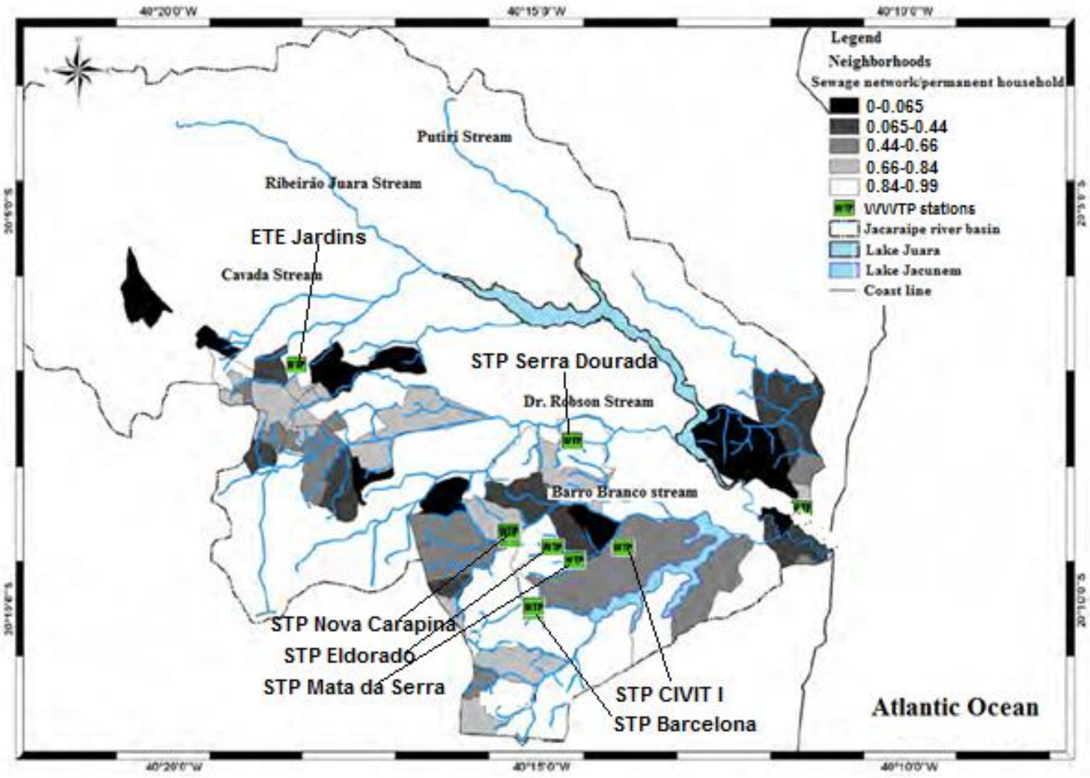

Figure 1.8*. Populated area connected to the sewage network within the River Jacaraipe basin, Serra (ES) (PMS (2008) and IEMA (2009), adopted and modified from Lellis, 2010)

*Values are based on the number of permanent households. Values close to 0 represent districts with the worst condition of sewage collection practices; values around 1 represent neighborhoods with better conditions of sanitation.

Out of ten WWTPs (Wate Water Treatment Plants) located in the river Jacaraipe basin, seven of them is using Jacunem lagoon as a final recipient body (Table 1.8). Even though there are 7 treatment plants covering the area, lake Jacunem basin still presents the neighborhoods with a quite critical situation in relation to the sewage, especially those drained by the stream Barro Branco (Figure 8) (Lellis, 2010).

Table 1.1 WWTPs around the lake Jacunem, Serra, ES

Basin	**WWTP**	**Flow rate (l/s)**		**Type of treatment**	**Receiving body**
		Projected	Measured		
Jacunem Lagoon	CIVIT I	43.6	4.0	Anaerobic lagoon + Facultative lagoon	Barro Branco Stream
	Nova Carapina	12.7	11.0	Anaerobic lagoon + Facultative lagoon	Barro Branco Stream
	Eldorado	14.0	10.0	Anaerobic lagoon + Facultative lagoon	Barro Branco Stream
	Mata da Serra	6	4.6	Facultative lagoon	Barro Branco Stream
	Porto Canoa	5.0	4.0	Anaerobic lagoon + Facultative lagoon	Jacunem Stream
	Barcelona	27.0	23.0	Facultative lagoon	Jacunem Stream
	Maringa	5	3	Anaerobic lagoon + Facultative lagoon	Jacunem Stream
	Total		**59.4**		**Jacunem Lagoon**

Source: PMS (2012) and IEMA (2009)

When it comes to a portion of the river Jacaraipe’s basin, population having their sewage collected into the septic tanks (44.025 inhabitants/around 30%) are using this type of sewage waste disposal (Figure 1.9).

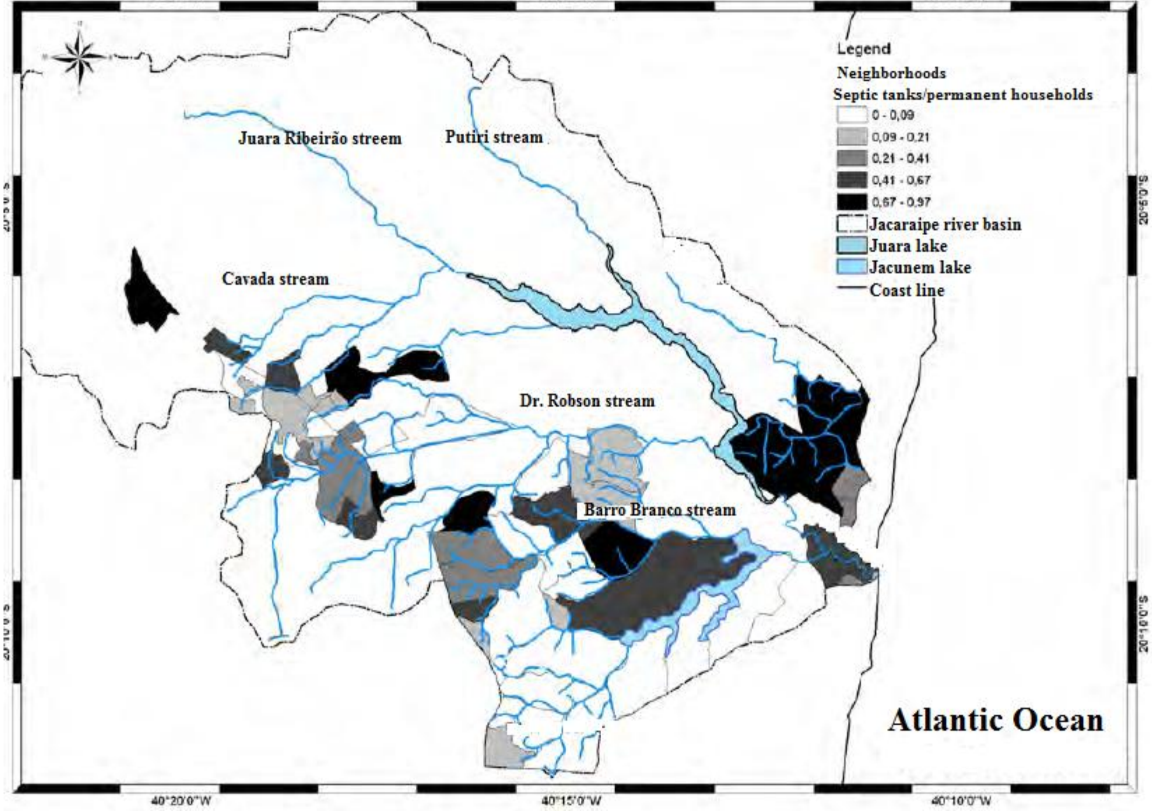

Figure 1.9**. Populated area covered by the septic tank sewage collection, within the Jacaraipe river basin, Serra (ES). (PMS (2008) and IEMA (2009), adopted and modified from Lellis, 2010)

** Values are based on the number of permanent households. Values close to 0 represent the neighborhoods whose population are less covered by the septic tanks (majority is connected to the central sewage system); values close to 1 represent the neighborhoods with high number of septic tanks (higher risk of groundwater contamination).

Finally, despite the fact that the municipality of Serra has the best coverage of sewage network, some neighborhoods are still under the contemplation. 10% of the inhabitants of the basin (some 15.000 people) are releasing their sewage “in the open”.

The flow of open sewage does not represent only a factor of landscape aesthetic degradation, resulting in depreciation of the quality of life of local residents, but more importantly poses a high threat to human health due to the risk of contagion by waterborne diseases.

1.3.3. Macrophytes

1.3.3.1. Eichhornia crassipes

Eichhornia crassipes is an angiosperm, monocotyledonous that belongs to Order of *Commelinales,* Family of *Pontederiaceae* and Genius of *Eichhornia*. *E. Crassipes* forms a shoot consisting of a branched, stoloniferous rhizome, 6cm in diameter and up to 30cm in length, with several short internodes (Figure 1.10). Each node bears a leaf and roots. Axillary buds, which can also form stolons, grow at an angle of 60 degrees from the rhizome and remain at that angle or bend upward in dense stands, or become horizontal in open stands. Plants on the edge of a mat form stolon buds while those in the middle may not. Stolons are purplish violet and extend up to 50cm or more in length and are highly variable in diameter (Gopal 1987, in Batcher Undated).

Figure 1.10. Water hyacinth (*Eichhornia crassipes*) (IFAS, Center for aquatic plants, University of Florida, Gianesville, 1996.)

E. Crassipes at the lake Jacunem, moved by the wind currents, has a tendency to form impassable “live” banks at the narrow parts of the lake branches aggravating the access to some lake parts. Both phenomena mentioned are tightly connected to the high content of organic matter present in water and sediments of Jacunem lake. Despite this, frequently, recreational fishing and swimming can often be seen close to the lake shore. Water hyacinth (*Eichhornia crassipes*) is a clonal, aquatic weed with a cosmopolitan distribution. It forms dense mats that interfere with navigation, recreation, irrigation, and power generation in tropic and subtropic regions. This plant's invasive ability results mainly from the extensive clonal growth by stolons and free-floating life forms (Barrett, 1992), so that the number of ramets can double in less than 1 week and allows an easy dispersal via water current.

The impact of *E. crassipes* on the physico-chemical characteristics of the water in general are decline of temperature, pH, biological oxygen demand (organic load), and nutrient levels (Rai and Datta Mushi 1979). Sometimes there is a complete decline of dissolved oxygen, leading to the deaths of a great number of fish. On the other hand, many studies prove that the water hyacinth *(Eichhornia crassipes)* is an important plant species being a hyper-accumulator of metals enabling the detection of these elements using currently available methodologies. Campaneli *et al.* (2010) and Shaban *et al.* (2005) demonstrated as well that the non-living roots of the water hyacinth can rapidly remove arsenic from water.

1.3.3.2. Typha domingensis

Typha domingensis is an angiosperm, monocotyledonous that belongs to an order of *Typhales,* family of *Typhaceae* and genus of *Typha*. *T. domingensis* has a strong stem which reaches up to a length of 2 m. Its leaves are knife-shaped, varying from 4 to 14 mm. The pistil is faint brown and together with anther are pointed out and separated by a gap that ranges from 1.5 to 7 cm.The color of the pistil is faint brown (Figure 1.11).

Typha domingensis is a plant that grows throughout the warm-temperate and tropical regions (Eid E.M. *et al.,* 2012). This plant is rhizomatous specie which forms dense stands in many continental aquatic ecosystems of Brazil such are marshlands, lagoon banks, lakes, rivers and artificial channels. Its major importance to the ecosystems is due to a large amount of organic matter produced by decomposition, but also they often stabilize shorelines and channels from wave action erosion and have been used to reduce salinity in rice fields. *Typha* was widely studied due to its high productivity, high tolerance and ability for contaminant removal. For these reasons, it has been largely used in constructed wetlands for the treatment of different effluents (Mufarrege *et al.,* 2014). However, This specie can act as an aggressive invader and can completely choke lakes, ditches and canals (Hegazy *et al.,* 2011).

Figure 1.11. Cattail (*Typha domingensis*), (University of Florida/IFAS Center for Aquatic and Invasive Plants, (Available at: www. http://idtools.org/)

There are numerous studies proving that *T. domingensis* is an excellent bioaccumulator of heavy metals (Yadav and Chandra, 2011). For example, Mojiri et. al (2013) conducted a research estimating the effectiveness of *T. domingensis* for phytoremediation of heavy metals from municipal waste leacheate. In the optimum conditions, the amount of removed Pb, Ni and Cd were 0.9725, 0.4681, and 0.3692 mg/kg, which proved that *Typha domingensis* is an effective accumulator plant of these heavy metals.

Due to a high content of vegetation and organic matter present in the Jacunem lagoon, in recent years a temporal variation of dissolved oxygen content is observed and a tendency to the formation of hypoxic/anoxic condition within the lake. When the anoxic event occurs, a series of biogeochemical reactions get initiated compromising the quality of the water in the lagoon. For instance, in oxidizing conditions (presence of oxygen) a significant portion of phosphorus binds to Fe^{3+}, and precipitates in the sediment. In the case of anoxic event at the bottom, reducing conditions will prevail and consequently, the reduction of Fe^{3+} to Fe^{2+} resulting in the phosphorus release from the sediments to the water column (Gächter & Müller, 2003). As phosphorus is the primary nutrient for the growth of the phytoplankton, it is expected an increase of algal biomass, thereby producing more organic matter to sediment. On the other hand, a long time anoxia coupled with high content of organic matter could create a reducing sediment condition which will facilitate the remobilization of metals resulting in high heavy metals availability (Suoza *et al*. 1986, Lacerda *et al.* 1992).

1.3.4. Phytoremediation

The applications of phytotechnologies can be used as tools for Ecohydrology because they involve the enhancement of the capacity of natural ecosystem to protect water resources and shoreline ecosystems (UNEP, 2002).

The definition of phytoremediation evolved over time. According to Schnoor (1997), phytoremediation is a technology for *in situ* treatment of contaminated sites that is attractive due to its low cost and versatility. Later phytoremediation was defined as the use of green plants to remove pollutants from the environment or render them harmless (Becker, 2000). According this author *green technology* uses plants to 'vacuum' heavy metals from the soil through the roots. While acting as vacuum cleaners, the plants must be able to tolerate and survive high levels of heavy metals in soils. We can use plants to extract, degrade, contain, or immobilize pollutants in soil, groundwater, surface water, and other contaminated media (EPA, 2010). During the last years, phytoremediation is defined as the direct use of green plants and their associated microorganisms to stabilize or reduce contamination in soils, sludge, sediments, surface water, or ground water. Sites with low concentrations of contaminants over large cleanup areas and at shallow depths present especially favorable conditions for phytoremediation (U.S. EPA, 2011). The term actually refers to a diverse collection of plant-based technologies that use either naturally occurring or genetically engineered plants for cleaning contaminated environments (Moosavi and Seghatoleslami, 2013).

In the environments such are shallow coastal lagoons, wetlands and others, phytoremediation is the most featured technique in water systems decontamination. Phytoremediation provides the best results in decontamination of cites polluted with low or medium levels of heavy metals. In phytoremediation, the plants are used to stabilize or to remove metals from soil or water contaminated through four mechanisms (Privetz, 2001):

1. Degradation (for destruction or alteration of organic contaminants)

    a) Rhizodegradation: enhancement of biodegradation in the below-ground root zone by microorganisms.

    b) Phytodegradation: contaminant uptake and metabolism above or below ground, within the root, stem, or leaves.

2. Accumulation (for containment or removal of organic and/ or metal contaminants).

    a) Phytoextraction: contaminant uptake and accumulation for removal.

    b) Rhizofiltration: contaminant adsorption on roots for containment and/or removal.

3. Dissipation (for removal of organic and/or inorganic contaminants into the atmosphere).

    a) Phytovolatilization: contaminant uptake and volatilization

4. Immobilization (for containment of organic and/or inorganic contaminants).

    a) Hydraulic Control: control of ground-water flow by plant uptake of water.

    b) Phytostabilization: contaminant immobilization in the soil.

1.4. Objectives

1.4.1. General Objective

The general objective of this study was to conduct an environmental assessment of heavy metals pollution from anthropogenic sources of the Jacunem coastal lake, Serra, ES, Brazil in order to define an ecohydrological strategy for restoration of the assessed lagoon.

1.4.2. Specific Objectives

- To compare the spatial distribution of specific heavy metals in eight sampling points of the Jcanuem lagoon, attending sediments, water and macrophyte species - *Typha domingensis* and *Eichhornia crassipes*;

- To relate the heavy metal contamination with human pressure around the lagoon with;
- To determine the heavy metals distribution among the organs (roots, stems and leaves) of two macrophyte species;
- To estimate the phytoremediation capacity of *Typha domingensis* and *Eichhornia crassipes* to define an ecohydrological approach to remove metals from the lagoon;

With this purpose, sediments, water and biomass of *Typha domingensis* and *Eichhornia crassipes* were collected in May 2015 for further analyses.

2. MATERIALS AND METHODS

2.1. Sampling

Sample collection of sediment, plants and water column of Jacunem lagoon(29º09’33.28” S; 40º13’12.34” W was carried out at 8 different sampling points along the Jacunem lagoon (Figure 2.1) on May 2015 (dry season/winter) .

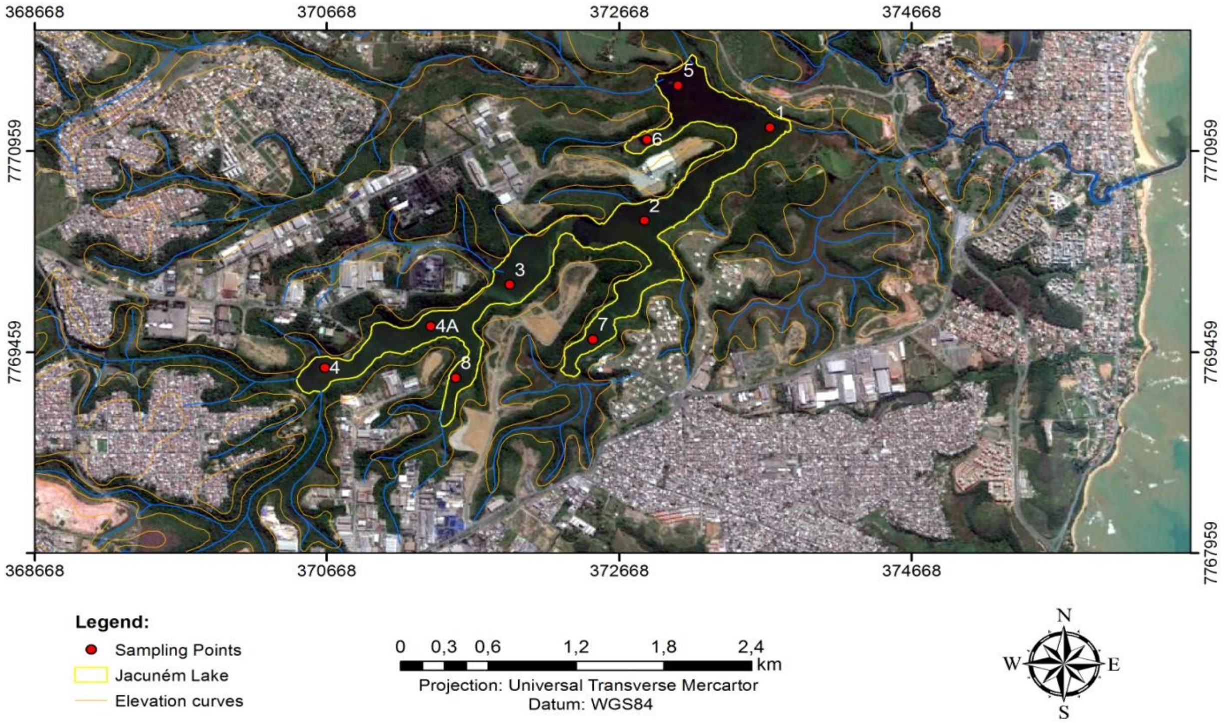

Figure 2.1. The sample collection site at Jacunem lagoon, Serra, Brazil (satellite image adapted from Google Earth, using GIS software)

Macrophytes

Plants were collected at 8 different points of Jacunem lagoon(1,,3,4,4A,5,6,7,8). At each point one unit of Cattail (*Typha domingensis*), and one unit of water hyacinth (*Eichhornia crassipes*) were collected. Water hyacinth was collected as a free floating plant while Cattail was uprooted from the bank soil around the lagoon together with roots and rhizomes. Plants were stored in the dark plastic bags and placed in the fridge until dried (within the next 5 days). Later on, in the laboratory, the plants were separated into roots, stems, and leaves.

Water

Water samples were collected for the heavy metals analyses at 8 different sampling points (1,3,4,4a,5,6,7,8) at the Jacunem lake. The samples were collected in previously decontaminated plastic bottles (volume max. 1 l) at the depth of 10 cm below the lake surface and stored in the Styrofoam containers (Max 5° C) with the ice tablets until frozen (the same day) in the lab freezer.

Sediments

Sediments were collected separately for the organics and heavy metals analyses and placed in aluminium containers (Max vol. 400 g). Using Bentic Grab Sampler, sediments were collected at 8 different points of the lake (1,3,4,4a,5,6,7,8) in a depth of 0-5 cm. In the storage containers, the sediment was collected from the upper central part of the Grabber (with the plastic spoon for the metal analyses and metal spoon for the organic analyses), closed with the waterproof paper cover and placed in Styrofoam containers (Max 5° C) with the ice tablets until frozen in the lab freezer.

Physico-chemical parameters (temperature, turbidity, conductivity, dissolved oxygen, pH, redox potential, Phycocyanin and Chl*a*) of a water column were determined using portable multianalyser analyser (Horiba 50) only at point number 4 due to the time constraints of the sampling day. They are presented in the Results and Discussion chapter under the Water Characterization.

2.2. Samples Treatment

2.2.1. Plants (Above- and Belowground Tissues)

Plant samples were manually separated into three organs (leaves, roots and stems) (Figure 2.2), carefully rinsed with distilled water to remove dust and remaining sediments, weighted and placed into the oven on 60 °C during approximately 96 hours for drying. After drying, the plants were stored at the desiccator until cooled down. After weighting it again (dry biomass) using an analytical balance (Scaltec SBC31) sensitive to 0.01 mg, plants were ground with an agate mortar for further analysis.

Grinding of the plants was done using traditional mortar and pestle made from agate until obtaining substance of very fine granulometry, after storing in a small zip bags and placed into a desiccator with silica until further analyses.

a) b)

Figure 2.2 a) One unit of each plant (*Typha domingensis* and *Eichhornia crassipes*),separated into leaves, stems and roots ready to be oven dried; b) dry plants after being 72h in the oven (Personal images)

2.2.2. Water

Water samples were filtered using the MCE (Mixed Cellulose Esters) membrane filters (0,45 µm, previously decontaminated with 10 % HNO_3 acid solution) and a vacuum pump assisted filtration system. After filtering 100 ml of each water sample, dissolved material was stored in polypropylene flasks, preserved by adding nitric acid (HNO_3) until reaching pH < 2 and stored in freezer until further analyses.

Filters containing particulate material were oven dried for 24 hr at 60 °C, weighted using analytical balance (Scaltec SBC31) sensitive to 0.01 mg and frozen until the extraction, for further analyses.

Metal analyses were done separately in suspended particulate matter and dissolved fraction.

2.2.3. Sediments

At the laboratory sediments were placed into the oven on 40 °C during the 5 days and left there on 20 °C until ground. Each sample was divided into two parts. One for metal analyses and one for grain size determination. The first sample was homogenized using agate mortar and pestle until obtaining a fine substance similar to the powder ready for further analyses.

2.2.4. Sediment Grain Size Determination

Particle size analysis in the superficial sediments of the Jacunem Lagoon were held in Geological Oceanography Laboratory of the Federal University of Espirito Santo, following the procedure below.

Approximately 5g of dry sediment was subjected to elimination of the organic material by the addition of hydrogen peroxide (H_2O_2), through the following procedure: The samples were placed in pre-cleaned glass beakers followed by addition of H_2O_2. After the reaction was repeated several times, in the samples was added hydrochloric acid HCl in order to eliminate the remaining carbon. After the procedure was done, the samples were washed three times with distilled water and were ready to be used in a laser particle analyzer (Mastersizer 3000 - MALVERN) (also used in Costa *et al*., 2015).

2.2.5. Total Organic Matter Determination

The organic matter contents of the sediments were determined by loss on ignition (LOI) at 600 ºC for 2 h (Otte, 1991).

2.3. Microwave-assisted digestion of samples for heavy metals analyses

The microwave digestion methods remove the subjectivity of the analyst from the digestion process through the efficiency of the heating and the direct monitoring of conditions inside the vessel. Additionally, closed vessel microwave methods continually reflux and retain the reagents thus much smaller volume of reagent are used, further reducing reagent contamination. These improvements in reproducibility and efficiency due to microwave-assisted digestion, reduce the sources of error (Richter *et al*., 2001).

2.3.1. Sediments and Particulate Material Digestion

For the analysis of sediment samples, 0.25 g of each sample was digested in a Teflon tube (X-press) using 10 ml of concentrated nitric acid (according to EPA 3051A). Before the sediment samples were placed in the Microwave, they were left two hours on the room temperature for the pre digestion for 2 hours. The extracts were digested in Microwave, model X-press Mars (CEM) for 40 minutes (15 minutes - Ramp and 25min - Hold) on the temperature of 185 ± 5 °C and power 1600W. After cooling (2 h), the final extract was filtered on Whatman 40 filter paper, ready for injection. Digestion of the 8 filters containing the particulate matter after water sample filtration, was conducted in the same way.

2.3.2. Plant Digestion

0.25g of each plant sample was digested adding 9ml of distilled nitric acid ($HNO_{3,}$ 65%) and 2ml of Hydrogen Peroxide (H_2O_2, 30%) (according to EPA 3052) using the Teflon tubes (X-press). Before placing them into Microwave, model X-press Mars (CEM) on for further digestion, the plant samples were previously left for two hours at room temperature for predigestion. In Microwave, digestion was conducted as follows: 5.5 min of heating on 180 ºC; 9.5 min of digestion on constant temperature on 180 ºC and approximately 2 hours of cooling time. After being digested and cooled down, the samples were filtrated using Whatman 40 filter paper, porosity 0.45 µm.

2.4. Metal Analyses

Plant, water, sediment and particulate material extracts were analyzed by mass spectrometry with inductively coupled plasma (ICP-MS), Agilent model 7500 cx. The analytical conditions of the equipment are presented in the Table 2.1 Possible interference caused by fluctuations in the operating parameters have been minimized using a internal standard mix (Bi, Ge, In, Li, Sc, Tb and Y) (Agilent Technologies).

Table 2.1. The analytical conditions of the ICP-MS

Equipment characteristics	
Instrument	Agilent 7500 cx
Cone e skimmer	Ni
Nebulizador	Micro flow
RF Power	1500 W
Carrier Gas	0,94 L/min
Makeup Gas	0,15 L/min
Nebulizer Pump	0,10 L/min
S/C Temp	2 °C

Certified reference materials, blanks and preparation of spiked water samples were used by laboratory quality control. Metal analysis in the certified reference material *Environ*MAT Contaminated Soil (SS-2) and Tomato Leaves (NIST 1573a) (Table 2.2), for sediment and particulate material, and plants respectively, were performed. The water samples were spiked using multielemental solution, diferent of the solution used in the calibration curve (Table 3). 5 replicas of all sample analyses was done, and the results were expressed as the mean and standard deviation.

Table 2.2. Recuperation values (Average ± SD) of different certification materials and water spiking expressed in percentage (%).

Certified Reference Material		Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
NIST 1573A	n=18	97.16± 2,81	80.09± 4,35	106.82± 22,03	101.52± 4,98	94.96± 2,85	109.09± 8,41	93.13± 12,15	97.51± 7,53	85.33± 10,05	92.56± 6,73	*
Contaminated Soil SS2	n=16	92.5± 10,60	93.38± 1,48	92.22± 4,44	96.57± 1,95	99.27± 2,16	94.64± 4,68	93.37± 3,07	99.77± 1,83	94.79± 3,83	97.69± 6,09	85.65±3,67
Water spiking		98.35± 1,25	97.80± 2,46	100.79± 1,98	101.54± 0,56	96.76± 2,65	101.03± 1,38	95.36± 0,69	108.05± 1,13	99.45± 0,84	101.04± 1,87	92.73±0,54

* Pb has no certified values for this reference material
1573A – NIST- Tomato leaves
SS2 – Contaminated soil from

2.5. Data Analyses of the Results

All results were organized according to the established objectives and all statistical analyzes were performed using the computer program STATISTICA 10.0. Correlation analysis were used as descriptive statistical analyses for the results obtained in superficial sediments. The Kruskal Wallis variance test was used to assess significant variation in the level of $\alpha = 0{,}05$ between the sampling points and botanical material. In order to observe possible correlations between the studied parameters of which did not show a normal distribution, we used the Spearman correlation coefficient (Costa *et al*., 2015.) Metal concentrations in sediments and water samples were compared with Brazilian legal reference about environmental quality standards for surface sediments (CONAMA, 2012) and freshwater (CONAMA, 2011).

Enrichment Factor of Sediments

In order to evaluate the anthropogenic contribution to metal accumulation, the enrichment factor (EF) of sediment was calculated as below:

$$\left. \frac{M}{Sc}\,Sample \middle/ \frac{M}{Sc}\,Background \right.$$

(Salomons and Förstner, 1984)

where,

M (sample) – concentration of metal in sample
Sc (sample) – concentration of Al in sample
M (background) – background value of metal concentration
Sc (background) – background value of Al concentration

This index is used as a tool for studies of trace metals in order to evaluate the anthropogenic contribution to metal accumulation (Baptista Neto *et al.*, 2000; Karageorgis *et al*., 2009; Costa *et al.*, 2015). Usually, Al or Fe is used as a conservative lithogenic marker since anthropogenic sources are much smaller compared to natural. In this work, Al was used. For the background values used for calculation of enrichment factor, were considered the average values of the three deepest points in sediment core of geographically closest to the lagoonal system Piraquê-Mirim (Aracruz-ES), analyzed by Costa (2015).

According to Birch (2003) EF indicates:

EF <1 – no enrichment;
EF <3 – small enrichment;
10 < EF <25 – severe enrichment;
3 < EF < 5 – moderate enrichment;
5< EF< 10 – moderately severe;
25 < EF < 50 – very severe enrichment

However, Qi *et al*. (2010) consider the values of EF between 0.5 and 2 may be typical of natural background variability.

Enrichment Factor of Roots of Typha domingensis

To evaluate whether *T. domingensis* accumulate heavy metals in roots, enrichment factors EF were calculated (found *in* Moreira da Silva, 2008) as:

$$EF = [Me]\ \text{roots} / [Me]\ \text{sediment, were calculated,}$$

where,

[Me] roots – sum of heavy metal concentration found in roots
[Me] sediment – heavy metal concentration found in sediments

Translocation Factors of E. crassipes and T. domingensis

In order to evaluate the capability of the studied plants to translocate metal (Me) to the aerial organs (leaves and stems), translocation factors (TF) were calculated as (Deng *et al.*, 2004):

$$[Me]_{\text{in leaves}} / [Me]_{\text{in roots}} \text{ and } [Me]_{\text{in stems}} / [Me]_{\text{roots}},$$

where,

$[Me]_{\text{in leaves}}$ – concentration of heavy metals in leaves

$[Me]_{\text{in roots}}$ – concentration of heavy metals in roots

$[Me]_{\text{in stems}}$ – concentration of heavy metals in stems,

3. RESULTS AND DISCUSSION

3.1. Heavy Metals in Sediments

The necessity to consider sediments in water quality management at the watershed scale has been conclusively established and documented by the introduction of policy and legislation (Owens 2005, 2008). The European Water Framework Directive (WFD) is example of the incorporation of sediment issues in river and lake basin management within the European Union (Casper 2008). In South America by contrast, and particularly in Brazil, only few quality indices for water and sediments have been established so far such is Brazil: CONAMA 1986, 2005.

3.1.1. General Characterization of Sediments

Organic matter share and grain size of the superficial sediments (sand, silt and clay) of Jacunem lagoon were determined and presented in the Table 3.1. Due to technical limitations, redox potential (Eh) and pH of sediments weren't determined in this work.

Table 3.1 Organic matter and grain size observed in the surface sediments of the Jacunem lagoon

Sampling points	Organic Mater (LOI %)	Sand (%)	Silt (%)	Clay (%)
1	40.49	7.24	87.45	5.31
3	40.05	8.3	86.69	5.02
4	49.5	23.51	73.79	2.7
4A	38.49	9.72	85.67	4.62
5	58.34	20.6	76.6	2.8
6	52.7	13.35	82.61	4.04
7	39.56	8.57	84.84	6.6
8	51.14	20.07	76.74	3.18
Mean	46.28	13.92	81.80	4.28
SD	7.55	6.52	5.31	1.37

Results from the composition analyses of the sediments from eight sampling points revealed that the sampled surface sediment from the Jacunem lagoon bottom was predominantly silt (around 80%), sand and clay jointly constituted about 20% of the sediment.

The organic matter varied between 38.5 and 58.3 % with mean and SD of 46.28 and 7.55, respectively.

Grain size distribution plays an important role regarding the content of heavy metals in sediments. Many investigations indicated that sediments composed of smaller grain sizes contain more metals than those formed of coarser ones (Gibbs, 1977; Salomons & Forstner, 1984). This was attributed to the fact that the smaller grains have a larger surface area that retains high amounts of heavy metals (Wang, Qin, & Chen, 2006). However, others investigations showed that the coarser size fractions contain high concentration of metals (Singh, Hasnain, & Banerjee, 1999).

3.1.2. Heavy Metal Concentrations

Metal concentrations in the superficial sediments of Jacunem lagoon were determined and are present in the Table 3.2. Aluminium and Fe are presented in percentage due to their high levels in environment and other metals (V, Cr, Mn, Ni, Cu, Zn, As, Cd and Pb) in mg/kg of dry mass. On Table X, are reffered too Brasilian legal values to heavy metals in surface sediments according to CONAMA (2012).

Statistical analyses show that there is no significant differences ($p<0.05$) between the metal concentrations, determined in the 8 sampling points in the lagoon. However, according CONAMA (2012) references Zn is higher then the one in Level 2 (315 mg/kg) and can be a problem in terms of toxicity, especially in points 4 and 4A. In sampling point 1, 6 and 8 were found higher concentrations then Level 1(5.9 mg/kg). For other metals from anthropogenic sources, concentrations are below then the ones in Level 1 of CONAMA (2012). In general, sampling point 8 presented the highest concentrations of V, Cr and second highest concentrations for Ni and As. These data are according to different industries distribution around the lagoon (Figure 3.1). Points 4, 4A and 8 are the nearest to the industrial zone and are receiving effluents. Zinc (Zn) is introduced into aquatic systems through industrial process, such as smelting and use of fertilizers in agriculture (Eisler, 1993). Zn is of special interest because it is both an abundant metal toxicant and an essential micronutrient with important properties indispensable for life. Zn plays a critical role in cellular metabolism, serving as a co-factor in a number of enzymatic reactions and as an intracellular signaling agent. Zn also acts as an antioxidant and a vital constituent of N200 enzymes (Bury *et al.,* 2003; Hogstrand, 2012). However, at higher concentrations, metal such is Zn is able to disrupt physiological and biochemical mechanisms causing both many disturbances and oxidative damage in fish (e.g. Spry and Wood, 1985; Gioda *et al.*, 2007; Lushchak, 2011; Loro *et al*., 2012).

Spearman correlation coefficients (r^2) were calculated, between different constituents of sediments (sand, silt and clay), organic matter and heavy metal concentrations and are presented in Table 3.2. Significant values ($p<0.05$) are shown in red. Important correlations were found between some metals from anthropogenic sources, namely: V and Cr; V and As; Cr and Ni; and Zn and Cd. It is well known that all of these metals have the same anthropogenic origin, namely from municipal and industrial effluents, mining and combustion of fossil fuels combustion (Ceci *et al*., 2012).

Spearman correlation coefficients (r^2) were calculated, between different constituents of sediments (sand, silt and clay), organic matter and heavy metal concentrations and are presented in Table 3.3. Significant values ($p<0.05$) are shown in red. Important correlations were found between some metals from anthropogenic sources, namely: V and Cr; V and As; Cr and Ni; and Zn and Cd. It is well known that all of these metals have the same anthropogenic origin, namely from municipal and industrial effluents, mining and combustion of fossil fuels combustion (Ceci *et al*., 2012).

Figure 3.1 Anthropogenic pressure around the Jacunem (modified Google Earth image)

Table 3.2 The concentrations of heavy metals (average and standard deviation) observed in the superficial sediment of Jacunem lake.

Sampling point	**Al (%)**	**V (mg/kg)**	**Cr (mg/kg)**	**Mn (mg/kg)**	**Fe (%)**	**Ni (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**As (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**
1	2.38±0.25	913.±18.2	23.11±1.12	170.5±4.1	3.51±0.09	3.45±0.41	5.65±0.27	75.44±6.33	7.27±0.13	<QL	6.29±0.21
3	2.34±0.40	934.5±21.1	27.68±1.75	296.4±5.6	3.59±0.08	4.09±0.58	13.44±0.87	96.64±2.00	5.70±0.15	<QL	11.00±0.52
4	1.66±0.38	508.8±23.9	16.63±1.90	294.5±9.8	2.50±0.09	3.58±0.68	11.73±5.48	1516.4±114.0	3.52±0.19	0.34±0.01	9.59±0.43
4A	2.57±0.21	835.3±12.0	27.96±0.48	356.8±9.1	3.84±0.06	5.21±0.26	23.89±1.23	1256.7±90.1	5.43±0.10	0.15±0.03	12.35±0.13
5	2.06±0.16	830.6±33.5	16.00±1.20	183.0±8.5	3.30±0.21	3.07±0.34	19.04±0.68	67.45±13.69	5.40±0.32	0.12±0.02	8.18±0.63
6	3.38±0.19	946.4±68.8	28.95±1.36	267.3±19.3	4.38±0.07	6.37±0.21	8.45±0.19	16.18±1.11	6.30±0.61	<QL	8.04±0.10
7	4.35±0.05	1009.4±28.6	32.76±0.82	200.8±3.9	3.48±0.06	11.87±1.65	13.16±0.27	87.04±4.61	5.68±0.10	<QL	13.20±0.94
8	3.34±0.14	1270.6±44.4	34.77±0.12	145.8±1.9	4.37±0.04	10.16±1.40	8.47±0.69	19.61±1.22	6.77±0.33	<QL	10.58±0.67
Average±SD	2.76±0.87	906.1±212.0	25.98±6.91	239.4±74.7	3.62±0.60	5.98±3.32	12.98±6.00	391.9±618.5	5.76±1.13	<QL	9.91±2.33
CONAMA(2012)											
Level 1*	--	--	37.3	--	--	18.0	37.3	123	5.9	0.6	35.0
Level 2*	--	--	0.486	--	--	35.9	90.0	315	17.0	3.5	91.3

*Level 1 – threshold below which there is less likelihood of adverse effects to biota;

*Level 2 – threshold below which there is a greater likelihood of adverse effects to biota

QL – quantification level; QL (Cd) = 0.019

-- – value not available

Table 3.3 Correlation coefficient (r^2) between sand, silt, clay, organic matter (O.M.) and heavy metals (N=8, $p < 0.05$)

Variable	Sand	Silt	Clay	O.M.	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Sand	1,00														
Silt	-0,99	1,00													
Clay	-0,91	0,86	1,00												
O.M.	0,81	-0,79	-0,81	1,00											
Al	-0,37	0,31	0,59	-0,21	1,00										
V	-0,26	0,25	0,28	-0,05	0,69	1,00									
Cr	-0,44	0,41	0,51	-0,39	0,83	0,82	1,00								
Mn	-0,17	0,21	0,02	-0,35	-0,30	-0,56	-0,12	1,00							
Fe	-0,29	0,32	0,15	0,04	0,58	0,82	0,76	-0,17	1,00						
Ni	-0,12	0,04	0,40	-0,16	0,92	0,67	0,82	-0,35	0,45	1,00					
Cu	0,01	0,01	-0,07	-0,09	-0,20	-0,29	-0,20	0,54	-0,16	-0,18	1,00				
Zn	0,29	-0,29	-0,30	-0,17	-0,49	-0,74	-0,39	0,69	-0,55	-0,32	0,45	1,00			
As	-0,50	0,52	0,38	-0,14	0,44	0,80	0,54	-0,56	0,74	0,27	-0,45	-0,76	1,00		
Cd	0,51	-0,52	-0,40	0,04	-0,56	-0,81	-0,56	0,52	-0,80	-0,33	0,37	0,85	-0,96	1,00	
Pb	-0,18	0,13	0,37	-0,47	0,46	0,17	0,53	0,36	0,05	0,60	0,51	0,26	-0,30	0,25	1,00

To compare the concentration levels in sediments of this lagoon with the geographically closest lagoonal system according to Costa *et al*. (2015), Enrichment Factors were calculated and are presented in Table 3.4.

Table 3.4 Enrichment factors (EFs) calculated for superficial sediments of Jacunem lagoon.

[Me] mg/kg	**Al**	**V**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Costa *et al.* (2015)	46285.91	63.40	73.45	301.52	57327.57	16.90	10.83	68.66	46.41	0.72	18.16
Current study	27637.55	906.08	25.99	239.40	36262.97	5.98	12.98	391.93	5.76	0.11	9.91
EF		23.94	0.59	1.33	1.06	0.59	2.01	9.56	0.21	0.27	0.91

As it is presented in the Table 3.4, in terms of metals from anthropogenic origin, Cu showed a small enrichment (EF=2.01), Zn a moderately severe enrichment (EF=9.56) and V severe enrichment (EF=23.94).

Vanadium, the 5th most abundant element in transition metals, is widely distributed in the earth's crust with an average abundance of 0.14 mg/kg (Amorim *et al.*, 2007). In recent decades, evidence of increasing levels of vanadium in the environment has raised concern over its release into the atmosphere from anthropogenic sources, mainly due to hydrocarbon fuel combustion (Ceci A., 2012). Vanadium may therefore have an important environmental impact, particularly in the food chain. The vanadium levels present in many cereals, fishes, fresh fruits and vegetables exceed 40 mg per gram of food. Mushrooms are another type of food that is rich in vanadium (Mukherjee *et al*., 2004). Although vanadium has been hypothesized to have numerous biochemical and physiological functions, this metal's role in higher forms of life has yet to be clearly defined (Baran, 2003). Recent evidence suggests that vanadium may be essential for organisms (animals, fungi, bacteria) (Anke, 2004; Berry *et al*., 1999; Hubregtse *et al*., 2005; Kraepiel *et al*., 2009). Moreover, in recent decades, research has led to a change in vanadium's status from a "slightly" toxic and cancerogenic metal to an essential trace element with anti-diabetic and anti-carcinogenic properties (Mukherjee *et al*., 2004).

On the other hand, major anthropogenic source of Zn is considered to be industrial and domestic wastewaters (Belabed *et al*., 2013). Earlier studies also found that Cd, Cu and Zn in the inflow parts of the lakes always exceeded the environmental quality standards for sediments (Jiao *et al*., 2010).

Concentrations of V found within the lake sediments are far above the once found in similar researches such is from author El Sayed *et al.*(2015). In this work, the average concentration of V was found to be 162.77 mg/kg where the current study shows the concentration of 906.08 mg/kg proving very intensive anthropogenic load, showed also by the EF at the Table 3.4.

3.2. Heavy Metals in Water

3.2.1. Physico–chemical Characteristics and Phytoplankton Indicators

Being shallow, Jacunem lagoon it is prone to constant mixing by wind. The water sample shows quite uniform drop of Temperature (ºC), pH and DO (mg/L) with depth (Figure 3.2), while the Conductivity (µS/cm) and the Redox Potential (mV) are gradually increasing with the lake depth.

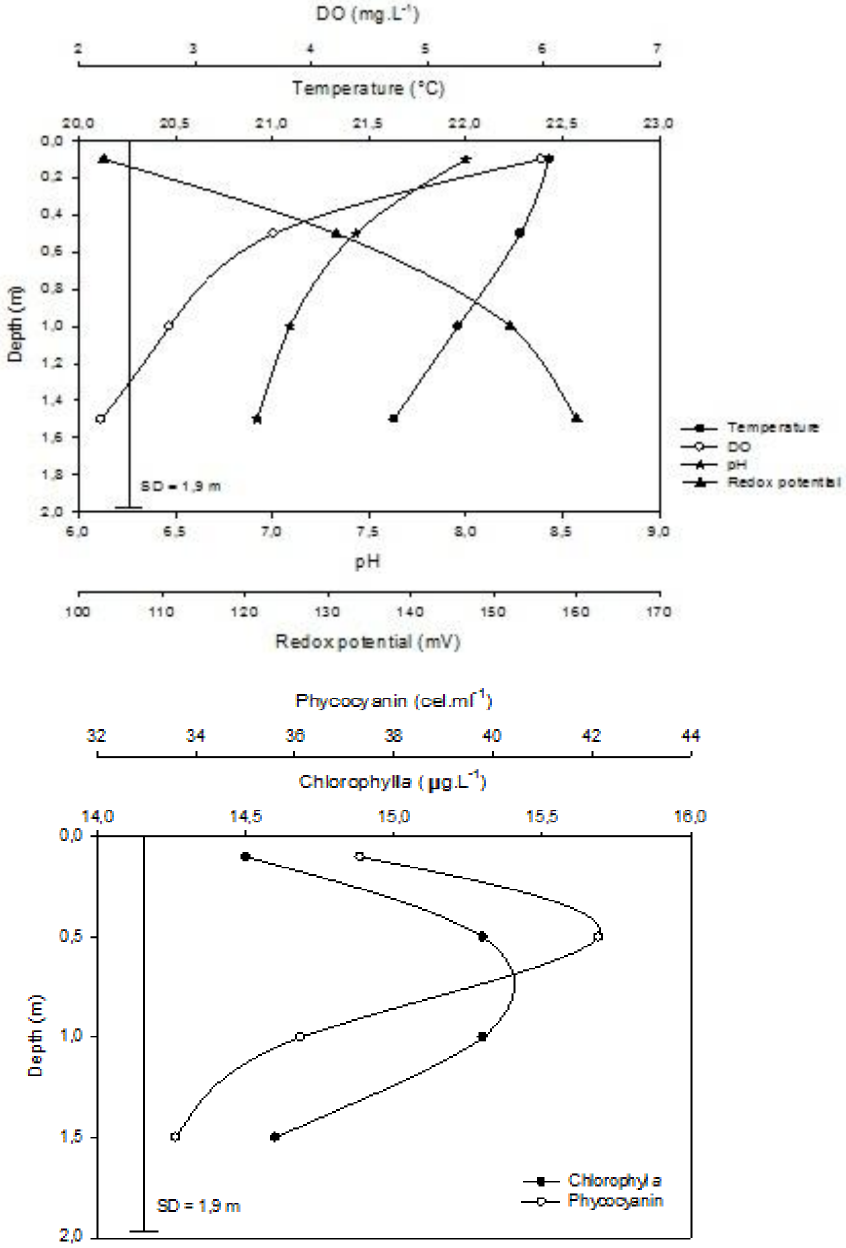

Figure 3.2 Physico-chemical parameters of the water (sampling point 4)

Chlorophyll *a* (Cl*a*), in average showed values of 15 µg/L, exceeding by 30% the Maximum Values presented in Brazilian Water Quality Standards (CONAMA, 2011). Similarly, the concentration of Phycocyanin was found extremely high (42.140 cel./ml), exceeding the standards by more than 50 % (Table 3.5). These results show that Jacunem lagoon is functioning as an euthropic aquatic (Figure 3.3 a,b and d) ecosystem confirming that water pollution from the surrounding human activities either industrial or domestic, is a major problem in this lagoon (Lellis, 2010). This previous study showed that this lagoon receives large amount of nutrients (particularly nitrogen and phosphorus) from the surrounding areas.

Table 3.5 Physico-chemical parameters of the water (sampling point 4)

Depth (m)	Temperature (°C)	Turbidy (UNT)	Conductivity (µS/cm)	DO (mg/l)	Eh (mV)	Chl a (µg/L)	Phycocyanin (cel./ml)	pH
0.10	22.43	43.5	266	5.98	+103.0	14.5	37.318	8.0
0.50	22.28	40.6	268	3.68	+131.0	15.3	42.140	7.43
1.00	21.96	43.0	280	2.78	+152.0	15.3	36.102	7.09
1.50	21.63	41.4	283	2.19	+160.0	14.6	33.588	6.92
CONAMA (2011)*	--	40.0	--	6.00	--	10.0	20.000	6-9

* Maximum values according to Brazilian Environmental Water Standards

a) b)

c) d)

Figure 3.3 a) Starting sampling point - lake Jacunem with obvious cyanobacteria bloom, b) lagoon borders with rich vegetal growing (majority *Typha domingensis* and *Eichhornia crassipes*), c) sediment sample rich in organic matter, d) heavy lake load with water hyacinth (Personal images)

According to Duarte (2012), Jacunem lagoon has been greatly exposed to the textile industry effluents, which were also observed on the plants and water on the sampling site of a current study (see the blue color on the leaves and stems on Figure 3.4).

Figure 3.4 Image of *Eichornia crassipes* in the lagoon Jacunem.

According Wang et al. (2011) in over the planet 25 million persons die as result of water pollution.

3.2.2. Heavy Metals Concentrations in Dissolved Fraction and Suspended Matter

Heavy metal concentrations in dissolved fraction and suspended matter were determined and are presented respectively, in Tables 3.6 and 3.7.

Statistical analyses show that there is no significant differences ($p<0.05$) between the metal concentrations, determined in the 8 sampling points in the lagoon.

Aluminium, Mn and Fe were presented in percentage due to naturally high concentrations of these elements in lagoon environment.

Table 3.6 shows that all metal concentrations quantified in the Dissolved Fraction, were lower than the Maximum Levels (CONAMA, 2011). However these reference values for V, Cr, Mn, Ni, Zn, As, Cd and Pb are Total Concentrations of metals in the water.

As it is shown, at some sampling points the concentrations of heavy metals from anthropogenic origin, namely V, Cr, Ni, Cu, Zn and Pb are very high.

The sampling point 7 shows the highest concentrations of V (185.65 ± 7:00 mg / kg), Cr (77.21 ± 6.61 mg / kg) and Pb (88.16 ± 7.10) in suspended matter. This might be due to the proximity (see Figure 3.1) of urban and industrial effluent discharge and runoff of agriculture. Point 1 was the one with the highest Ni content in suspended matter. This point, located in the NE of lagoon, is relatively close to the sea and to one WWTP therefore, pollution is likely coming from the sea (coastal urbanization) and from the WWTP. At the high tide events, the lagoon is suffering the seawater intrusion, often contaminated by urban effluents.

Much of the suspended matter is expected to be organic and therefore has a great capacity for adsorption of metal cations present in the water column, thus these metals are not bioavailable. If these particles are ingested by aquatic organisms, bioaccumulation of heavy metals will occure in their tissues throughout the trophic chain, causing damage not only to the environment but also for the human health, through consumption of products coming from this lagoon.

Moreover, these organic particles, once deposited in sediments or even suspended in water, are gradually decomposed by microorganisms, over time and in accordance with the surrounding biogeochemical conditions. In this way, they can function as heavy metals pools which can cause metals mobilization to the water column and promote their bioavailability. Consequently, heavy metals will enter again in the trophic chain, through e.g., remediation by plants.

Table 3.6 . Concentration of heavy metals found in the dissolved fraction of water samples of Jacunem lake

Sampling Points	Al (mg/L)	V (μg/L)	Cr (μg/L)	Mn (μg/L)	Fe (μg/L)	Ni (μg/L)	Cu (μg/L)	Zn (μg/L)	As (μg/L)	Cd (μg/L)	Pb (μg/L)
1	0.210±0.07	3.04±0.09	7.12±0.35	10.22±0.70	16.33±0.75	2.33±0.17	<QL	0.85±0.1	1.14±0.14	<QL	3.32±0.15
3	1.10±0.01	1.61±0.01	3.71±0.15	9.36±0.41	16.69±0.31	1.53±0.15	0.61±0.16	3.52±0.57	1.15±0.07	0.32±0.0023	<QL
4	0.14±0.03	2.75±0.06	6.49±0.33	18.36±0.20	18.76±0.87	1.52±0.16	0.36±0.11	3.29±0.26	1.20±0.06	<QL	0.95±0.07
4A	0.14±0.02	3.87±0.05	9.42±0.72	12.48±0.90	23.24±1.57	1.40±0.04	5.49±0.34	14.99±0.39	1.14±0.16	<QL	0.78±0.01
5	0.09±0.02	1.65±0.05	7.46±0.56	15.84±0.10	24.02±1.89	0.78±0.05	1.15±0.11	4.85±0.35	0.97±0.05	<QL	<QL
6	0.15±0.02	2.62±0.05	7.27±0.84	21.41±1.32	22.35±1.50	1.39±0.11	<QL	1.35±0.25	1.25±0.04	<QL	<QL
7	0.11±0.01	2.27±0.02	5.73±0.52	9.60±0.37	17.76±1.46	1.53±0.15	3.18±0.39	6.87±0.67	1.31±0.12	<QL	<QL
8	0.13±0.02	3.10±0.03	12.99±2.40	20.22±0.87	31.85±1.22	2.01±0.17	4.95±0.01	18.84±3.66	1.44±0.17	<QL	0.97±0.23
Average±SD	0.26±0.34	2.26±0.76	7.53±2.74	14.69±4.92	21.38±5.19	1.57±0.46	<QL	6.83±6.59	1.21±0.14	<QL	<QL
CONAMA (2011)	0.1	100*	50*	100*	300	25*	9	180*	10*	1*	10*

* Total concentration in water

QL –quantification level; QL (Cr) = 0.009; QL (Cu) = 0.514; QL (Zn) = 0.067; QL (As) = 0.083; QL (Cd) = 0.019

Table 3.7 Concentrations of heavy metals found in suspended matter in water

Sampling Points	Al (%)	V (mg/kg)	Cr (mg/kg)	Mn (%)	Fe (%)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
1	1.95±0.11	33.69±2.37	13.20±2.72	0.33±0.00	3.01±0.12	1432.3±165.3	32.07	322.05	<QL	<QL	67.17
3	3.46±0.07	41.83±0.75	33.11±2.16	0.35±0.00	2.82±0.08	272.9±17.1	10.24	<QL	<QL	<QL	25.06±2.06
4	2.08±0.09	21.00±0.76	<QL	0.37±0.01	2.59±0.06	95.7±2.5	<QL	<QL	<QL	<QL	34.10±3.28
4A	2.72±0.03	12.02±0.51	10.36±2.04	0.34±0.01	3.08±0.01	101.4±1.2	<QL	<QL	<QL	<QL	37.50±1.36
5	2.28±0.13	21.04±0.69	<QL	0.46±0.01	3.79±0.03	352.2±29.1	<QL	<QL	<QL	<QL	41.54±2.41
6	1.53±0.04	8.17±1.32	<QL	0.47±0.01	3.61±0.03	231.5±29.00	<QL	<QL	<QL	<QL	35.35±3.55
7	24.79±0.66	185.65±7.00	77.21±6.61	0.46±0.01	10.10±0.25	231.3±3.9	<QL	<QL	<QL	<QL	88.16±7.10
8	2.53±0.03	32.31±0.21	6.43±0.45	0.36±0.00	2.89±0.02	98.7±1.8	<QL	<QL	<QL	<QL	16.89±8.80
Average±SD	5.17±7.95	44.47±58.16	<QL	0.4±0.06	3.99±2.50	352.0±446.4	<QL	<QL	<QL	<QL	43.22±23.29

QL –quantification level; QL (Cr) = 0.06; QL (Cu) = 0.24; QL (Cd) = 0.15; QL (Pb) = 0.6

3.3. Heavy Metals in Macrophytes

3.3.1. *Eichhornia crassipes*

The capacity of water hyacinth (*Eichhornia crassipes*) as a very promising plant with tremendous application in wastewater treatment is being studied during the last years (Jafari and Trivedy, 2005).

3.3.2. Heavy Metal Concentrations in Different Organs of *Eichhornia crassipes*

Heavy metal concentrations in different organs (leaves, stems, roots) of *Eichhornia crassipes* were determined and presented in the Table 3.8.

Aluminium, Fe and Mn (only in roots) are presented in percentage due to naturally much higher concentrations present, than the concentrations of other metals, which were expressed in mg/kg.

Results showed that except for Al, Fe and Mn, the highest metal concentrations were always present in the roots of *E. crassipes.*

The explanation for lower bioaccumulation of Fe and Mn in roots, is their relative essentiality for the growth of plants, due to their importance in chlorophyline aerial organs (stems and leaves) for the biochemical reactions of photosynthesis (Taggarta *et al*., 2005; Moreira da Silva, 2008).

The most abundant metal in the roots of *E. crassipes,* in all sampling points was V. The point where the highest concentration of V in the roots, was sampling point 1 (438.6 ± 20.7 mg / kg), which was also the point with the highest concentration of V in dissolved fraction of water (3.04 ± 0.09 µg /L).

The second most concentrated metal in the roots of *E. crassipes* was Zn, although its dominance in roots is not verified at all sampling points.

The third most abundant element in the roots, at all sampling points was Cr, reaching the maximum concentration of 4.62 ± 0.20 mg/kg in the sampling point 1. In this point, Ni also displayed the highest concentrations in roots of *E. crassipes* (2.54 ± 0.10 mg / kg), and just like V, this result concurs with the highest concentration in dissolved fraction of water too (2.33 ± 0.17).

Table 3.8 Heavy metals concentration in different organs of *Eichhornia crassipes* (mg/kg of dry mass)

Sampling stations	**Plant organs**	**Al (mg/kg)**	**V (mg/kg)**	**Cr (mg/kg)**	**Mn (mg/kg)**	**Fe (mg/kg)**	**Ni (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**As (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**
1	*Leaves*	47.19±1.69	0.09±0.00	1.13±0.08	336.4±6.4	127.0±4.7	0.63±0.19	1.06±0.59	12.42±1.23	<QL	0.16±0.02	<LQ
	Stems	164.5±12.3	0.46±0.02	1.03±0.13	600.6±21.3	204.3±4.8	<QL	0.01±1.03	13.62±2.01	<QL	0.06±0.01	0.15±0.08
	Roots	0.58±0.03*	438.6±7.20	4.62±0.20	0.19±0.00*	0.98±0.02*	2.54±0.10	<QL	19.82±1.98	3.53±0.19	0.01±0.004	1.36±0.24
3	*Leaves*	74.3±3.3	0.15±0.01	1.05±0.28	213.3±7.4	158.1±17.9	<QL	1.29±0.17	18.21±1.54	<QL	<QL	<LQ
	Stems	134.4±20.1	0.44±0.05	1.28±0.38	280.6±8.2	167.0±7.9	<QL	1.33±0.49	13.35±1.46	<QL	0.01±0.01	0.69±0.06
	Roots	0.47±0.02*	209.4±3.2	3.45±0.12	0.11±0.00*	0.38±0.01*	1.49±0.06	6.16±1.16	31.46±2.48	1.49±0.02	0.17±0.01	2.57±0.07
4	*Leaves*	612.3±44.1	0.82±0.04	1.12±0.12	289.4±7.5	272.4±17.1	0.51±0.06	0.85±0.03	27.25±2.03	<QL	<QL	0.61±0.08
	Stems	186.6±8.2	0.56±0.03	1.21±0.03	498.1±5.7	198.4±4.0	<QL	1.98±1.30	15.10±1.58	<QL	0.10±0.04	0.15±0.07
	Roots	0.49±0.03*	199.6±12.1	3.95±0.30	0.24±0.01*	0.47±0.03*	1.27±0.17	7.54±1.23	22.74±0.51	<QL	0.01±0.02	1.04±0.08
4A	*Leaves*	89.11±8.38	0.12±0.04	0.69±0.05	300.5±10.9	176.6±8.0	0.37±0.05	0.68±0.10	25.53±0.59	<QL	0.02±0.01	0.69±0.06
	Stems	57.08±5.24	<QL	1.17±0.77	477.5±40.0	107.2±6.5	<QL	1.16±0.08	16.33±2.61	<QL	0.11±0.01	0.71±0.08
	Roots	0.32±0.06*	254.9±10.2	2.63±0.22	0.24±0.01*	0.42±0.03*	0.74±0.16	0.36±0.18	21.29±0.51	<QL	0.007±0.02	1.32±0.12
5	*Leaves*	105.3±9.9	0.20±0.01	1.00±0.09	242.4±1.5	227.6±3.1	0.36±0.08	0.65±0.10	18.78±0.85	<QL	0.04±0.02	0.56±0.07
	Stems	114.2±2.9	0.34±0.01	1.11±0.09	517.5±2.8	178.1±13.5	<QL	1.21±0.22	16.14±1.53	<QL	0.15±0.01	<QL
	Roots	0.27±0.00*	169.0±2.2	1.99±0.19	0.32±0.01*	0.52±0.09*	<QL	<QL	18.40±1.95	1.44±0.06	<QL	0.55±0.08
6	*Leaves*	26.00±3.29	<QL	0.47±0.02	477.3±8.2	102.0±12.9	0.22±0.09	0.57±0.59	20.91±4.23	<QL	0.06±0.02	<QL
	Stems	81.20±6.87	0.51±0.01	0.63±0.06	830.0±17±.3	270.4±9.0	<QL	1.23±0.13	16.21±2.95		0.15±0.01	<QL
	Roots	0.14±0.01*	20.48±0.81	1.66±0.15	0.23±0.01*	0.53±0.03*	0.68±0.07	5.51±0.42	19.28±0.53	2.35±0.09	<QL	<QL
7	*Leaves*	41.08±4.00	<QL	0.51±0.05	305.2±2.9	123.5±7.6	<QL	0.34±0.06	18.80±2.50	<QL	0.15±0.04	<QL
	Stems	82.64±4.00	<QL	0.60±0.11	500.04±36.48	126.56±5.32	<QL	2.81±0.75	17.09±0.40	<QL	0.17±0.01	<QL
	Roots	0.25±0.03*	20.35±1.54	2.63±0.21	0.25±0.02*	0.33±0.03*	0.93±0.02	2.73±0.2	21.85±2.67	2.18±0.17	0.21±0.02	0.68±0.07
8	*Leaves*	126.2±4.2	0.31±0.01	0.61±0.03	295.9±3.9	155.9±14.7	<QL	0.68±0.18	25.83±0.74	<QL	0.10±0.02	0.21±0.18
	Stems	336.0±39.9	1.22±0.10	0.84±0.06	485.3±11.9	241.0±20.8	1.06±0.02	4.76±0.31	27.22±0.56	<QL	0.24±0.03	<QL
	Roots	0.48±0.05*	318.31±0.20	3.73±0.20	0.36±0.02*	0.40±0.02*	1.59±0.12	9.28±1.80	54.29±4.10	2.28±0.11	0.24±0.02	1.68±0.15

*values expressed in %

QL – quantification level; QL (V) = 0.011; QL (Ni) = 0.129; QL (Cu) = 0.017; QL (As) = 0.084; QL (Cd) = 0.010; QL (Pb) = 0.152

In terms of spatial distribution, sampling point 1 represents the highest concentration levels of V, Cr, Ni, Zn, As and Pb in the roots of *E. crassipes*,. This could be related with the high concentrations of metals in the lagoon in particular, dissolved metals in water, due to the proximity of the sewage, industrial discharge and occasional sea water inflow, as explained earlier.

If the plant as a whole is considered (not separated by organs), it can be concluded that the highest concentrations of V, Cr, Ni and As are present in the sampling point 1, the highest concentration of Pb in sampling point 3, the point 7 revealed the highest concentrations of Cd and finally, point 8 showed the highest concentrations of Cu and Zn (Table 3.9).

Table 3.9. Heavy metal concentrations in the whole plant (*E. crassipes*)

Sampling points	**Al (%)**	**V (mg/kg)**	**Cr (mg/kg)**	**Mn (%)**	**Fe (%)**	**Ni (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**As (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**
1	0.60	439.19	6.79	0.29	1.02	3.31	1.10	45.87	3.83	0.23	1.62
3	0.50	209.99	5.80	0.17	0.42	1.72	8.79	63.03	1.78	0.19	3.37
4	0.58	201.00	6.29	0.32	0.52	1.92	10.38	65.10	2.37	0.12	1.80
4A	0.34	255.20	4.51	0.33	0.46	1.25	2.21	63.16	2.25	0.15	2.73
5	0.30	169.43	4.01	0.38	0.57	0.58	1.32	55.97	1.82	0.12	1.69
6	0.15	20.51	2.62	0.33	0.56	1.04	6.67	61.12	2.65	0.22	0.35
7	0.27	20.38	3.66	0.31	0.36	1.15	3.43	59.47	2.52	0.53	0.93
8	0.51	318.95	4.97	0.42	0.44	1.81	10.65	105.97	2.69	0.45	2.02
Average ± SD	0.41 ± 0.16	204.33 ± 141.31	4.81 ± 1.41	0.32 ± 0.07	0.54 ± 0.2	1.60 ± 0.83	5.57 ± 4.04	64.96 ± 17.64	2.49 ± 0.64	0.25 ± 0.15	1.81 ± 0.95

In spite of being noxious weed, the water hyacinth (*E. crassipes*) has been an important choice for phytoremediation of heavy metals from waste water due to its several advantages over other species (Maine *et al.*, 2001). Its enormous biomass production rate, its high tolerance to pollution, and its heavy metal and nutrient absorption capacities qualify it for use in wastewater treatment ponds (Liao and Chang, 2004; Jayaweera and Kasturiarachchi, 2004).

Previous studies (Agunbiade *et al.*, 2009) revealed that the *E. crassipes* accumulated toxic metals such as Cr, Cd, Pb and As both in the roots and in the shoots in high degree, which indicates that the plant that forms a large biomass on the water surface, and is not fed upon by animals, can serve as a plant for both phytoextraction and rhizofiltration in phytoremediation technology. De Souza *et al*. (1999) studied the phytoaccumulation of trace elements Cd (II), Cr(VI), Cu(II), Ni(II), Se(VI) with the specie *E. crassipes*, under hydroponic conditions and concentrations found were ranging from 0.1 to 10 mg/L in a period of 14 days. For a concentration level of 0.10 mg/L the bioaccumulation capabilities were: Cd (1.85 mg/kg/d); Cu (1.15 mg /kg/d); Cr (0.53 mg /kg/ d); Se (0.58 mg /kg/d) and Ni 1.04 mg/kg /d. Shaban *et al*. (2005) demonstrated that the non-living roots of the water hyacinth can rapidly remove arsenic from water (Alvardo *et al.*, 2008).

3.3.3. *Typha domingensis*

Previous studies showed that *T. domingensis* has capacity to absorb and accumulate heavy metal from wastewaters and this accumulation is mainly done in roots, rhizomes and old leaves (Hegazy *et al*., 2011).

3.3.4. Heavy Metal Concentrations in Different Organs of *Typha domingensis*

Heavy metal concentrations in different organs of *T. domingensis* were determined and presented in the Table 3.11. Aluminium and Fe (only in roots) are presented in percentage due to naturally higher concentrations found compared to other metals expressed in mg/kg.

In all sampling points, the highest concentrations of V, Cr, Cu and Zn (except in point 4A), As, Pb (exept in point 4A) were found in the roots of *T. domingensis*. Curiously, Ni showed a different behavior. Concentrations in vegetal tissues were higher in aerial organs (stems and leaves) than in roots in sampling point 5 and were higher in stems than in roots in sampling points 6,7 and 8. As shown before, this didn’t occur with *E. crassipes.*

In terms of spatial distribution, the roots of *T. domingensis* in sampling point 4 present the highest concentrations of Cr, Ni and Zn (concuring with the highest Zn concentration quantified in sediments), and the roots of sampling point 8 present the highest concentrations of Cu, Cd and Pb. The sampling point 7 presented the highest concentration of As on the roots of *T. domingensis*.

If the plant as a whole is considered (not separated by organs), it can be concluded that the highest concentrations of Cr, Ni and Cd are present in the sampling point 4, the highest concentration of V was found in point 6, while point 7 revealed the highest concentrations of As. The point 8 showed the highest concentrations of Cu, Zn and Pb, this is according the results obtained for *E. crassipes*. The Table 3.11 shows the values discussed.

Table 3.10 Heavy metals concentration among the different organs of *Typha domingensis* (mg/kg of dry mass)

Sampling stations	**Plant organs**	**Al (mg/kg)**	**V (mg/kg)**	**Cr (mg/kg)**	**Mn (mg/kg)**	**Fe (mg/kg)**	**Ni (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**As (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**
1	*Leaves*	28.11±2.76	<QL	0.54±0.02	99.20±5.36	78.68±4.55	0.09±0.00	2.23±0.04	16.44±1.92	0.08±0.01	0.16±0.008	<QL
	Stems	97.22±6.94	0.12±0.02	0.26±0.01	54.93±3.02	337.46±5.58	<QL	0.50±0.24	18.51±1.24	<QL	<QL	<QL
	Roots	0.21±0.01*	19.53±0.29	2.62±0.10	400.5±1.5	0.63±0.01*	0.75±0.18	3.05±0.31	20.67±0.82	1.64±0.04	<QL	1.50±0.07
3	*Leaves*	135.73±8.98	0.32±0.02	0.62±0.06	293.0±12.0	338.7±19.6	<QL	4.74±0.91	28.33±3.62	0.16±0.03	0.16±0.06	<QL
	Stems	105.23±4.97	0.17±0.04	0.21±0.02	166.6±25.1	429.8±32.7	<QL	0.80±0.37	40.15±1.14	<QL	<QL	<QL
	Roots	0.20±0.01*	15.27±0.21	1.64±0.12	327.4±9.3	1.08±0.01*	0.37±0.04	13.16±0.21	92.33±0.82	1.76±0.04	<QL	1.64±0.11
4	*Leaves*	101.87±6.44	<QL	0.61±0.03	56.04±1.24	119.16±5.37	<QL	2.53±0.72	11.64±2.35	0.12±0.01	0.23±0.02	<QL
	Stems	396.3±2.6	2.15±0.09	0.33±0.06	328.3±9.3	312.3±2.6	1.42±0.10	<QL	10.57±0.28	<QL	<QL	0.39±0.10
	Roots	0.79±0.03*	353.4±2.3	8.09±0.32	618.2±17.5	0.70±0.01*	2.55±0.19	10.33±0.10	127.0±1.6	2.09±0.10	<QL	4.46±0.30
4A	*Leaves*	53.36±2.36	<QL	0.49±0.06	259.9±27.4	101.3±6.7	<QL	5.22±0.55	20.69±4.28	0.12±0.02	0.26±0.03	2.14±0.30
	Stems	6.84±0.93	<QL	<QL	140.1±14.0	<QL	0.57±0.07	<QL	8.41±0.93	<QL	<QL	0.53±0.18
	Roots	0.17±0.01*	351.7±11.02	1.57±0.04	160.3±2.4	0.84±0.02*	0.88±0.16	3.25±0.53	20.12±2.20	2.44±0.07	<QL	0.63±0.17
5	*Leaves*	23.85±2.20	<QL	0.18±0.04	125.3±6.3	37.84±2.18	1.41±0.83	<QL	8.86±2.87	<QL	<QL	0.21±0.21
	Stems	22.99±2.43	<QL	0.28±0.03	82.25±3.61	<QL	0.82±0.15	<QL	10.43±1.72	<QL	<QL	<QL
	Roots	0.48±0.02*	14.23±0.05	3.25±0.07	105.0±3.9	0.96±0.02*	0.70±0.07	3.02±0.26	11.85±1.02	1.53±0.04	<QL	1.54±0.12
6	*Leaves*	63.48±2.67	<QL	0.04±0.04	155.8±2.8	43.36±7.67	0.45±0.03	<QL	11.95±1.10	<QL	<QL	0.15±0.04
	Stems	17.10±0.51	<QL	<QL	82.80±1.87	<QL	1.28±0.50	0.48±0.01	21.34±2.86	<QL	<QL	0.30±0.04
	Roots	0.52±0.04*	679.2±18.9	3.81±0.15	65.03±1.24	0.93±0.01*	1.08±0.03	3.37±0.71	35.84±1.05	2.81±0.11	0.21±0.02	2.92±0.07
7	*Leaves*	50.98±2.88	<QL	0.07±0.01	201..±3.8	24.89±0.54	0.70±0.1	<QL	9.87±0.92	<QL	<QL	<QL
	Stems	44.57±59.12	<QL	0.05±0.1	121.8±1.5	46.79±89.23	2.00±0.18	<QL	15.43±0.82	<QL	<QL	0.70±0.07
	Roots	0.42±0.01*	537.1±10.0	3.95±0.07	492.4±14.6	1.42±0.02*	1.13±0.11	6.66±0.68	17.29±1.36	3.17±0.05	0.04±0.01	2.67±0.06
8	*Leaves*	78.97±4.56	<QL	0.08±0.04	248.5±15.6	44.98±4.79	0.76±0.00	<QL	24.34±3.40	<QL	<QL	0.71±0.04
	Stems	19.43±20.60	<QL	0.08±0.12	92.64±9.32	<QL	1.55±0.04	<QL	35.39±0.82	<QL	<QL	0.08±0.11
	Roots	0.29±0.01*	584.9±28.4	1.99±0.12	225.3±4.7	0.58±0.01*	0.94±0.09	28.53±2.28	120.3±3.9	2.28±0.15	0.31±0.02	6.66±0.51

*values expressed in %

QL – quantification level; QL (V) = 0.011; QL (Cr) = 0.029; QL (Ni) = 0.129; QL (Fe) = 0.351; QL (Cu) = 0.017; QL (As) = 0.084; QL (Cd) = 0.010; QL (Pb) = 0.152

Table 3.11 Heavy metals concentration in *Typha domingensis*

Sampling points	Al (%)	V (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Fe (%)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
1	0.23	19.67	3.43	554.65	0.67	0.93	5.80	55.63	1.82	0.18	1.76
3	0.23	15.78	2.49	786.99	1.16	0.56	18.71	160.82	2.01	0.35	1.90
4	0.85	355.55	9.04	1002.61	0.75	4.07	12.87	149.20	2.30	0.44	4.96
4A	0.18	351.70	2.09	560.32	0.85	1.55	8.49	49.23	2.65	0.32	3.32
5	0.49	14.25	3.72	312.50	0.96	2.95	3.05	31.16	1.68	0.02	1.91
6	0.53	679.21	3.88	303.64	0.94	2.83	3.86	69.14	2.96	0.23	3.39
7	0.43	537.10	4.08	815.49	1.43	3.84	6.69	42.60	3.32	0.07	3.48
8	0.31	584.95	2.17	566.48	0.59	3.26	28.55	180.01	2.43	0.34	7.45
Average± SD	0.41± 0.22	319± 273.82	3.86± 2.24	612.84± 244.19	0.92± 0.27	2.50± 1.33	11.00± 8.76	92.22± 60.44	2.40± 0.56	0.24± 0.15	3.52± 1.92

Enrichment Factors of *T. domingensis* were calculated in all sampling points and are presented in the Table 3.12.

Table 3.12 Enrichment Factors (EF) of *Typha domingensis*

Sampling Points	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
1	0.09	0.02	0.11	2.35	0.18	0.22	0.54	0.27	0.23	--	0.24
3	0.09	0.02	0.06	**1.10**	0.30	0.09	0.98	0.96	0.31	**1.49**	0.15
4	0.48	0.69	0.49	**2.10**	0.28	0.71	0.88	0.08	0.59	0.57	0.47
4A	0.07	0.42	0.06	0.45	0.22	0.17	0.14	0.02	0.45	0.34	0.05
5	0.24	0.02	0.20	0.57	0.29	0.23	0.16	0.18	0.28	--	0.19
6	0.15	0.72	0.13	0.24	0.21	0.17	0.40	**2.21**	0.45	**10.50**	0.36
7	0.10	0.53	0.12	**2.45**	0.41	0.10	0.51	0.20	0.56	0.52	0.20
8	0.09	0.46	0.06	**1.55**	0.13	0.09	**3.37**	**6.13**	0.34	**7.00**	0.63

As it is shown, this macrophyte had capability to remove Cd from sediments (EF > 1) in several sampling points (see Table 3.4), where Cd concentrations in sediment were below than in the roots.

In sampling point 8, as well EFs > 1 were found for Cu and Zn. Similarly, EF > 1 was found for Zn in sampling point 6.

Comparing concentrations of metals in roots of the two macrophytes it is important to remember that they are different.The roots of *T. domingensis* are in contact with the sediments and the roots of *E. crassipes*, are floating. Therefore, EFs were calculated only for *T. domingensis*.

On the other hand, as we can see in the Figures 1.10 and 1.11, *T. domingensis* roots have much larger diameters and therefore by weight a much smaller surface sorption on the roots surface than do *E. crassipes*.

3.3.5. Heavy Metal Distribution Among the Different Organs of *E. crassipes* and *T. domingensis*

The percentage of metals in different organs of macrophytes, in all sampling points, are calculated and are shown in Figures 3.5 and 3.6.

Aluminium, Fe (although less in *T. domingensis*) and Mn showed high percentages of metals accumulated in aerial organs of both species.

For V and As, just residual percentages were found in aerial organs of both species, in all sampling points of the lagoon. For Cr this distribution pattern was observed just for *T. domingensis*, while in *E. crassipes* were found relevant percentages in aerial organs.

For Zn and Ni were observed relevant (in some cases higher than 50%) percentages of accumulated metals in stems and leaves, in majority of sampling points of the lagoon.

In the case of Cd in *E. crassipes*, metal was accumulated mainly in stems, then in leaves and just a small percentage in roots, except in sampling points 6, 7 and 8 where Cd distribution, was uniform among all organs (roots, stems and leaves). Analyzing the distribution of Cd among *T. domingensis* organs, a different accumulation pattern was observed. Cadmium is mainly accumulated in leaves (sampling points 1, 3, 4, 4A and 5) and in roots (sampling points 6, 7 and 8). The percentage of Cd in stems of *T. domingensis* is residual in all sampling points.

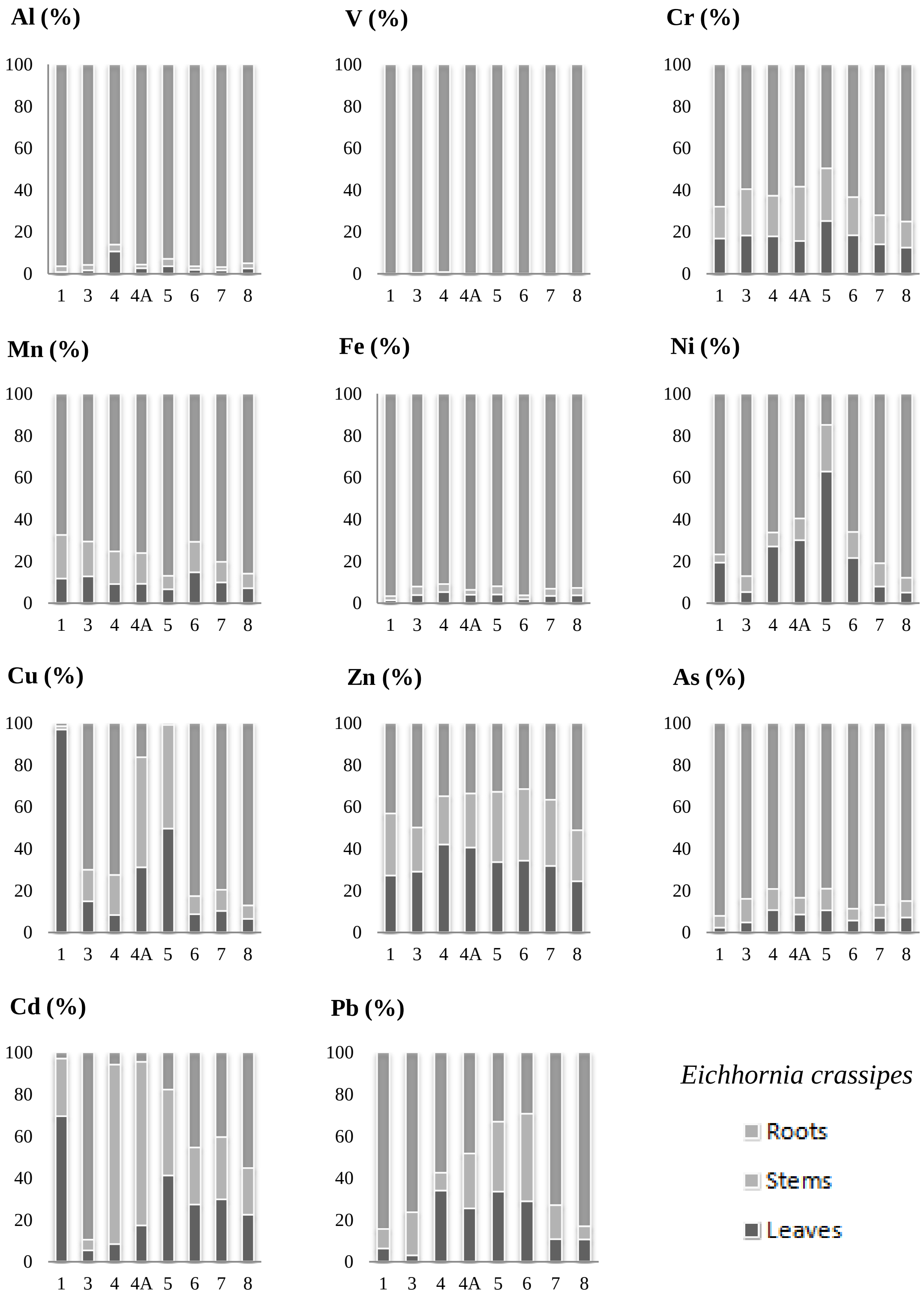

Figure 3.5 Heavy metals distribution among the different organs (roots, stems, leaves) of *Eichhornia crassipes*

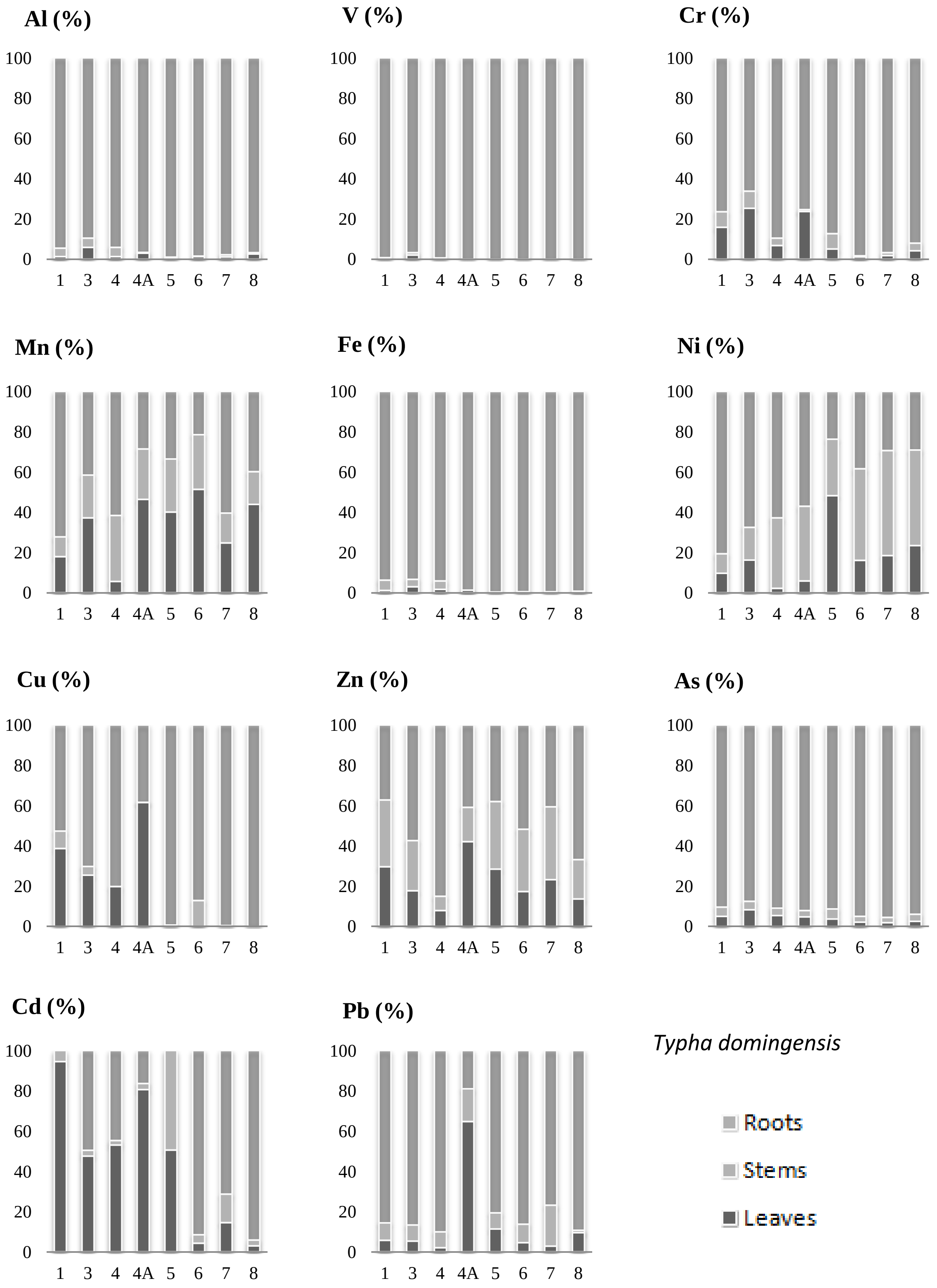

Figure 3.6. Distribution of heavy metals among the different organs (roots, stems, leaves) of *Typha domingensis*

Copper in *E. crassipes* didn’t show a general distribution pattern among the organs in the lagoon, meaning that different points show different pattern of Cu distribution. Copper in *T. domingensis* was accumulated mainly in roots in sampling points 5, 6, 7 and 8, but in the other points relevant percentages were found in leaves (and minor percentages in stems).

In order to evaluate the capability of these macrophytes to translocate metals to aerial organs, Translocation Factors were calculated, using the mean values of metal concentrations, and are presented in Table 3.13

Table 3.13 Translocation Factors for leaves and stems of *E. crassipes* and *T. domingensis*

TF	Macrophyte	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Leaves	***E. crassipes***	0.0367	0.0011	0.2684	0.1243	0.0329	0.2549	0.1946	0.8021	0.0767	0.7388	0.2661
	T.domingensis	0.0172	0.0002	0.0992	0.6010	0.0110	0.4391	0.2070	0.2968	0.0416	0.8479	0.1645
Stems	***E. crassipes***	0.0379	0.0024	0.3197	0.2116	0.0366	0.2088	0.4578	0.6458	0.0810	1.2928	0.2330
	T.domingensis	0.0227	0.0010	0.0472	0.4467	0.0158	0.9308	0.0257	0.3598	0.0378	0.0761	0.1128

It was expected that EFs of Mn and Fe were higher attending to their importance in aerial organs, but curiously EF for Cr, Ni, Cu, Zn and Pb presented higher values mainly in *E. crassipes*. This fact can be related the higher available concentrations of these heavy metals from human activities. Iron is closely related to chlorophyll formation and all plants have iron-containing enzymes (Marshner, 1995). Manganese is activator of a number of enzymes involved in the tricarboxylic acid cycle and some studies reported accumulation in aerial organs about 90% the whole Mn tha plant absorbed (Min *et al*., 2007).

Analysing the data of heavy metals from anthropogenic sources, *E.crassipes* showed higher EF than *T. domingensis* of leaves and stems for V, Cr, Zn, As and Pb and lower for Ni. In the cases of Cu and Cd, EF of *E. crassipes* was higher than *T. domingensis* in stems, but lower in the leaves.

4. FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES

This study confirmed that Jacunem lagoon is an euthropic aquatic ecosystem, surrounded by several human activities which promote the entrance of heavy metals in the lagoon.

High concentrations of Zn were quantified in sediments, particularly in two sampling points (4 and 4A) above in concentrations related with a greater likelihood of adverse effects to biota (CONAMA, 2012). The Enrichment Factors calculated for sediments of this lagoon showed a severe contamination with V. Note that Brazilian legislation has no reference value to V concentrations in sediments. The spatial distribution of the highest concentrations of heavy metals in sediments, in general, was according the proximity to anthropogenic sources of pollution, particularly WWTPs and industries.

Concentrations of all studied heavy metals in dissolved fraction of water, were below to reference values (CONAMA, 2011). However, in suspended matter were found high concentrations of metals, mainly of Ni and Pb in sampling point 1, near the connection to the sea and next to a WWTP serving a big coastal urbanization.

Both *E. crassipes* and *T. domingensis* showed capacity to absorb and accumulate heavy metals from human activities around the Jacunem Lagoon. The distribution of metals among the organs of these macrophytes presented some distinct patterns, according species and depending of metals. Metals were mainly accumulated in roots of both species, however, higher concentrations of Cd, Zn were quantified in leaves and stems.

To develop an ecohydrological approach to the sustainable management of this lagoon we can use the abilities of *E. crassipes* and *T. domingensis* to remove the studied heavy metals from ecosystem. Both species showed high ability to remove V from aquatic environment and accumulate this metal in the roots. In the case of Zn (which can cause environmental damages), both macrophytes phytoremediated this metals and distributed it among roots, stems and leaves. EF of *T. domingensis* were promising for Cu, Zn and Cd (respectively EF = 3.37; EF = 6.17; EF = 10.50) revealing ability of this plant to phytoremediate these metals.

However, it would be important to complement this study with more information about: hydrodynamics of the lagoon, to understand the movement of dissolved and suspended substances and to identify the most stagnant zones; the biogeochemistry of these sediments (in need of sediments characterization, at least through the Redox potential, pH, organic matter and granulometry) to better understand the bioavailability of accumulated heavy metals in sediments; and more water quality parameters should be studied, in particular nutrients of urban and agricultural sources (Nitrogen and Phosphorous), pesticides and organic pollutants from industry (e.g. hydrocarbons).

In future the utilization of invasive plants, as *E. crassipes* and *T. domingensis*, in heavy metals pollution abatement can certainly assist for aquatic ecosystems sustainable management. Plants can be removed using manual or mechanical technics and be disposed in landfills, ensuring the inertia of metals. Moreover a large number of useful byproducts can be developed like power plant energy (briquette), ethanol, biogas, composting and fiber making (Rezania *et al*., 2015).

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