Metal accumulation by *Typha dominguensis* Pers. From a hygrophilous forest fragment in Brazil

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Resumo

Florestas alagadas são formações ribeirinhas, frequentemente degradadas nas regiões mais industrializadas do Brasil devido à crescente interferência da agricultura, indústria e urbanização. Esse cenário é típico para os arredores da Mata Santa Genebra, Estado de São Paulo, onde são observadas alterações químicas do solo e das águas naturais. Neste trabalho foram coletadas amostras de taboa (*Typha dominguensis* Pers.) para testar a capacidade dessa espécie nativa como acumuladora de metais e também para investigar as interações químicas entre planta, solo e água. A composição química da água foi determinada por cromatografia iônica e ICP-MS em amostras coletadas nas estações seca e chuvosa, enquanto que as amostras de solo foram analisadas por fluorescência de raios X e as de plantas por ICP-MS. A água superficial foi classificada como bicarbonatada sódico-potássica para a maioria das amostras e foi observado que as concentrações de PO_4^{3-}, Fe e Mn excederam os limites regulamentados. As amostras de solo apresentaram concentrações elevadas de Ba, Cu e V quando comparadas com os valores de referência. Os conteúdos mais altos de metais nas plantas foram encontrados para Ba, Sr, Zn, Cu, V e Pb , principalmente nas raízes, e para Mn nas folhas. O enriquecimento em metal da planta em relação a solo e água confirma a eficiência da taboa como espécie fito-acumuladora, em particular, para o vanádio, mesmo em baixas concentrações do metal no ambiente. Estes resultados esclarecem o papel desta espécie de planta na reciclagem de elementos no ecossistema ao qual pertence.

Palavras-chave: Mata Santa Genebra, *Typha dominguensis* Pers., fito-acumuladora

Abstract

Hygrophilous forests are riverside formations that are frequently degraded in the most industrialized region of Brazil as a result of increasing interference of agriculture, industry and urbanization. This scenario is typical for the surroundings of the Santa Genebra Forest, Southeastern Brazil, where chemical alterations in soil and natural waters are observed. In the present study samples of cattail (*Typha dominguensis* Pers.) were collected to check the capability of this native species to act as accumulator of metals as well as to investigate the chemical interactions of plant, soil and water. The water chemical composition was determined by ionic chromatography and ICP-MS in dry and wet seasons whereas the soil samples were analyzed by XRF Spectrometry and the plants by ICP-MS. Surface water was classified as Na-K bicarbonate water for the majority of samples and concentrations of PO_4^{3-}, Fe and Mn exceeding the limits established by Brazilian regulations were noted. The soil samples yielded elevated concentrations for Ba, Cu and V when compared to regulated reference values. The highest metal contents in plants were found for Ba, Sr, Zn, Cu, V and Pb, rather in the roots, and for Mn in the leaves. Metal enrichment in plant in relation to soil and water attests the efficiency of cattail as phyto-accumulator, in particular for vanadium even at low metal contents in the environment. These results also highlight the role played by this species in recycling elements in the ecosystem to which it belongs.

Keywords: Santa Genebra Forest, *Typha dominguensis* Pers., phyto-accumulator

1. INTRODUCTION

Economic growth and increasing urbanization certainly meet several societal needs but also promote a number of environmental problems related to misuse of natural resources. The care for a better quality of life and the quest for the rational use of natural resources in modern society have awakened the preoccupation with contamination of soil and water systems, which can cause not only environmental damage but also health problems for humans.

The increasing interest in the study of environmental contamination by metals even at low concentrations is a warning against damage to living organisms. From a biological point of view, some of metals are considered essential to life, but even these, under specific conditions, can cause negative impacts to land and water ecosystems.

The majority of the chemical elements occur naturally in soils and their concentration both in soil and water depends on several variables, such as the chemistry of rocks from which they derive biogeochemical processes and atmospheric deposition. The availability of these elements to plants depends on their chemical form, on the soil-plant and water-plant interactions, and on the microbial activities (Carranza-Álvarez *et al*. 2008).

The organisms of an ecosystem, such as many plant species, can accumulate chemical elements, in special heavy metals, due to the adaptability to the chemical variations in the environment (Kabata-Pendias & Pendias 2001). Hence, these organisms can be used as bio-indicators or biomonitors to inform on the environment quality (Markert 1993).

The biomonitoring of pollutants using accumulator species is based on the capacity of plants or animals to accumulate large quantities of polluting elements, even from much diluted solutions and without apparent harmful effects. According to Ravera *et al*. (2003), aquatic macrophytes are considered excellent indicators of environmental pollution in wetlands because they can absorb large quantities of different chemical elements of the environment where they grow.

The aquatic macrophyte *Typha* sp. has been object of several studies in the past as cited below. The capacity of this plant to accumulate trace elements enables its use as a phyto-remediator in different areas. Some examples are: effluent treatment in the plastics recycling industry (Gondim 2007), treatment of acid drainage of uranium (Groudev *et al*. 2008) and coal mines (Freitas *et al*. 2007), and the environmental biomonitoring in different parts of the world (Goulet & Pick 2001, Freitas et al. 2007, Martins *et al*. 2007, Almeida *et al*. 2007, Bose *et al*. 2008, Alonso-Castro *et al*. 2009).

This plant is common in hygrophilous forest at the Santa Genebra Forest, which is considered the largest remnant of the Atlantic Forest in the region (Campinas municipality in the State of São Paulo) and the second largest urban forest in Brazil after the Tijuca Forest (Rio de Janeiro). In that wetland, most of the native vegetation was replaced by grasses, such as Napier grass (*Pennisetum purpureum*) and guinea grass (*Panicum maximum*), by cattails (*Typha dominguensis* Pers.), and by sugar cane plantations (*Saccharum oficinrum* L.) in the surrounding areas (Coelho & Chiba 2006).

In the present study, samples of *Typha dominguensis* Pers. were analyzed to test the efficiency of this species as a phyto-accumulator of metals in its natural habitat. Additionally, the local water-soil-plant interactions were observed to trace probable anthropogenic interferences in the ecosystem.

2. MATERIALS AND METHODS

2.1 The study area

This investigation was carried out in an area of hygrophilous forest which is part of the Santa Genebra Forest, known as the largest remnant of the Atlantic Forest (252 ha) in the Campinas municipality, São Paulo State, Brazil. This area is limited by the UTM coordinates 7472950 to 7473253 N and 284078 to 283665 W (Figure 1).

A mesothermal dry winter climate is dominant in the area (Coelho & Chiba, 2006) where different rocks such as diabase and gneiss (Instituto Geológico, 1993) can be found. Local soils are part of a fluvial plain strongly influenced by the groundwater level and it is classified as Haplic Organosol-Gleisol, according to Coelho *et al*. (2008). The soil usually occurs in meadows, depressions and valleys, covered by hygrophilous vegetation, either grassland or forest. The strong hydromorphic conditions, due to the shallow groundwater level during most of the year, favor the occurrence of anaerobic conditions that limit the decomposition of organic matter and the development of the soil, resulting in the expressive accumulation of plant remains (Coelho & Chiba, 2006).

2.2 Sampling and analytical procedures

Samples of water and *Typha dominguensis* Pers. were collected in five sites of the semi-flooded areas of the hygrophilous Santa Genebra forest (Figure 1). Topsoil was sampled at three of those five sampling sites. Water sampling took place in two occasions, one in the dry season (September 2008) and the other in the rainy season (March 2009). The rainfall and temperature averages in the last ten years in the Campinas region have been respectively 162.3 mm and 24.7 °C in March and 59.5 mm and 21.8 °C in September, which are considered normal for the periods.

The water quality parameters (pH, conductivity, turbidity, dissolved oxygen, temperature, total dissolved solids and Eh) were measured *in situ*, parallel to sampling. The measured Eh, using a Pt-combined Ag:AgCl electrode, was recalculated to the Standard Hydrogen Electrode (*SHE*), according to the procedure suggested by Nordstrom & Wilde (2005). The alkalinity of water was determined by 0.009 mol/L HCl titration with bromocresol green and methyl red indicators.

The water samples were filtrated in (0.45 µm) cellulose acetate membrane and separated in two aliquots, one for major element analysis by ionic chromatography (Dionex, ICS 2500) and the other for trace-element analysis by ICP-MS, after acidification with super-pure HNO_3 Merck® (1% v/v). The Thermo X series II ICP-MS has a collision cell (CCT, Collision Cell Technology) for the attenuation of polyatomic interferences, as described in Cotta & Enzweiler (2009).

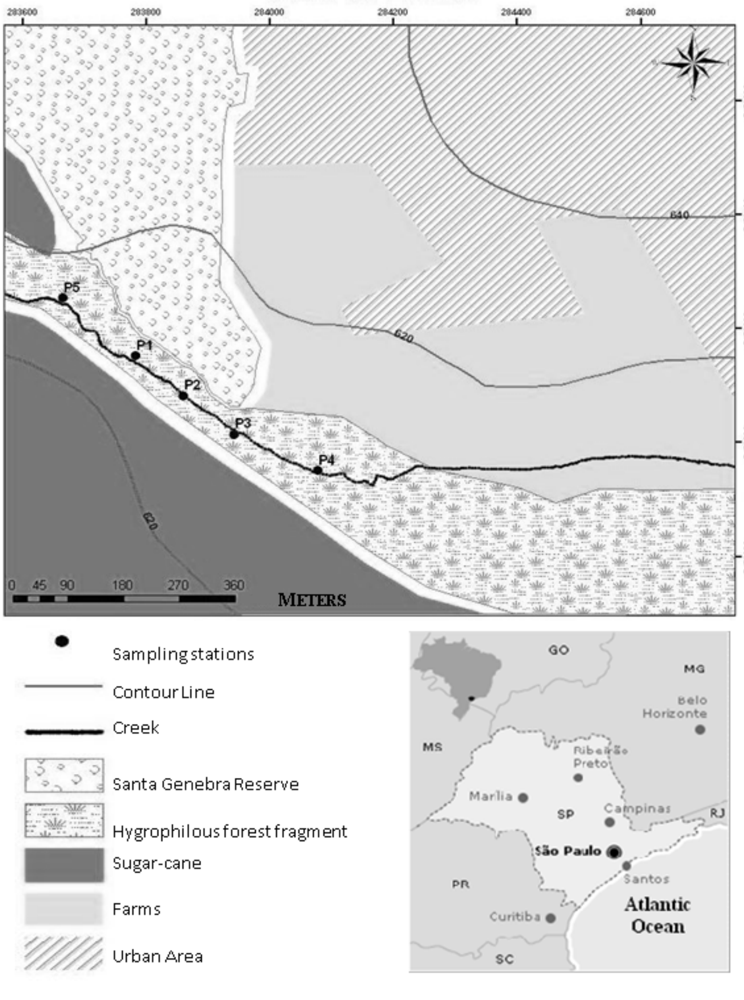

Figure 1. Location map of the study area indicating the State of São Paulo and the Campinas city.

The soil samples were collected at 0-20 cm depth, dried at room temperature, crushed and homogenized manually and sieved. The grain-size fraction lesser than 177 µm was ground in a planetary ball mill using agate grinding media for the preparation of pressed tablets (9.0 g of soil and 1.5 g of wax) for major and trace-element analysis by x-ray fluorescence spectrometry (PW2404, Philips, with rhodium tube) according procedures described by Zambello & Enzweiler (2002).

The organic matter (OM) content in the soil was determined by the Walkey & Black method, adapted from EMBRAPA (1997). In this method the carbon in the soil is exposed to an oxidizing solution ($K_2Cr_2O_7^{2-}$ in acid medium of concentrated H_2SO_4). The potassium dichromate titration was made with a reduced iron solution ($FeSO_4.7H_2O$) in acid medium, using diphenylamine as indicator. From this titration the percentage of organic carbon (OC) is obtained and applied to the formula: OM = % OC x 1.724, where 1.724 is the Van Bemmelen correction factor.

The pH of the soil was measured by the pH method in water (EMBRAPA 1997). Approximately 10 g of soil were dissolved in 25 mL of deionized water, homogenized with a glass stick and left to stand for an hour. Afterwards in was once again stirred and the electrode was introduced in the solution for the measurement.

The samples of *Typha dominguensis* Pers. were collected in duplicate in the same sites of water and soil sampling. One of the samples was used to prepare exsiccates necessary to identify the species. The other sample was washed in running water and deionized water for chemical analysis. After freezing, the plant material was lyophilized for 72 h as suggested by Padaki *et al.* (1992). The leaves and the rhizome were crushed manually and sent separately for chemical analysis in the Acme Analytical Laboratories, Vancouver (Canada). One gram aliquot of dry and sieved (fraction < 177 µm) sample was initially digested in concentrated nitric acid for an hour at room temperature and in heated bath for an additional one hour. After cooling, Aqua Regia (3:1 HNO_3-HCl) and deionized water were added until reaching 6 mg/L in volume. The samples were then conditioned in test tubes, heated at 95°C for two hours. After cooling, the solutions were filtered and analyzed for trace-elements via ICP-MS (Perkim Elmer Elan 9000).

The analytical quality was warranted by the analysis of blanks, replicates samples and certified reference materials. An ionic balance was carried out for major cations and anions contents obtained from the chromatography analyses and, electro neutrality percentages varying from –3.3 % to 5.8 % in both sampling campaigns were found. The certified materials SRM 1640, SRM 1643e (Trace Elements in Water) and SLRS-4 (River Water Reference Material) were used for water analyses by ICP-MS and the GSS-2 and GSS-5 materials (stream sediments and a soil, IGGE, China) for soil XRF analyses. For plant samples the reference materials STD V14 and STD V16 were used by the Acme Analytical Laboratories and certified by the British Columbia Certified Assayer.

2.3 Data treatment

The analytical data obtained for water, soil and plant were analyzed by basic statistics. In particular, the water major-element compositions were plotted at a Piper diagram for water classification purpose. Regarding the metal concentrations in plants, the concentration factor (CF) and the translocation index (TI) were calculated for each element. According to Salisbury & Ross (1992) the concentration factor is the ratio between the element concentration in the plant (leaves and roots) and the element concentration in the environment (soil and water). The TI values indicate the transference of ions from the absorption point in the root to another point, inside or outside the root (Malavolta et al. 1997). In this study, TI represents the percentage of the total absorbed quantity that was transferred to the aerial part of the plant (Abichequer & Bohnen, 1998), as indicated in the equation: IT = 100 x (element concentration in the leaves) / (element concentration in the leaves + element concentration in the roots).

3. RESULTS AND DISCUSSIONS

3.1 Chemical composition of water and soil

The physico-chemical parameters and the chemical composition of the surface water samples are presented in Table 1. The water is acid and oxidizing (dry season, average temperature of 18°C) to slightly acid (rainy season, average temperature of 27°C), with pH varying from 5.2 to 6.4 and Eh in the interval 79-462 mV. The dissolved oxygen concentrations are low (0.45 to

3.5 mg/L) and may reflect the lentic characteristics of the environment with stagnant water. The values obtained for TDS varied from 0.01 to 0.1 mg/L, and for turbidity from 10 to 75 UNT. The alkalinity (HCO_3^-) and conductivity of the water samples varied from 12 to 97 mg/L and from 10 to 180 µS/cm, respectively.

The average concentration of major ions in water in both sampling periods were plotted in the Piper´s diagram for classification purpose. Four samples plotted on the sodic-potassic bicarbonate water field whereas one sample (P03) was classified as mixed bicarbonate water. The highest ion concentrations in all sampling sites but sample P03 correspond to Na^+ (19.2 mg/L), Ca^{2+} (11.8 mg/L) and phosphorous in PO_4^{3-} (0.18 mg/L). Due to its low conductivity as well as its low major and trace-element contents, the water from sample P03 may be pristine and originate from one of several local springs.

The water chemical composition data were compared with regulated values by CONAMA (2005) for special water Class I, which deals with the quality of superficial hydric bodies suitable for the preservation of the natural equilibrium of the aquatic communities and environment in Brazilian integral-protection conservation units (Table 1).

It was noted that PO_4^{3-} (0.88 mg/L), Fe (6 mg/L) and Mn (184 µg/L) exceeded the limiting values established by CONAMA (2005). These metal contents were found in the same samples that yielded high phosphate content and the highest Ba, Mn, Sr, Zn, Cu, Ni, Pb and V concentrations (samples P01, P02, P04 and P05). These metal contents in water correspond to the rainy season when an increase in metal contents in water was favored by leaching of elements from the near cultivated land area where agrochemicals are applied.

According to Kabata-Pendias & Pendias (2001) and He *et al.* (2005), several chemical products such as fungicides, insecticides and herbicides may contain significant amounts of metals. In addition, spreading of elements such as Cu, Zn, Fe, and Mn, which are essential for plant growing, is a common practice to correct deficiencies in soil.

The chemical compositions of the soil samples are presented in Table 2. The clayey soil pH varied from 4.5 to 5.5 and organic matter contents from 4.2% to 17.4%. These figures can be explained by the low declivity of the area that favors the accumulation of organic matter in the soil and the lowering of pH due to the acid groups present in the organic matter.

The metal contents in the soil were compared to the reference values (Table 2) recommended for São Paulo State (CETESB, 2005). These reference values were conceived to support interventions against soil and groundwater pollution. Exceeding metal contents were noted for Ba, Cu and V concentrations whereas Ni, Pb and Zn concentrations were slightly above the established limits. These metal contents are higher than those found by Pereira (2005) for the natural soils of the same region, suggesting that soil in the study area might have undergone some chemical interference from nearby agriculture.

According to Levinson (1974), the use of agrochemicals containing Cu and Zn as well as lime with Ba, Pb and Zn in previous decades can be responsible for the anomalies found in soils of the cultivated areas. It is presumed that the agrochemicals used in the surroundings of the study area, once leached by rainfall, can reach flooded areas and be accumulated in the soil, leading to the increase of certain metal contents in the soil of the study area.

It is noted that V and Ni concentrations in the soils of the study area exceed the reference values established by CETESB (2005). However, both V and Ni contents are within the limits expected for soils that originate from diabase according to the study conducted by Fiorentino (2007). However, the copper contents in soil are excessive even considering that local soils may derive from basic rocks weathering.

Seasonal variation was noted both for water and soil chemical compositions (Tables 1 and 2). Water and soil pH values were slightly higher in the rainy season than in dry season. Less acidic and less oxidizing conditions prevailed in the rainy season. In general, concentrations for the most elements were higher in the rainy season than in dry season.

3.2 Concentration and transport of trace elements in *Typha dominguensis* Pers.

The trace-element concentrations in *Typha dominguensis* Pers. leaves and roots are presented in Table 3. The average metal concentrations in the plant were observed in decreasing order as following: Mn >Sr>Ba>Zn>Cu>V>Pb>Ni. The highest concentrations correspond to Ba, Cu, Pb, Sr, V, and Zn in the roots, and to Mn in the leaves. These metal contents in the plant, in water and soil from the Santa Genebra Forest are depicted in figure 2 for comparison.

According to Bose et al. (2008), different studies attest for a higher metal accumulation in roots than in other plant organs. Some plant species develop a strategy to avoid accumulation of toxic trace elements by storing them far away from the metabolically active structures, especially in the roots, so that even the elements absorbed in great quantities do not act as a phytotoxin to the plant (Carranza-Álvarez *et al*. 2008).

Table 1. Water quality parameters and chemical composition of water from two sampling campaigns (1) dry season and (2) rainy season and regulated values according to CONAMA 357

	P01		**P02**		**P03**		**P04**		**P05**		**CONAMA 357**
	(1)	**(2)**	**(1)**	**(2)**	**(1)**	**(2)**	**(1)**	**(2)**	**(1)**	**(2)**	
pH	5.2	6.4	5.2	6.4	5.3	6.2	5.2	6.3	5.2	6.4	6-9
Cond. (µS/m)	80	180	70	70	10	20	90	110	80	130	
Turb. (NTU)	41	10	10	10	75	17	48	20	66	10	<40
OD (mg/L)	0.45	0.82	2.10	1.87	3.50	2.51	1.50	0.45	0.66	0.83	>6
TDS (mg/L)	0.05	0.10	0.04	0.04	0.01	0.01	0.06	0.07	0.05	0.08	500
EH (mV)	189	79	222	172	462	457	213	185	225	114	
mg/L											
HCO3$^-$	63.7	96.95	79.95	35.1	12.5	15.15	68.7	95.4	58.6	93	
F$^-$	0.12	0.17	0.08	0.07	<0.01	0.03	0.13	0.17	0.11	0.18	1.4
Cl$^-$	7.4	12.1	21.8	11.3	1	1.2	9.9	12.4	6.7	12.3	250
SO_4^{2-}	0.55	1.1	3.3	2.5	0.18	0.16	1.2	3.5	0.84	1.6	250
NO_3^--N	<0.01	0.02	0.17	0.01	0.07	<0.01	<0.01	0.06	<0.01	0.02	10
PO_4^{3-}—P*	0.32	0.88	2.1	0.39	<0.02	0.02	0.26	0.62	0.22	0.97	0.02
Na$^+$	14.6	17.9	17	9.3	2.1	2.3	17.4	19.2	14.6	18.9	
NH4$^+$	1	2.3	1	0.06	<0.05	<0.05	2	2.6	0.85	2.3	3.7
K$^+$	2.2	5.4	32.1	8.9	0.13	0.56	2.9	5	1.9	4.9	
Mg^{2+}	2	2.9	3.4	1.7	0.79	0.85	2.2	3	1.9	2.9	
Ca^{2+}	7.4	11.6	8.7	5.2	1.3	1.7	8.3	11.8	7.1	11.3	
Fe	3.5	6	1.9	2	0.1	0.1	3.2	3.4	3.3	5.1	0.3
µg/L											
Al	24.3	29.3	46	96.7	28.1	24.4	37.6	21.1	29.8	30	100
As	0.25	0.46	0.19	0.31	0.02	0.06	0.23	0.36	0.16	0.38	10
B	14.1	23.2	26.7	23.6	2	1.5	14.9	25.5	12.9	23.4	500
Ba	28.9	38.4	29.6	26.7	30.7	19.5	30.5	27.1	28.9	33.8	700
Be	0.02	0.03	0.02	0.03	0.02	0.01	0.04	0.03	0.02	0.02	40
Cd	0.06	0.1	0.07	0.06	0.06	0.18	0.06	0.03	0.08	0.04	1
Co	0.53	0.9	0.58	0.9	0.21	0.4	0.56	0.8	0.46	0.8	50
Cr	0.14	0.5	0.19	0.3	0.04	0.1	0.16	0.3	0.13	0.3	50
Cu	0.8	3.3	1.5	4.9	0.9	3.1	1.1	1.9	0.8	1.7	9
Li	0.19	0.24	0.32	0.3	0.25	0.2	0.22	0.23	0.17	0.18	2500
Mn	112.8	184	140.1	84	8	15	124.3	176	89.5	159	100
Mo	0.05	0.08	0.09	0.04	0.02	<0.01	0.07	0.06	0.05	0.04	
Ni	0.58	1.1	0.61	1.1	0.23	0.6	0.61	0.8	0.44	0.7	25
Pb	0.1	0.35	0.19	0.74	0.4	0.18	0.24	0.4	0.25	0.4	10
Rb	5.05	8.7	20.45	9	0.31	1	5.72	8.7	4.48	8.3	
Sb	0.02	0.05	0.03	0.06	0.01	0.01	0.02	0.04	0.02	0.04	
Se	<0.02	0.08	0.09	0.05	0.03	0.06	0.05	0.07	0.05	0.08	10
Sr	52.1	76.3	57.2	32.1	9	10.3	55.9	73.9	46.4	70.3	
V	1.7	3.1	2.5	5.4	1.1	0.8	1.6	2.6	1.5	3.1	
Zn	2.6	48.9	8	64.7	7.3	45.7	2.7	28	2.5	22.5	180

Table 2 – Chemical composition of soil from two sampling campaign (1) dry season, (2) rainy season and CETESB (2005) regulated reference vaues. LOI – loss on ignition at different temperatures; OM – organic matter contente

Samples	P01		P03		P04		CETESB
	(1)	(2)	(1)	(2)	(1)	(2)	(2005)
pH	4.8	5.5	4.7	4.5	4.5	5.5	
%							
SiO_2	20.40	35.00	49.50	39.50	37.40	23.30	
TiO_2	1.28	4.81	4.11	3.41	2.33	1.22	
Al_2O_3	16.30	26.00	17.40	15.70	15.00	14.50	
Fe_2O_3	8.90	16.20	3.60	4.90	7.70	3.80	
MnO	0.02	0.11	0.04	0.04	0.08	0.02	
MgO	0.22	0.18	0.18	0.22	0.30	0.24	
CaO	0.88	0.21	0.39	0.28	1.17	0.33	
Na_2O	0.09	0.08	0.09	0.12	0.17	0.19	
K_2O	0.12	0.06	0.08	0.08	0.21	0.09	
P_2O_5	0.65	0.22	0.21	0.30	1.32	0.41	
LOI(105^{o}C)	8.3	3.1	4.3	5.8	6.7	8.2	
LOI(1000^{o}C)	43.1	14.1	20.2	29.5	27.9	47.6	
OM	12.8	13.9	4.2	17.4	12.3	13.9	
mg/kg							
As	5	5	<3	<3	3	4	3.5
Ba	158	95	135	162	317	211	75
Co	11	21	12	13	22	10	13
Cr	32	53	31	30	40	23	40
Cu	236	316	416	291	189	234	35
Ga	18	28	13	13	13	12	
Mo	2	3	<1	<1	<1	2	<4
Nb	22	52	36	36	30	20	
Ni	25	15	16	17	17	25	13
Pb	19	16	26	25	20	18	17
Rb	10	6	6	7	14	13	
Sr	32	17	20	22	48	29	
Th	15	35	29	20	18	14	
U	<3	3	5	4	<3	4	
V	381	365	239	233	184	344	275
Y	42	23	48	35	27	31	
Zn	43	75	65	62	99	52	60
Zr	171	632	518	446	276	176	

According to Bose et al. (2008), different studies attest for a higher metal accumulation in roots than in other plant organs. Some plant species develop a strategy to avoid accumulation of toxic trace elements by storing them far away from the metabolically active structures, especially in the roots, so that even the elements absorbed in great quantities do not act as a phytotoxin to the plant (Carranza-Álvarez *et al*. 2008).

Among the elements analyzed Cu, Mn, and Zn are considered essential micronutrients to plants, because they satisfy the essentiality criteria, being Cu and Zn physiologically involved in the redox reactions (Fitter & Hay 2002). Therefore, Cu and Zn concentrations in *Typha dominguensis* Pers. leaves and roots may reflect the respective concentrations of these elements in soil. The influence of Ba and Pb as beneficial elements or even as essential elements remains unknown and so far they are considered toxic to plants even at low concentrations (Malavolta *et al*.1997).

The accumulation of vanadium in plant species is less studied and information on how the metal affects them is still scarce in the literature. However, Panichev *et al*. (2006), who studied soils and grasses in the surrounding of a vanadium mine, reported vanadium concentrations varying from 1570 to 3600 µg/g in soils and 8 to 13 µg/g in grasses. Piispanen & Lähdesmäki (1983), in their study on vanadium accumulation by aquatic plant species, indicated concentrations of the order of 10 mg/L as beneficial for the growing of the algae species *Nitella mucronata* and *Chlorella* sp.. However, in the opposite way, the same concentration was considered toxic for other species (*Salvinia natans* and *Lemna minor*). In the present study, vanadium concentrations in *Typha dominguensis* Pers. roots varied from 12 to 41 µg/g which is suggestive of the potential of this species as phyto-accumulator for this element.

Carranza-Álvarez *et al*. (2008) have already indicated the capacity of *Typha* species to extract Pb, Cd, Cr, Mn and Fe from the environment and suggested its use in treatment systems for contaminated water. These authors believe that the hyper-accumulation of metals in emerging macrophyte roots is related to the simple fact that the roots expose a larger tissue area to water and soil, thus increasing the accumulation power.

A similar study carried out by Kumar *et al*. (2006) in an urban lake in India attested the role played by eight macrophyte species, including a *Typha* species, as bio-indicators for metals. The authors detected high Cd, Co, Cu, Ni, Pb, and Zn concentrations in sediments and water. The analysis of the macrophyte leaves and roots showed that the *Typha* species has a great capacity to accumulate metals from the environment, the larger concentration factors corresponding to Cu, Ni, Zn and Pb, which shows the applicability of the species in bio-remediation.

The enrichment or concentration factors for the metals were calculated in relation to their concentrations in water and soil in the same sampling sites. As expected, the concentration factors resulted high regarding the concentrations in water, but also significant values were obtained for the concentrations factors referred to soil. As mentioned, the highest accumulations of metals in roots were observed in decreasing order for V, Cu, Pb, Zn, Ni, Ba, Sr and Mn.

Regardless of the small Ba, Cu, Pb, Sr, V, and Zn contents in water and soil, in general, the elements that are most concentrated in soil were also most concentrated in the plant, especially in the roots. The species adopts the strategy cited by Bose *et. al*. (2008) to avoid translocation of elements and damages to reproduction. Furthermore, it is also suggested that even at low concentrations the species cannot avoid the accumulation of these elements by the roots once they are available in the environment.

It is also noted that regardless of the metal concentration in the environment, the physico-chemical conditions can exert a determining role in the bio-availability of these elements to plants. Changes in Eh, metal speciation and solubilization can facilitate the absorption of elements by plants as stated by Weis & Weis (2004).

Therefore, it can be inferred that the element contents in soil as investigated in this study reflect the lentic characteristics of the source-area. In turn, the plants accumulate metals more efficiently by their roots, evidencing that even at low concentrations the species *Typha dominguensis* Pers. is able to act as a bio-indicator and phyto-accumulator for these elements.

The behavior of the elements inside the plant is demonstrated by the translocation indices (TI) of the *Typha dominguensis* Pers. samples calculated for some metals as indicated in figure 3.

The lowest TI values correspond to the metals that are most accumulated in the roots such as vanadium. Also Cu, Pb and Zn accumulated in the roots and showed little translocation in the plant. Intermediate IT values were obtained for Ni, Ba and Sr. The element with the highest translocation index was manganese, fact that can be explained by the role played by this element in the activation of enzymes responsible for respiration at leaves.

Table 3. Major and trace-element contents in leaves (L) and roots (R) of Typha dominguensis Pers. (n = number of samples)

	P01 (n=2)		**P02 (n=1)**		**P03 (n=2)**		**P04 (n=2)**		**P05 (n=1)**	
	L	**R**	**L**	**R**	**L**	**R**	**L**	**R**	**L**	**R**
%										
Al	0,01	0,13	0,01	0,04	0,01	0,27	0,01	0,22	0,01	0,14
Ca	0,74	0,62	0,68	0,56	0,69	0,51	0,81	0,57	0,58	0,65
Fe	0,01	1,48	0,01	1,22	0,01	1,82	0,01	2,18	0,01	2,23
K	2,44	0,43	1,54	2,05	2,22	0,79	2,25	0,4	2,44	1
Mg	0,16	0,11	0,17	0,16	0,19	0,09	0,17	0,06	0,18	0,09
Na	0,46	0,77	1,26	1,26	0,73	0,99	1,13	1,28	0,55	1,71
P	0,15	0,22	0,13	0,24	0,16	0,24	0,18	0,2	0,19	0,29
S	0,13	0,44	0,13	0,34	0,19	0,29	0,2	0,55	0,14	0,75
mg/kg										
As	0,1	0,9	0,1	0,4	0,1	0,8	0,1	1,2	0,1	1
B	5,5	5,5	7	6	6,5	4	6	4,5	7	5
Ba	24,45	44,75	32,9	29	34,15	43,95	30,95	48,15	23,5	52
Bi	0,02	0,03	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
Cd	0,03	0,04	0,01	0,02	0,01	0,06	0,01	0,07	0,02	0,04
Co	0,08	4,47	0,07	2,15	0,16	6,26	0,1	6,09	0,04	5,55
Cr	1,55	2,3	1,3	1,8	1,5	2,65	1,45	2,85	1,4	2
Cu	3,33	29,42	2,77	9,33	3,93	52,71	3,8	34,58	2,48	23,19
Ga	0,1	0,6	0,1	0,2	0,1	1,2	0,1	0,9	0,1	0,7
Hg	8	13	6	10	9	11,5	9	21	12	18
La	0,18	3,66	0,17	1,03	1,06	5,08	0,22	3,76	0,08	2,9
Mn	147,5	45,5	209	41	237	39	209,5	44	214	41
Mo	0,08	0,48	0,04	0,18	0,07	0,36	0,13	0,59	0,04	0,47
Ni	0,75	1,75	0,6	0,7	1,05	2,2	0,85	2,1	0,4	1,4
Pb	1,15	3,63	0,13	0,91	0,23	3,89	0,24	3,1	0,23	2,21
Sb	0,05	0,24	0,06	0,1	0,03	0,18	0,05	0,27	0,04	0,23
Sc	0,2	0,65	0,1	0,5	0,25	1,05	0,2	0,8	0,2	0,4
Se	0,1	0,2	0,1	0,1	0,15	0,15	0,1	0,2	0,1	0,2
Sr	43,35	45,7	44,4	35,9	38,8	39,35	51,35	44,9	39,2	48,7
Te	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
Th	0,01	0,09	0,01	0,1	0,01	0,07	0,01	0,13	0,01	0,02
Ti	7,5	20	5	15	7,5	27	7	24	7	20
Tl	0,02	0,06	0,02	0,02	0,02	0,08	0,02	0,1	0,02	0,07
U	0,01	0,15	0,01	0,03	0,01	0,18	0,01	0,16	0,01	0,1
V	2	20	2	12	2	41	2	27	2	20
W	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Zn	16,55	64,55	14,7	20,9	16,8	39,3	16,35	35,45	11,2	25,7

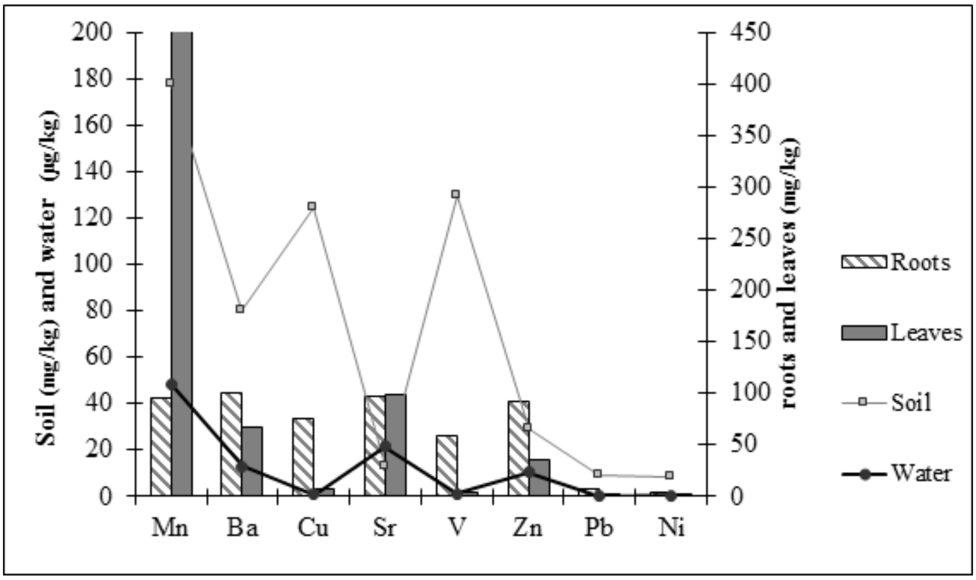

Figure 2 – Comparative values for some metal contents in water, soil and *Typha dominguensis* Pers. from the Santa Genebra Forest

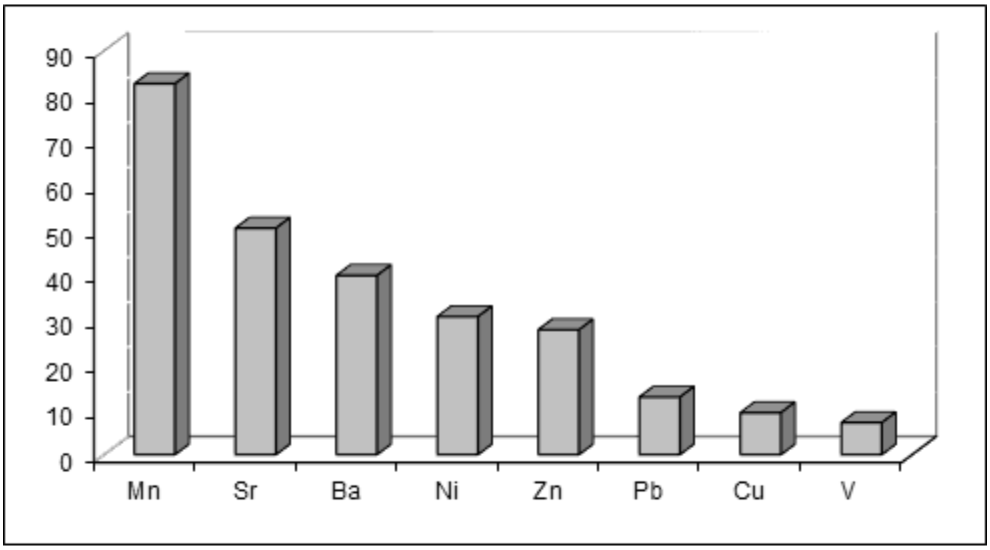

Figure 3 – Translocation index (%) for some metals in *Typha dominguensis* Pers.

4. CONCLUSIONS

Despite the proximity of the urban area and the presence of sugar cane crops in the surroundings of the hygrophilous forest, no exceptionally high metal concentrations in soil, water or in the *Typha dominguensis* Pers. species were found in this sector of the Santa Genebra Forest.

Na^+, Ca^{2+} and PO_4^{3-} and Fe and Mn yielded the highest ionic and metal concentrations in water, especially in the rainy season were more acidic and less oxidizing conditions prevailed in comparison with the dry season. Relatively low dissolved oxygen contents and high PO_4^{3-} and Mn concentration values found in water may indicate some eutrophication as well as anthropogenic interference in the environment.

Major and trace-element contents in soil can be considered normal in the study area. Nevertheless, copper contents in soil exceeded the expected concentrations for soils originated from diabase weathering and may reflect leaching of substances from agrochemicals used in sugar cane plantations or from another unknown source in the region.

Except for these changes, the chemical concentrations obtained in this study for the most elements can be used as local background for water, soil and *Typha dominguensis* Pers. and can be used as reference parameters in other studies in the region.

The metal accumulation by *Typha dominguensis* Pers. was greater in the roots than in the leaves. The highest concentrations correspond to Ba, Cu, Pb, Sr, V, and Zn in the roots and to Mn in the leaves. The metal enrichment in the plant occurred in decreasing order for V, Cu, Pb, Zn, Ni, Ba, Sr, and Mn, standing out the accumulation of vanadium by the roots. The data indicate the potential of the *Typha* species as vanadium phyto-accumulator and attest for its performance in the extraction and accumulation of metals, even at low concentrations in the environment. These results also explain the role played by the species in the recycling of elements in the ecosystem where it grows.

5. ACKNOWLEDGMENTS

The authors wish to thank the National Council for Science and Technology Development - CNPq - for the financial support and the directors of the José Pedro de Oliveira Foundation for permission to access the Santa Genebra Forest.

6. REFERENCES

Abichequer, A.D & Bohnen, H. 1998. Eficiência de absorção, translocação e utilização de fósforo por Reservada de trigo. *Rev. Bras. Ciên. Solo*, **22**:21-26.

Almeida, R.A; Oliveira, L.F.C; Kliemann, H.J. 2007. Deformação em inflorescência de taboa (*Typha angustifolia* L.) submetida a esgoto sanitário. *Pesq. Agropec. Trop*., **37(2)**: 125-129.

Alonso-Castro, A.J.; Carranza-Álvarez, C; Alfavaro-De la Torre, M.C.; Chávez-Guerrero, L.; García-De la Cruz, F.R. 2009. Removal and accumulation of Cadmium and Lead by *Typha latifolia* exposed to single and mixed metal solutions. *Arch. Environ. Contam. Toxic*. **57**: 688-696.

Bose, S; Vedamati, J.; Rai, V.; Ramanathan, A.L. 2008. Metal uptake and transport by *Typha angustata* L. grown on metal contaminatedwaste amended soil: An implication of phytoremediation. *Geoderma*, **145**: 136-142.

Carranza-Álvarez, C.; Alonso-Castro A.J.; Alfaro-De La Torre, M.C.; García-De La Cruz, R.F. 2008. Accumulation and Distribution of Heavy Metals in Scirpus americanus and *Typha latifolia* from an Artificial Lagoon in San Luis Potosí, México. *Water Air Soil Pollut*, **188**:297–309.

CETESB - Companhia de Tecnologia de Saneamento Ambiental 2005. Valores orientadores para solos e águas subterrâneas no Estado de São Paulo, São Paulo.

Coelho, R. M. & Chiba, M. K. 2006. Levantamento detalhado de solos da Área de Bens Naturais, Fragmentos “C’ e “D”, em Campinas, S.P- Relatório técnico - Centro de Solos e Recursos Ambientais Instituto Agronômico Campinas, S.P.

Coelho, R. M., Valladares, G. S., Chiba, M. K. 2008. Mapa pedológico semidetalhado do município de Campinas. 1:50.000. EMBRAPA and IAC. Available at http://www.cnpm.embrapa.br/publica/download/cot24_mapapedolog.pdf

CONAMA, Conselho Nacional de Meio Ambiente 2005. Resolução no. 357 de 15 de março de 2005. Brasília.

Cotta, A. J. B. & Enzweiler, J. 2009. Quantification of major and trace elements in water samples by ICP-MS and collision cell to attenuate Ar and Cl-based polyatomic ions, 01/2009, *J. Analyt. Atom. Spect*., **24**:1406-1413.

EMBRAPA - Empresa Brasileira de Pesquisa Agropecuária. 1997. Centro Nacional de Pesquisa de Solos. Manual de métodos de análise de Solo. 2 ed., Rio de Janeiro, 212 p.

Fiorentino, J. C. 2007. Geoquímica do mercúrio e outros elementos em perfil de solo desenvolvido sobre diabásio, Paulínia, SP, Dissertação de Mestrado, Instituto de Geociências, Unicamp, 68p.

Fitter, A. & Hay, R. 2002. *Environ. Phys. Plants*. 3 ed., Academic Press. 397 pp.

Freitas, M.; Zocche, J.J.; Esemann, J.Q. 2007. Metais pesados (Mn e Zn) em Typha dominguensis Pers em áreas de mineração de carvão. *Rev. Bras. Bioc*., **5 (1)**: 789-791.

Gondim, J.A. 2007. Tratamento de efluente de indústria recicladora de plásticos utilizando reator anaeróbio compartimentado e leitos cultivados. Dissertação de Mestrado, Faculdade de Engenharia Agrícola, UNICAMP, 286p.

Goulet, R. & Pick, F. R. 2001. The effects of cattails (*Typha latifolia* L.) on concentrations and partitioning of metals in surficial sediments of surface-flow constructed wetlands. *Water Air Soil Poll*., **132**: 275–291.

Groudev, S., Georgiev, P.; Spasova, I.; Nicolova, M. 2008. Bioremediation of acid mine drainage in a uranium deposit. *Hydrometallurgy*, **94**: 93-99.

He, L.Z.; Yang, X.E.; Stoffella, P.J. 2005. Trace elements in agroecosystems and impacts on the environment. *J. trace elem. Medic. Biol*., **19**: 125-140.

Instituto Geológico 1993. Mapa geológico do município de Campinas, escala 1:50.000. Subsídios do meio físico-geológico ao planejamento do município de Campinas (SP). Programa: Cartas geológicas e geotécnicas para o planejamento ambiental na região entre Sorocaba e Campinas. São Paulo: Secretaria do Meio Ambiente.

Kabata-Pendias, A & Pendias, H. 2001. *Trace Elements in Soils and Plants*. 3^{a} ed. Boca Raton: CRC. Press. 413 pp.

Kumar, J. I. N., Soni, H.; Kumar, R.N. 2006. Biomonitoring of selected freshwater macrophytes to assess lake trace element contamination: a case study of Nal Sarovar Bird Sanctuary, Gujarat, India. *J. Limnol*., **65(1)**: 9-16.

Levinson, A.A. 1974. *Introduction to Exploration Geochemistry*. Applied Publishing: Wilmette, 614 pp.

Malavolta, E.; Vitti, G.C.; Oliveira, S.A. 1997. *Avaliação do Estado Nutricional das Plantas: Princípios e Aplicações.* 2.ed. Piracicaba: Potafos, 319 pp.

Markert, B. 1993. *Plants as Biomonitors: Indicators for Heavy Metals in the Terrestrial Environment*. Weinheim: VCH- Verlagsgesellschaftmbh, 645p.

Martins, A.P.L.; Reissmann, C.B.; Favaretto, N.; Boeger, M.R.T.; Oliveira, E.B. 2007. Capacidade da *Typha dominguensis* Pers. na fitorremediação de efluentes de tanques de piscicultura na Bacia do Iraí – Paraná. *Rev. Bras. Eng. Agríc. Ambiental*. **11(3):** 324–330.

Nordstrom, D.K. & Wilde, F.D. 2005. Reduction-Oxidation Potential (Electrode Method), Capter A6. In: F. D. Wilde, B. D. Radtke, J. Gibs, R. T. Iwatsubo, (eds), National Field Manual for the Collection of Water-Quality Data, U. S. Geological Survey Techniques in Water- Resources Investigations: Reston, Book 9.

Padaki, P.M.; Mcwillians, E.L.; James, W.D. 1992. Use of Spanish moss as an atmospheric monitor for trace elements. *J. Radioanal. Nucl. Chem*., **161**: 147-157.

Panichev, N; Mandiwana, K; Moema, D; Molatlhegi, R; Ngobeni, P. 2006. Distribution of vanadium(V) species between soil and plants in the vicinity of vanadium mine. Journal of Hazardous Materials, **137**: 649–653.

Pereira, J.C. 2005. Geoquímica de solos e sedimentos e impacto antrópico por elementos-traço na microbacia do córrego da Fazenda Santa Cândida, Área periurbana de Campinas, SP. Dissertação de Mestrado, Instituto de Geociências, Unicamp, 102p.

Piispanen, R & Lähdesmäki, P. 1983. Effect of vanadium on some water plants. *J.. Geol. Soc. Sweden*. **105**: 23-27.

Ravera, O.; Cenci, R.; Beone, G. M; Dantas, M.; Lodigiani, P. 2003. Trace element concentrations in freshwater mussels and macrophytes as related to those in their environment. *J. Limnol*. **62(1):** 61-70.

Salisbury, F.B. & Ross, C.W. 1992. Plant physiology. 4ed. Wadsworth Publishing Company, Belmont, 682 pp.

Weis, J.S. & Weis, P. 2004. Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environ. Intern*. **30**:685-700.

Zambello, F.R. & Enzweiler, J. 2002. Multi-element analysis of soils and sediments by wavelength-dispersive X-ray fluorescence spectrometry. *J Soil & Sediments*, **2 (1)**: 29-36.