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Anthropogenic Influences on Cd, Cr,Cu, Ni, Pb and Zn Concentrations in Soils and Sediments in a Watershed with Sugar Cane Crops at São Paulo State, Brazil

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ABSTRACT: The use of fertilizers NPK and amendments in sugar cane crops may change the heavy metals concentrations in soils, making them available for plants and, consequently, they can be transferred to the human food chain. This study describes the redistribution of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in soils with sugar cane crops due to fertilizers NPK and amendments at Corumbataí River basin, São Paulo State. The heavy metals concentrations were determined in samples of fertilizers NPK (5:25:25) and amendments (limestones, KCl, and phosphogypsum) by atomic absorption spectrometry (AAS). Heavy metals incorporated in fertilizers NPK and amendments are annually added in the sugar cane crops, but if utilized in accordance with the recommended rates, they do not raise the concentration levels in soils up to hazards values. Those applications promote the decrease of heavy metals concentration in soils profiles with sugar cane crops due to their fractionation to water soluble and/or exchangeable fractions, and the results still indicate that the profiles do not possess hazard levels in relation to heavy metals concentration. In relation to metals concentration in a sediment core, Cu, Ni, Pb and Zn values increased progressively from 1974 to 2000 due to anthropogenic activities, mainly sugar cane crops, indicating adverse biological effects to the aquatic environment and to organisms living in or having direct contact with sediments.

Key words: Fertilizers, Geochemistry, Environmental, Crops

INTRODUCTION

The Brazilian soils are normally acid, with low content of organic matter and deficient in micronutrients, which may cause decreasing of the agricultural productivity in Brazilian crops. The addition of inorganic fertilizers to soils and crops is an ordinary practice in agriculture worldwide because they are sources of macro (N, P, K, Ca, Mg and S) and micronutrients (B, Cl, Co, Cu, Fe, Mn, Mo, Ni, Se, Si and Zn). Micronutrients improve the yield of many temporary and perennial crops, reducing the production costs, making the agricultural products cheaper in the international market and, consequently, more competitive for exportation with improvement in the quality of the agricultural products (Malavolta, 1994).Brazilian phosphate ore is commonly rich in metals (Conceição and Bonotto, 2006; Conceição *et al.*, 2009a) and the first step to obtain the industrial products derived from phosphate ore is the flotation-separation process, where the apatites ($Ca_{10}F_2(PO_4)_6$) are concentrated (Fig. 1). The apatite is destroyed by the action of sulphuric acid (H_2SO_4) to produce phosphoric acid (H_3PO_4) and phosphogypsum ($10CaSO_4nH_2O$). Fertilizers such as monoammonium phosphate (MAP – $NH_4H_2PO_4$) and diammonium phosphate (DAP – $(NH_4)_2HPO_4$) are obtained by reacting H_3PO_4 with ammonium (NH_3). Further details about the wet process used in Brazilian factories are described by Saueia and Mazzilli (2006).

The sugar cane is the main agricultural activity in São Paulo State, being the fertilizers NPK and amendments applications in theses crops a very common practice. The long-term continued application of fertilizers NPK and amendments can redistribute the metals concentrations in soil profiles and, consequently, their availability for plants and subsequent transfer to the human food chain, mainly in acid soils (Martínez and Motto, 2000; Matos *et al.*,

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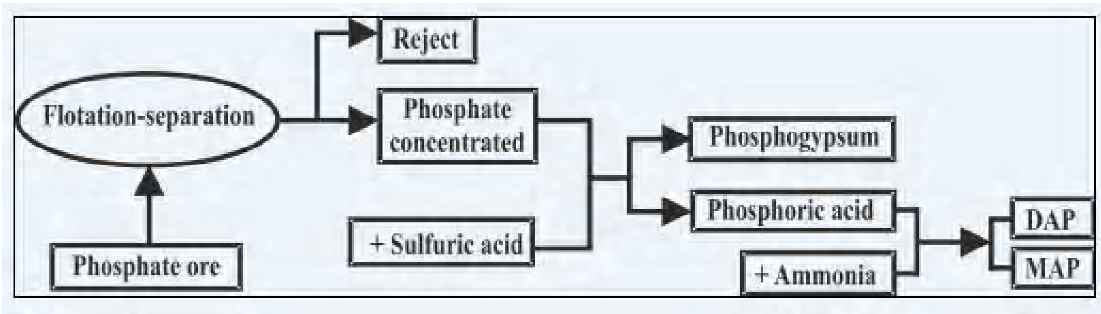

Fig. 1 . Simplified route of industrial (by) products from phosphate ore

2001; Cao *et al.*, 2003; Cao *et al.*, 2004; Panwar *et al.*, 2005; Li and Huang, 2007; Liu, *et al.*, 2007; Chen *et al.*, 2007; Cao *et al.*, 2008; Conceição *et al.*, 2009b). Additionally, these applications may also raise the heavy metals concentration in irrigation runoff/ drainage or in fluvial sediments from fertilized lands. Estimating metal concentration in fluvial sediments, associated with ^{210}Pb-derived chronology, which it provide a reliable method of dating over the last 100-150 years, is important to show the historical information on the temporal changes of pollution growth in a watershed, manly in urbanized or agricultural areas (Krishnaswami *et al.*, 1971; Farrington *et al.*, 1977; Goldberg *et al.*, 1978; Benninger *et al.*, 1979; Carpenter *et al.*, 1984; Crusius and Anderson, 1991; Ivanovich and Harmon, 1992; Baskaran and Naidu, 1995; Ravichandran *et al.*, 1995; Baskaran *et al.*, 1996; Godoy *et al.*, 1998; Santschi *et al.*, 2001; Bonotto and Lima, 2006).

Thus, the first objective of this paper was to evaluate the annual additions of Cd, Cr, Cu, Ni, Pb and Zn from fertilizers NPK and amendments applications to soils with sugar cane crops in one important hydrographic basin located in the middle-east part of the São Paulo State, Brazil, i. e. the Corumbataí River basin (Fig. 2a). This basin was chosen because it is affected by agricultural processes and wastes derived from the sugar cane crops (Conceição and Bonotto, 2003 and 2004). Two soil profiles, with different land use (PS-1 – soil with sugar cane crops and PS-2 – natural soil without anthropogenic activities) were also measured in the same metals in order to confirm the long-term effect of fertilizers NPK and amendments applications in agricultural soils that covered the Corumbataí River basin. Besides, the Cd, Cr, Cu, Ni, Pb and Zn concentrations in sediments also were estimated to indicate the history of possible anthropogenic influences. Moreover, a contamination index has been applied to provide basis for comparison of potential heavy metals hazards.

The Corumbataí River basin extends over an area of about 1710 km^2 in the middle-east part of the São Paulo State (Fig. 2a). It lies between 22º05' and 22º40' S and 47º25' and 47º55' W, being about 250 km west of the Atlantic Ocean coast. The Corumbataí River basin occurs in an eroded belt in the cuestas zone of the Depressão Periférica Geomorphological Province (Penteado, 1976). This province delimits the northeastern edge of the basaltic flows in the Paraná sedimentary basin and the crystalline plateau. Topographically, the region is a great plain, with maximum altitude of 800 m and minimum of 470 m. The Corumbataí River and tributaries start flowing in the cuestas zone, reaching the Piracicaba River after crossing Rio Claro city, the most important municipality in the basin, with 180,000 inhabitants. The average monthly flow rate at Santa Terezinha, close to the confluence with Piracicaba River, was 26.45 m^3/s, with a maximum value of 168.36 m^3/s (February 1995) and a minimum value of 5.96 m^3/s (September 1994) (Conceição and Bonotto, 2004).

The climate of the region is Cwa type (Köeppen´s classification), i. e. tropical rainy weather characterized by wet summer (October through March) and dry winter (April through September); mean temperature in almost all months is higher than 18ºC, reaching 22ºC in the hottest one (December). The area often has 55 - 65 days of rain per year, with more than 80% of the precipitation falling between October through March (Conceição and Bonotto, 2003). For more than 50% of the year (October - April) the area is dominated by tropical and equatorial air masses, with the winds coming from the S and SE. The mean annual rainfall was 1,572 mm (Conceição and Bonotto, 2004). The Corumbataí river basin comprises several stratigraphic units of the giant Paraná sedimentary basin (Paleozoic - Cenozoic) (IPT, 1981): the Tubarão Group (Itararé Subgroup and Tatuí formation), Passa Dois Group (Irati and Corumbataí formations), São Bento Group (Pirambóia, Botucatu and Serra Geral formations) and different types of Cenozoic covers like the recent deposits, terrace sediments and the Rio Claro formation. Following USDA (1999) nomenclature, the major soil types in the Corumbataí river basin are ultisols and oxisols, which cover about 75% of the basin area (Fig. 2a). Other minor soil types at Corumbataí River basin include alfisols, orthents, entisols and quartzipsamment. The land use is mainly used for sugar cane crops (55%) and pasture (28%) (Fig. 2b).

MATERIALS & METHODS

The soils that recovered the Corumbataí River basin are acids with low cation exchangeable capacity (CEC) and organic matter (Conceição and Bonotto, 2003). Herewith, a large amount of fertilizers NPK and amendments are applied every year in sugar cane crops. To measure the annual additions of Cd, Cr, Cu, Ni, Pb and Zn due to fertilizers NPK and amendments applications, two sample of 2 kg of fertilizers NPK 5:25:25 type (5% of nitrogen, 25% of phosphate and 25% of potassium – F-1) and amendments (KCl – F-2, limestones – F-3 and phosphogypsum – F-4) utilized in sugar cane crops at Corumbataí River basin were collected. Two soil profiles in Ultisols were sampled in 1 m deep backhoe pits (Fig. 2 and Table 1). At each site, two samples of 2 kg of soil were collected from every depth range. The PS-1 soil profile is located in areas with sugar cane crops, where the application of fertilizers NPK and amendments has occurred for 40 years. The PS-2 soil profile was collected in the same soil type (derived from the same rock - Corumbataí

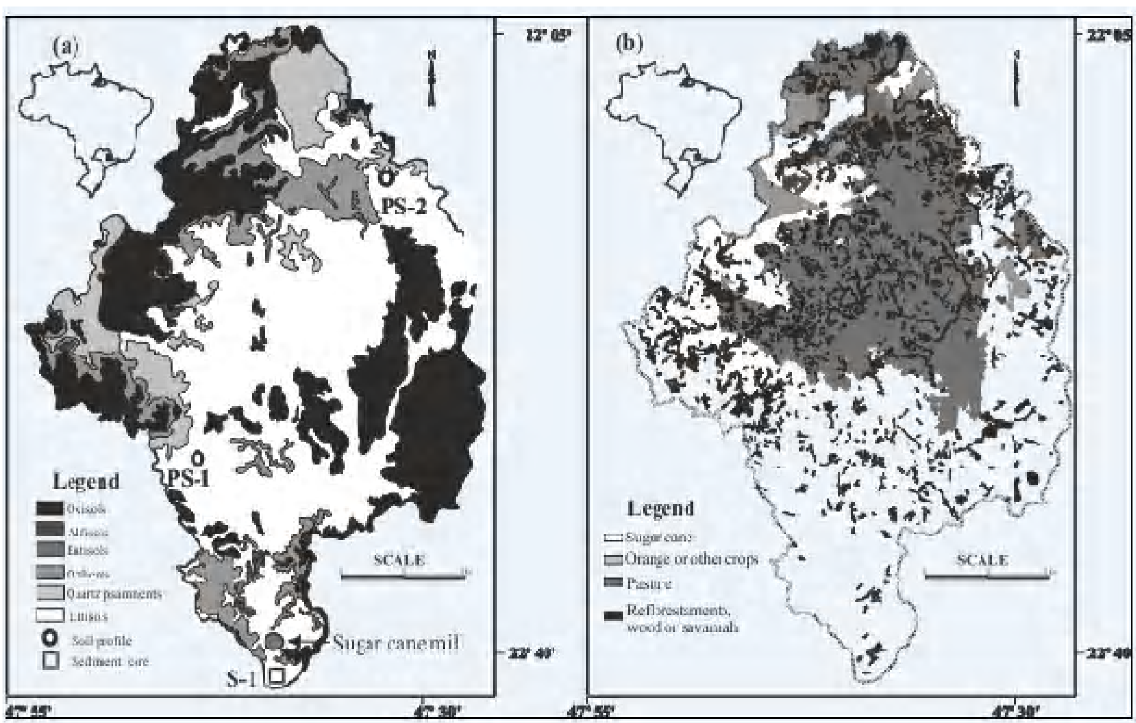

Fig. 2. Maps of soils (a), with sampling points of soil profiles, and land use (b) at Corumbataí River basin

Table 1. Main characteristics of the soil profiles sampled at Corumbataí River basin

Code	Depth range (cm)	Sampling depth (cm)	Grain size[a]	Color[b]
		Soil profile PS-1		
PS-11	0 to -18/20	-10	Clay loam and clay	Yellow red
PS-12	-18/20 to -33/35	-30	Clay loam and clay	Yellow red
PS-13	-33/35 to -70/74	-50	Clay loam and clay	Yellow red
PS-14	-70/74 to -97/103	-80	Clay loam and clay	Yellow red
		Soil profile PS-2		
PS-21	0 to -14/15	-10	Clay loam and clay	Yellow red
PS-22	-14/15 to -40/48	-30	Clay loam and clay	Yellow red
PS-23	-40/48 to -60/63	-50	Clay loam and clay	Yellow red
PS-24	-60/63 to -70/92	-80	Clay loam and clay	Yellow red

[a]ABNT (1980) classification [b] Munsell (1975) classification

Formation) in an area covered by natural vegetation (forest) and identical depths of the PS-1 soil profile. Because such site is located in areas without anthropogenic inputs, it was possible to perform evaluations concerning the heavy metals redistribution caused by continuous application of fertilizers NPK and amendments.

The sediment core samples were collected at the confluence of Corumbataí and Piracicaba rivers, downstream from Rio Claro city, agricultural areas and a sugar cane mill (Fig. 2a and 2b). This sampling point was chosen because it is located in the mouth of the Corumbataí River, and, consequently, all modification in sediment quality related to land use of the Corumbataí River basin may be identified. The sediment core was collected with a Wildco Model 77263 hand core sediment sampler, which it is composed by a steel liner core tube with a plastic eggshell core catcher to hold the sample intact during the extraction (no compaction or perturbation). After the sampling, the core was transportation to the laboratory and the sediment extruded with a polyethylene embolus and cut into 7 sections (SE-1 up to SE-7) with thickness of 3.4 cm each.

All samples of fertilizers NPK, amendments, soil profiles and sediments were air-dried, disaggregated and crushed a 200 mesh. The Cd, Cr, Cu, Ni, Pb and Zn concentration in all samples was measured through the use of atomic absorption spectrometry (AAS - *Varian*, model 240FS) in 0.5 g of crushed sample digested with HCl (30 mL) + HNO_3 (10 mL) (Gomes, 1984). The lower AAS detection limits are Cd = 1 mg/kg; Cr, Cu, Ni and Zn = 2 mg/kg; Pb = 5 mg/kg, being the upper AAS limit of 5000 mg/kg to all analyzed elements. The soils pH were determined by mixing fresh soil and deionized water (1:2, w/v), being the sample agitated for 1 h, filtered (0.45 μm Millipore Membrane) and the pH measured by *Analion* digital meter coupled to a combination glass electrode (Malavolta, 1994).

RESULTS & DISCUSSION

The Cd, Cr, Cu, Ni, Pb and Zn concentrations in fertilizers NPK and amendments used in sugar cane crops at Corumbataí River basin are shown in Table 2. The phosphogpsum contributes with all metals, being the phosphate fertilizers NPK and limestones responsible for the highest input of Cr, Cu, Ni and Zn and Cd and Pb, respectively (Fig. 3). The KCl, fertilizers NPK and limestones possess the lowest Ni and Zn, Cd and Pb and Cr and Cu concentration, respectively. If the comparison is performed with the world range for phosphate rocks used worldwide as phosphate fertilizers, i.e. Cd = 1-100 mg/kg, Cr = 7-500mg/kg, Cu =1-1000 mg/kg, Ni = 0-100 mg/kg, Pb = 0-10 mg/kg and Zn = 4-1000 mg/kg (Malavolta, 1994), then, it is possible

Table 2. Heavy metals concentration (ppm) in fertilizers NPK and amendments used in sugar cane crops at Corumbataí River basin

Sample	Code	Cd	Cr	Cu	Ni	Pb	Zn
Fertilizers NPK	F-1	1	19	19	21	27	63
		2	18	20	23	27	57
KCl	F-2	2	4	10	11	33	18
		2	7	14	15	30	18
Limestone	F-3	5	3	5	18	43	34
		5	3	5	20	44	30
Phosphogypsum	F-4	3	8	10	18	33	29
		3	7	6	14	27	27

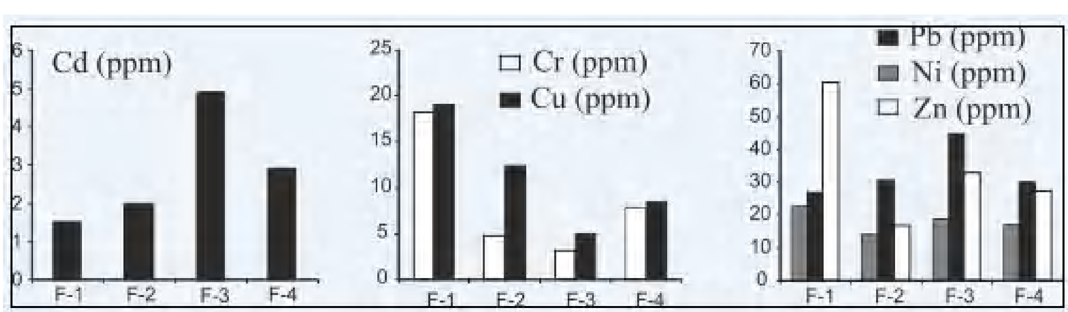

Fig. 3. Average of heavy metals concentration in fertilizers NPK and amendments used in sugar cane crops at Corumbataí River basin. F-1 = phosphate fertilizers NPK; F-2 = KCl; F-3 = limestones; F-4 = phosphogypsum

to verify that the Cd, Cr, Cu, Ni and Zn concentration is within the world range, whereas the Pb concentrations are higher in all products.

In general, the cultivation of the sugar cane starts in September/October at Corumbataí River basin, when are applied at rates of 600 kg/ha (1 ha = 10,000 m^2) of phosphate fertilizers NPK, 2 ton/ ha of limestones, 200 kg ha^{-1} of KCl and 1.5 ton/ha of phosphogypsum per year. Using the average data presented in Table 2 and these applied rates, it is possible to evaluate the maximum average annual addition of metals distributed per arable land unit, which corresponds to 17.8, 31.2, 75.2, 69.5, 138.8 and 114.9 g/ha for Cd, Cr, Cu, Ni, Pb and Zn, respectively. Micronutrients as Cu, Ni and Zn are essential for plant life, without evidencing hazards to the human health. The sugar cane crops must receive an annual addiction of micronutrients of 172.8 and 460.8 g/ha of Cu and Zn, respectively (Malavolta, 1994), and the phosphate fertilizers and amendments application in sugar cane crops are responsible for annual addition of 75.2 and 114.9 g/ha of Cu and Zn, respectively. Thus, these lower inputs of Cu and Zn in relation to the necessary values for sugar cane crops make indispensable the use of other sources of micronutrients, such as oxides, acids, salts and chelates.

Table 3 exhibits a comparison of the maximum allowable release of Cd, Cr, Cu, Ni, Pb and Zn into Brazilian and British soils. The Brazilian limits are higher than the British ones, except for Pb, because they refer to the addition of sewage mud into soils. The metals addition is greatly lower than the annual tolerance limits. The number of years of continuous application to reach the maximum annual Brazilian tolerance limits ranged from 107 (Cd) to 1218 years (Zn). Therefore, the metals, being micronutrients or not, determined in fertilizers NPK and amendments and applied in sugar cane crops at Corumbataí River basin, if used according to the recommended rates, do not raise their concentration in soils to harmful levels in a short/ medium periods of time. Such finding is supported by various international (Mulla *et al.,* 1980; Mortvedt, 1985; Alcordo and Reigheigl, 1993) and national (Malavolta, 1994; Conceição and Bonotto, 2006; Conceição *et al.,* 2009a) studies.

The results of Cd, Cr, Cu, Ni, Pb and Zn concentrations in two soils profile with different land use at Corumbataí River basin are presented in Table 4 and Fig. 4. The pH values were higher in PS-1 (mean = 5.89) than in PS-2 (mean = 4.85), reflecting the use of large amount of limestones in sugar cane crops. Using the world range for these metals in agricultural soil (Malavolta, 1994), i.e. Cd = <1-2 ppm, Cr = 100-300 ppm, Cu = 6-40 ppm, Ni = 20-40 ppm, Pb = 2-200 ppm and Zn = 26-94 ppm (Malavolta, 1994), then, it is possible to observe that the Cd, Cr, Cu, Ni and Pb concentrations are within this world range, whereas the Zn concentrations are lower than the reference values.

The higher annual use of limestones ($CaCO_3$) may decrease the metals mobility in soils profile (Malavolta, 1994; Martínez and Motto, 2000). The use of fertilizers NPK may also induce the metals immobilization, mainly lead with the formation of pyromorphite ($Pb_5(PO_4)_3(F,Cl)$) (Cotter-Howells, 1996; Cao *et al.*, 2003; Cao *et al.*, 2004; Cao *et al.*, 2008). Thus, it is expected that the metals concentrations in the soil profile with sugar cane crops will be higher than in the natural soil profile. However, as indicated by results shown in Table 4 (Fig. 4), this fact does not occur, so there is not accumulation of metals in the soil profile where there are fertilizers NPK and amendments applications. On the other hand, the Cd, Cr, Cu, Ni, Pb and Zn concentrations decreased in PS-2 (soil profile with sugar cane crops). Large amounts of N (as fertilizer NPK, being N = NH_4Cl), SO_4^{2-} (as phosphogypsum - $CaSO_4.2H_2O$) and K and Cl^- (as KCl and fertilizer NPK, being K = KCl) are applied in the studied area. The comprehension regarding the mobility of all metals must also be associated with these products. The higher K, N and SO_4^{2-} inputs increase the mobility of all metals, mainly to Cr, Cu and Ni, as indicated by Eriksson (1990), Martínez and Motto (2000), Matos *et al.,* (2001), Chen et al. (2007) and Liu et al. (2007). This increase in heavy metals mobility is attributed to fractionation of these metals to water soluble and/or exchangeable fractions (Eriksson, 1990; Bringham *et al.,* 1984; Tu *et al.,* 2000; Liu *et al.,* 2007).

Thus, the change in the speciation and mobility of these metals may be associated not only with the use of fertilizers NPK, but mainly the amendments application in sugar cane crops at Corumbataí River basin, allowing their lixiviation during the wet period or uptake by sugar cane crops and, consequently, decreasing their concentration in PS-1. Only more detailed studies based on progressive and selective chemical extractions could give more information about the (non) incorporation of metals in both soils profiles, i.e. the different distribution of these heavy metals in exchangeable cations, organic matter, “free” oxides of Fe, Mn and Al and soils residues that can be separated into size fractions (sand, silt and clays).

Table 5 presents the soil quality guidance for agricultural soils found at São Paulo State (CETESB, 2005). The quality reference values are the heavy metals concentrations in soils that define a soil as clean at São Paulo State. It is considered prevention values the heavy metals concentrations in an agricultural soil whose values are higher than these ones that might cause prejudicial changes in soil quality. On its turn, the intervention values are the heavy metals concentrations in soils and, if they are greater than such values, there are potential risks, direct or indirect,

Table 3. Tolerance limit, estimated annual addition of metals, and number of expected years for reaching the allowable limit

Element	Annual allowable limit (UK)[a] (kg/ha)	Annual allowable limit (Brazil)[b] (kg/ha)	Annual addition (kg/ha)	Number of years (UK)	Number of years (Brazil)
Cd	0.166	1.9	0.02	9	107
Cr	33.33	-	0.03	1068	-
Cu	9.33	75.0	0.07	124	997
Ni	2.33	21.0	0.07	34	302
Pb	33.33	15.0	0.14	240	108
Zn	18.66	140.0	0.11	162	1218

[a]Adriano (1986) [b]CETESB (1999)

Table 4. pH and heavy metals concentration (ppm) in soils profiles with different land use at Corumbataí River basin

Code	Ph	Cd	Cr	Cu	Ni	Pb	Zn
			Soil profile PS-1				
PS-11	5.81	<1	41	13	10	29	12
		<1	39	12	9	25	14
PS-12	6.02	<1	41	14	11	27	14
		<1	40	15	9	26	15
PS-13	5.93	<1	42	15	11	28	15
		<1	40	14	12	25	11
PS-14	5.81	<1	42	15	12	29	15
		<1	41	16	10	26	12
			Soil profile PS-2				
PS-21	4.88	1	70	21	15	35	18
		1	67	19	13	31	17
PS-22	4.82	1	70	22	16	33	17
		1	66	20	14	31	19
PS-23	4.78	1	72	20	14	33	18
		1	69	22	16	30	18
PS-24	4.92	1	68	22	15	32	18
		1	71	19	13	35	17

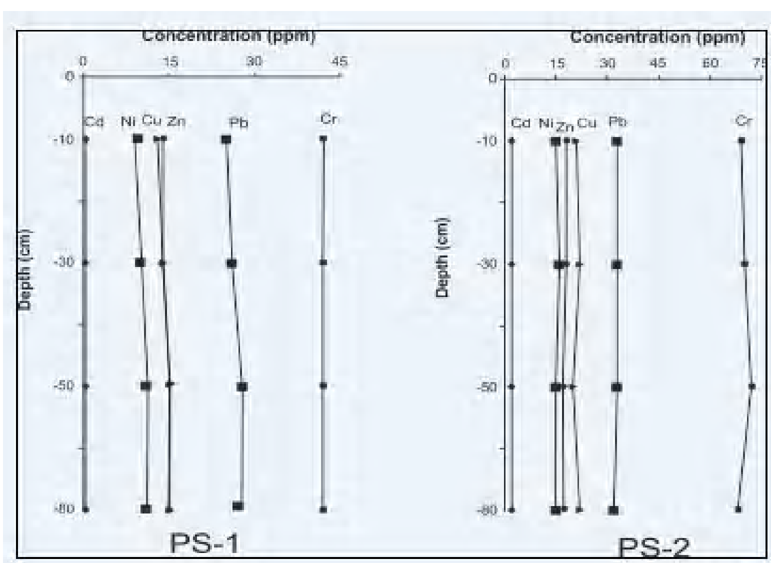

Fig. 4 . Distribution in depth (cm) of average of metals concentration (ppm) in soils profiles at Corumbataí River basin. PS-1 = soil profile with sugar cane crops; PS-2 = soil profile with natural vegetation

Table 5. Soil quality guidance (mg/kg) for agricultural soils found at São Paulo State, according to CETESB (2005)

Heavy metal	Values of quality reference	Values of prevention	Values of intervention
Cd	<0.5	1.3	3
Cr	40	75	150
Cu	35	60	200
Ni	13	30	70
Pb	17	72	180
Zn	60	300	450

to human health. In both soils profiles, all Cu and Zn concentrations are lower than the quality reference values, with the Ni concentrations values slightly higher than these values only in the PS-2. The Cd, Pb and Zn concentrations, in both profiles, are lower than the prevention values. Thus, the results indicate that both profiles do not possess hazard levels of heavy metals concentration. Besides, these values should be utilized as reference values to control the introduction of some substances in the soils that recovered the Corumbataí River basin.

The results of Cd, Cr, Cu, Ni, Pb and Zn concentrations in sediment core are shown in Table 6. Such table also reports the expected deposition year for each sediment layer. The age of each sediment section was evaluated by Sieber (2002), through the use of ^{210}Pb-derived geochronology; model CRS - constant rate of supply of unsupported/excess (Robbins, 1978; Appleby and Oldfield, 1978). The deposition year was plotted against depth in Fig. 5, depicting linear feature of the graphical solution involving these parameters. The deposition rate (mm/yr) value corresponded approximately to 4.7 mm/yr. This result is inside the range of the sedimentation rate obtained by Orlando (1993) and Bonotto and Lima (2006).

The historical trends of selected metals are plotted in Fig. 6. As shown in this fig, there was not significant variation in the concentrations of all metals during the 1953 and 1966, fact that may be considered as a natural background of the area. The Cd and Cr concentrations values were practically constant in 40 years of deposition and the Cu, Ni, Pb and, mainly, Zn concentrations enhance progressively from 1974 to 2000, probably as a consequence of increasing

Table 6. Metal concentrations in sediments from Corumbataí River basin (mg/kg)

Code	Depth (cm)	Deposition year[a]	Cd	Cr	Cu	Ni	Pb	Zn
S-1	-1.7	1995	1	18	45	28	35	161
S-2	-5.1	1988	1	20	38	24	33	159
S-3	-8.5	1982	1	20	36	20	31	142
S-4	-11.9	1974	1	18	29	18	28	134
S-5	-15.3	1966	1	23	23	13	26	47
S-6	-18.7	1959	1	21	22	13	26	39
S-7	-22.1	1953	1	18	21	11	27	40
TEL[b]	---	---	0.6	37.3	35.7	18.0	35.0	123.0
PEL[b]	---	---	3.5	90.0	197.0	35.9	91.3	315.0

[a]Sieber (2002) [b](CONAMA, 2004)

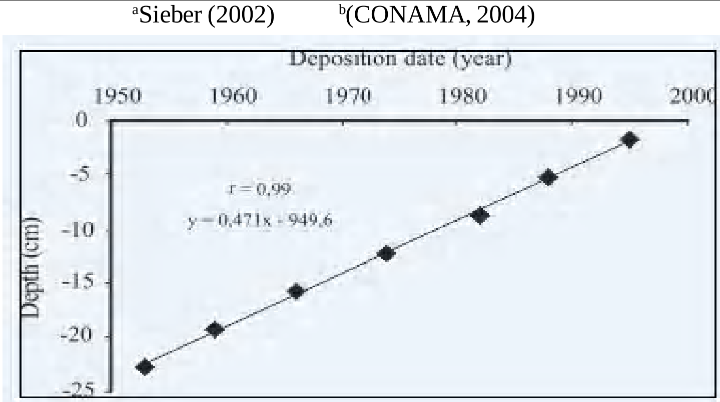

Fig. 5. Depth versus deposition date of sediment core from Corumbataí River basin

anthropogenic activities in the drainage basin of the Corumbataí River. As discussed in this work, the fertilizer NPK and amendments application is responsible for an annual anthropogenic input of Cd, Cr, Cu, Ni, Pb and Zn. However, concentrations of these metals did not increase in soils from Corumbataí River basin, indicating that the Corumbataí River receives from laminar erosion large quantities of these metals, mainly in wet period, due to agrichemical activities. Conceição and Bonotto (2003) also reported that the higher concentrations of dissolved uranium and phosphate in Corumbataí River are more pronounced during wet periods, when natural and fertilizer-derived U are more easily released from the soil cover.

In the Corumbataí River basin, the main industrial development has been associated with of the sugar cane mill located in the mouth of the Corumbataí River and surrounding neighborhoods (Fig. 2a), which started its activities in 1938. Expressive development of this sugar cane mill occurred in the middle of 1970s (Garcia, 2000), with the sugar cane activities build up its crops area from 10% up to 55% of the total area of the Corumbataí River basin during 1974-2000. With this progressive enhance of sugar cane crops area, there also is an enhance of annual inputs of all metals due to fertilizer NPK and amendments and, consequently, the amounts of all metals released from soil cover to Corumbataí River. Thus, this fact can explain the increase of Cu, Ni, Pb and Zn concentrations in sediments core during 1974-2000. The Resolution CONAMA n$_o$ 344 suggests the orienting values for sediment quality guidelines used in Brazil, which provides the maximum concentration limits in sediment quality for the protection of aquatic life due to the possibility of assimilation into the environment and recognized human hazards. The threshold effect level (TEL) represents the concentration below which adverse biological effects are expected to occur rarely and the probable effect level (PEL) defines the level above which adverse effects are expected to occur frequently. The criterion established by such resolution is based in the Canadian Sediment Quality Guideline (Environment Canada, 2002). As indicated in Table 6, all metals concentrations are lower than the probable effect level (PEL).

For a better evaluation of the metal distributions in the sediment core, it was used the normalization of all metal concentration for TEL values (Fig. 7). This factor is frequently utilized and indicates if the metal find more enrichment (EF>1) or depletion (EF<1) in

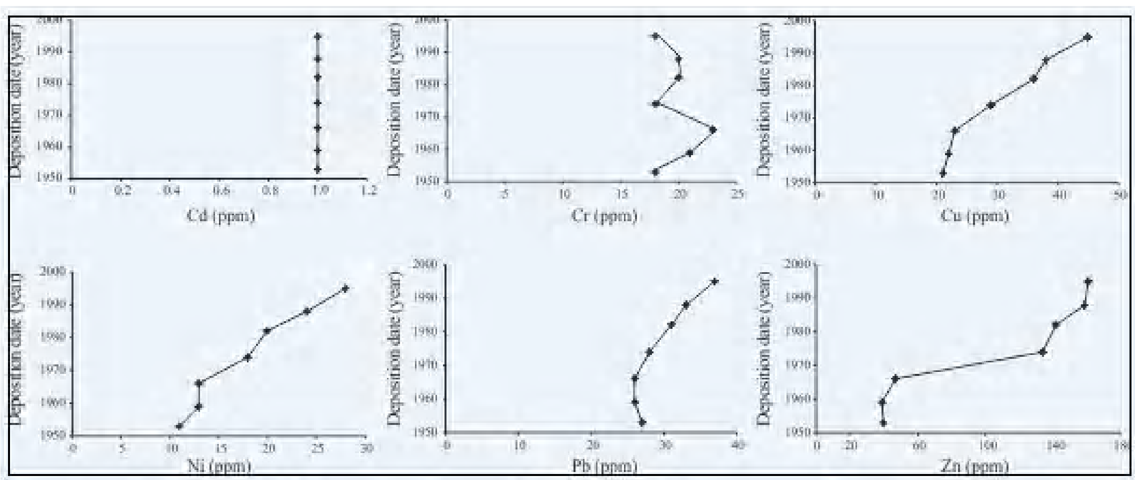

Fig. 6 . Metal concentrations profiles in sediment core from Corumbataí River basin

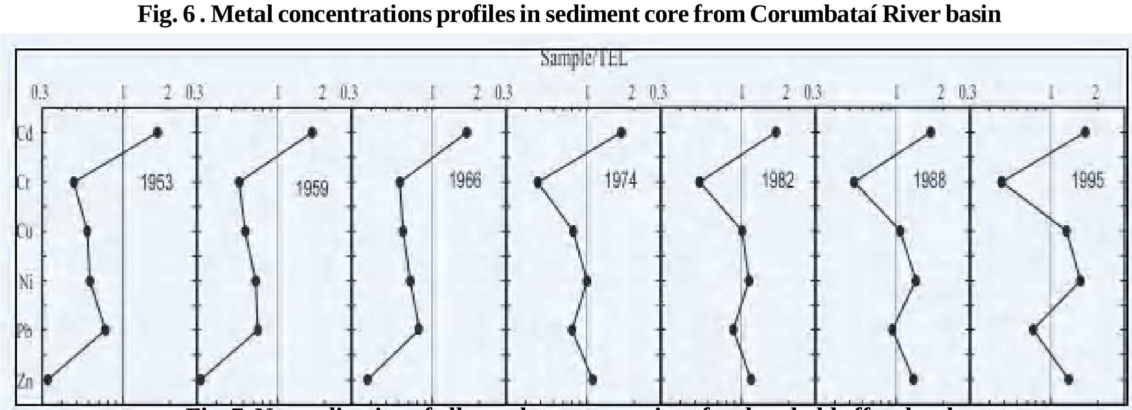

Fig. 7. Normalization of all metals concentrations for threshold effect level

relation to TEL values. The concentrations values of all metals in sediments during the 1953 and 1966 were lower than the TEL values, except for Cd. The Cr and Pb concentrations are lower than the TEL values. However, Cu, Ni and Zn concentrations are higher than the TEL limits, mainly after 1982. The increase of Cu, Ni and Zn concentrations above the TEL limits can indicate adverse biological effects to the aquatic environment and to organisms living in or having direct contact with sediments. In addition, toxicity test should be used to identify the relationship between the Cu, Ni and Zn concentrations in benthic and epibenthic organisms. Besides, the elevate values of Cu, Ni and Zn suggest the necessity of the implantation and evaluation of sediment quality monitoring or managements programs, as benchmarks, targets or prioritization tools for the assessment and remediation.

CONCLUSION

The Cd, Cr, Cu, Ni, Pb and Zn concentrations in fertilizers NPK and amendments used in sugar cane crops at Corumbataí River basin are within the worldwide range for these products. These metals environmental hazards to population due to fertilizers NPK and amendments are also negligible. The addition of inorganic phosphate fertilizers to soils and crops has become a common practice in sugar cane crops and the results show that these metals concentrations decrease in the agricultural soil, in relation to natural soils, probably due to fractionation of these heavy metals to water soluble plus exchangeable fractions. Besides, in both soil profiles, the Cd, Cr, Cu, Ni, Pb and Zn concentrations always presented below the reference values utilized in São Paulo State, Brazil. With this study, it is possible confirming that the increase of heavy metals concentration in soils with sugar cane crops must not be associated with fertilizers NPK and amendments applications, but to other anthropogenic sources such as domestic and industrial residues/wastes, sewage sludge and pesticides. Besides, the increasing concentrations of Cr, Ni, Pb and Zn in sediments were resulted from increasing anthropogenic activities in the drainage basin of the Corumbataí River, confirmed by sugar cane crops growth observed in this basin during 1974-2000. The Cu, Ni and Zn concentrations are above the TEL limits, suggesting the necessity of sediment quality monitoring or managements programs, as benchmarks, targets or prioritization tools for the assessment and remediation.

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