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Metal Concentrations in Soil in the Vicinity of a Municipal Solid Waste Landfill with a Deactivated Medical Waste Incineration Plant, Ribeirão Preto, Brazil

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Concentration of metals in many environments have increased as a direct result of anthropogenic activities such agricultural practices, mineral exploration, industrial processes and solid waste management. Among these activities, it is known that the municipal solid waste incineration can release metals into the environment with potential health hazards (Alumaa et al., 2002; Llobet et al., 2002).

In Brazil, according to IBGE (Brazilian Institute of Geography and Statistic), 76% of solid wastes have their final disposal in dumps or illegal landfills, 13% in controlled landfills, 10% in sanitary landfills 0.9% in composting plants, and 1% in recycling or incineration plants. The Brazilian population generates 90,000 metric tons per day of solid waste, while it is also estimated that 1000 tons per day of medical waste are generated in the country (IBGE, 2002).

Although municipal governments cannot guarantee that all hospitals, clinics and other pathogenic activities have their contaminated waste properly treated, in many hospitals waste is incinerated or disinfected with microwave technology. Incineration of medical waste includes a number of different products such as paper, plastic materials (vacutainer caps, plastic bags and packings, glass), organic and inorganic chemicals, metals, as well as biological materials such as blood, tissues, body members, urine and stool. Due to their toxicity and potential hazards, the emission of toxic metals is an issue of great concern (Weir, 2002).

Ribeirão Preto (São Paulo State, Brazil) has a population of more than 500,000 inhabitants. A municipal landfill site (MLS) for urban waste disposal has been operating since 1989. It was integrated with a medical waste incinerator plant (MWIP). The MWIP, even been considered a small-size plant with a capacity of 3300 tons/year, was deactivated in February 2002, because it was outdated. Nowadays, a microwave system technology for treatment of Ribeirão Preto and region medical waste is being utilized.

A study conducted in 2000, before MWIP deactivation, which evaluated some metals levels in soils in distances up to 500 m from the MLS/MWIP, showed that seven metal levels significantly increased when compared to a local protected area (Segura-Muñoz, 2002). The purpose of the present study was to assess the

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magnitude and distribution of As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Sn, Tl and V around the MLS/MWIP by measuring their concentrations in soil within 2 km of distance, and to compare metal level variations in the MLS-MWIP area with the concentrations obtained in the 2000 survey (Segura-Muñoz, 2002).

MATERIALS AND METHODS

The MLS/MWIP is located in the South-Western region of Ribeirão Preto, with an extension of approximately 150,000 m^2, surrounded by agricultural areas. The soil in this area is classified as dusky latosol (Alvarenga et al., 1986). A total of 32 duplicated surface soils were sampled in 2003 along four transects established at the north (N), east (E), west (W) and south (S) directions from the border of the MLS/MWIP (Fig. 1). Six duplicated soil samples from the Santa Teresa Forest Ecological Station of Ribeirão Preto were also collected as control samples. This area, which is located 8 km away from the MSL/MWIP, is the best preserved forest in Ribeirão Preto, and it is characterized by having the same soil type. All samples were transported in polyethylene boxes. All materials used for sampling and storage were previously soaked overnight in 30% (v/v) HNO_3 65% Suprapur (E. Merck, Darmstadt, Germany).

Soil samples were air-dried at room temperature until constant weight. Samples were then hand-crushed in a mortar and sieved through a 1.5 mm mesh screen. About 0.5 g of soil were treated with 65% nitric acid Suprapur (E. Merck, Darmstadt, Germany) in teflon bombs. All samples were kept at room temperature during 8 h, and then heated at 90°C for 8 h. After cooling, solutions were filtered and made up to 25 ml with deionized water. Arsenic, Be, Cd, Cr, Hg, Mn, Pb, Sn, Tl, V were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer Elan 6000). The levels of Ni were analyzed by atomic absorption spectrophotometry with graphite furnace atomization (AAE-GF, UNICAM 939/959) (Schuhmacher et al., 2002).

The accuracy of the instrumental methods and analytical procedures was checked by using certified soil samples (121-S, 127-S) from Quality Control Technologies Pty. Ltd. (Queensland, Australia). Detection limits in soils were the following: 0.02 ppm for Ni; 0.03 ppm for Cd, Mn, Pb and Tl; 0.05 ppm for Hg and Sn; 0.1 ppm for As, and 0.25 ppm for Be, Cr and V.

Statistical analysis was performed using the Statistical Program GraphPad Prism (Version 3.02 for Windows, GraphPad Software, San Diego, CA, USA). The statistical significance of the differences was checked using the Kruskal-Wallis Rank Sum Test followed by a Multiple Comparisons Test and Mann-Whitney Rank Sum Test (Motulsky, 1999). A probability of 0.05 or less was considered to be significant. The results were compared with the Guideline Values for Intervention Levels established for São Paulo State Soils by the São Paulo Environmental Sanitation Company (CETESB, 2001).

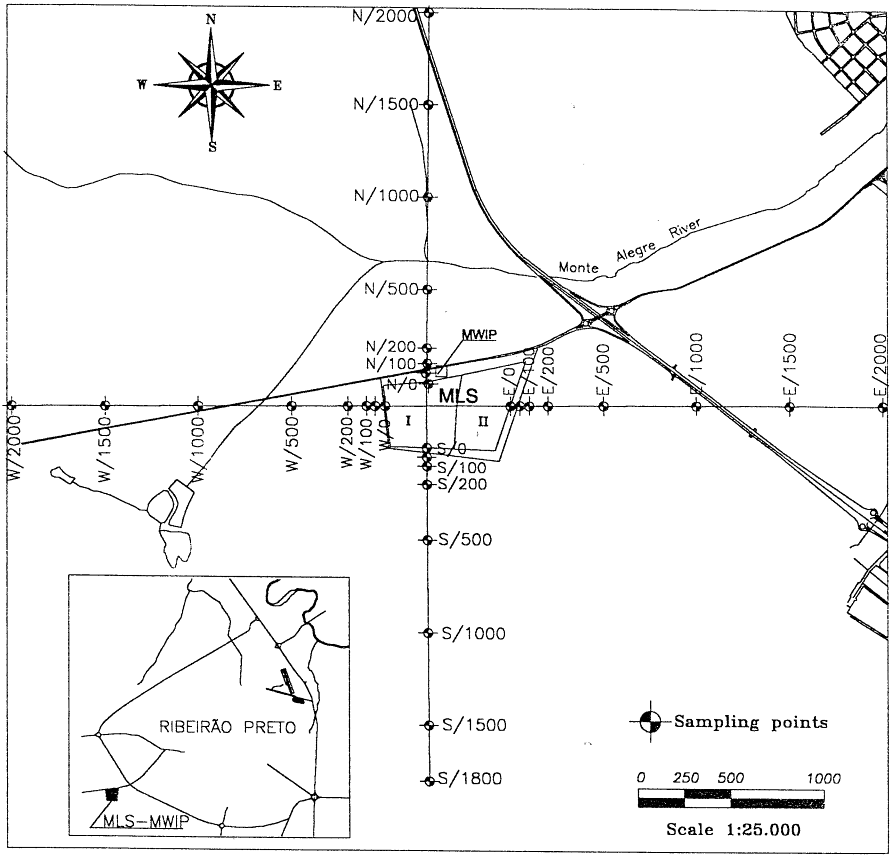

Figure 1. Location of sampling points in the area of Ribeirão Preto Municipal Landfill Site (MLS)/Medical Waste Incineration Plant (MWIP), Ribeirão Preto, São Paulo, Brazil. Numbers represent the distance in meters from the MLS limits.

RESULTS AND DISCUSSION

The concentrations of the 11 elements analyzed in the 32 soil samples are shown in Table 1. In general terms, the current concentrations were comparable to those commonly reported in the literature for urban areas (Pichtel et al., 1997; CETESB, 2001). Results showed that soils in the vicinity of the MLS/MWIP contained not significantly higher concentrations of metals when compared to Santa Teresa Forest control samples ($p>0.05$). Most metal levels did not exceed critical limits for agricultural soil defined by São Paulo Environmental Sanitation Company (CETESB, 2001). The highest levels correspond to Mn and V, showing values belong to the *"contaminated soil"* and *"slight contaminated soil"* categories according to the HMSO - London Classification of contaminated soils (HMSO, 1991).

Table 1. Metal concentrations in soil samples collected in the vicinity of the MSL/MWIP (n = 32).

Metal	Mean	Standard Deviation	Median	Minimum Value	Maximum Value	Maximum value for agricultural soil*
As	2.45	1.04	2.37	1.11	6.58	25
Be	1.02	0.42	0.95	0.40	2.13	--
Cd	0.23	0.04	0.23	0.16	0.34	10
Cr	32.3	22.5	24.2	17.4	100.6	300
Hg	0.05	0.02	0.05	0.02	0.08	2,5
Mn	636.9	398.9	429.6	288.3	1602.3	--
Ni	16.6	8.0	14.0	10.6	46.8	50
Pb	8.59	1.90	8.32	6.05	13.85	200
Sn	0.37	0.16	0.33	0.80	0.12	--
Tl	0.09	0.04	0.09	0.04	0.19	--
V	309.7	23.2	308.8	282.6	411.4	--

Results are given in mg kg^{-1} (dry weight).
* (CETESB, 2001)

For most elements, no significant differences ($p<0.05$) were noted between samples collected at increasing distances within a radius of 2000 m from the MSL/MWIP (Table 2). Only Pb and Tl showed significant differences between distances. Lead values were notably lower than the maximum values accepted for agricultural soil in São Paulo (CETESB, 2001), while Tl levels were comparable with previously reported concentrations in soils near municipal solid waste incinerators (Schuhmacher et al., 1997; Meneses et al., 1999; Llobet et al., 2002).

Table 2. Concentrations of metals in soils at increasing distances (m) from the MLS/MWIP.

Metal	0-500	500-1000	1500-2000	p
As	2.46 ± 1.19	2.46 ± 1.06	2.43 ± 0.81	NS
Be	1.21 ± 0.44	0.81 ± 0.29	0.84 ± 0.32	NS
Cd	0.22 ± 0.03	0.21 ± 0.03	0.25 ± 0.05	NS
Cr	24.03 ± 6.02	35.01 ± 23.36	46.26 ± 35.21	NS
Hg	0.05 ± 0.02	0.05 ± 0.02	0.05 ± 0.01	NS
Mn	665.7 ± 431.6	598.4 ± 349.4	617.9 ± 423.5	NS
Ni	14.93 ± 3.96	17.63 ± 8.06	18.95 ± 13.10	NS
Pb	7.61 ± 1.23^{a}	9.52 ± 2.59^{b}	9.60 ± 1.31^{b}	<0.05
Sn	0.33 ± 0.11	0.37 ± 0.17	0.46 ± 0.21	NS
Tl	0.11 ± 0.03^{a}	0.08 ± 0.03^{b}	0.07 ± 0.02^{b}	<0.05
V	304.0 ± 16.5	320.5 ± 39.2	310.3 ± 7.1	NS

Different superscripts (a, b) indicate significant differences at $p< 0.05$. NS: not statistically significant ($p>0.05$).

Cadmium, Mn, Pb, Cr and Hg concentrations in soil samples collected in 2000 and 2003 are shown in Table 3. It was only possible to compare the levels in samples collected until 200-500 m from the stack, having as limitation the distances reached in the 2000 survey. The percentage of variation between both studies, as well as the statistical significance are also given.

Table 3. Metal concentrations (mg kg^{-1} ± SD) in soil samples collected in the vicinity of the MLS/MWIP in 2000 and 2003, up to 500 m from the complex.

Metal	2000	2003	% variation	p
Cd	16.73 ± 5.80	0.22 ± 0.03	-98.7	< 0.0001
Cr	29.53 ± 10.08	23.06 ± 4.76	-21.9	NS
Mn	1063.61 ± 385.05	648.34 ± 445.43	-39.0	< 0.05
Pb	24.20 ± 3.55	7.83 ± 1.60	-67.6	< 0.0001
Hg	< 0.025	0.05 ± 0.02	---	---

NS: not statistically significant (p>0.05).

In general, the results indicate that Cd, Cr, Mn and Pb concentrations in soil around the MLS area decreased between 2000 and 2003. The current metal concentrations are comparable and even lower than soil samples from the Santa Teresa Forest Ecological Station of Ribeirão Preto (Fig. 2).

The medical waste incineration plant was deactivated in February, 2002, being in operation since 1989. It was outdated and had not an adequate standard pollution control system to remove acids, organic compounds and heavy metals from the flue gases emissions (Segura-Muñoz, 2002). Since the operation conditions of the MLS were basically unchanged during this period, the observed reductions would correspond to the elimination of potential sources of metal emission in the environment from the MWIP.

Taking into account that approximately 80% of biomedical waste is composed of items such as paper, cans, bottles and plastic materials (Weir, 2002), where metals such as Cd, Cr, Hg, Mn and Pb are found, it can be considered that during incineration they could vaporize, forming fine fumes that entered to the environment.

The current results show that Cd level decreased notably and significantly when compared with the 2000 survey (Fig. 2). In the 2000 study, the Cd content found in soil samples made this area improper for agriculture, taking into account that the maximum limit for Cd concentration accepted in São Paulo State is 10 mg kg^{-1} (CETESB, 2001). Cadmium could be present in vapor and fumes generated by MWIP. Sao Paulo State medical waste contains more than 40% plastic materials that release Cd when incinerated (PRODAM, 2002).

In 2000, Cr levels were lower than the maximum Cr concentration accepted for agricultural soil in São Paulo: 300 mg kg^{-1} (CETESB, 2001). Current results showed a no statistically significant attenuation of Cr levels. Chromium levels were in accordance with some recent investigations on municipal solid waste

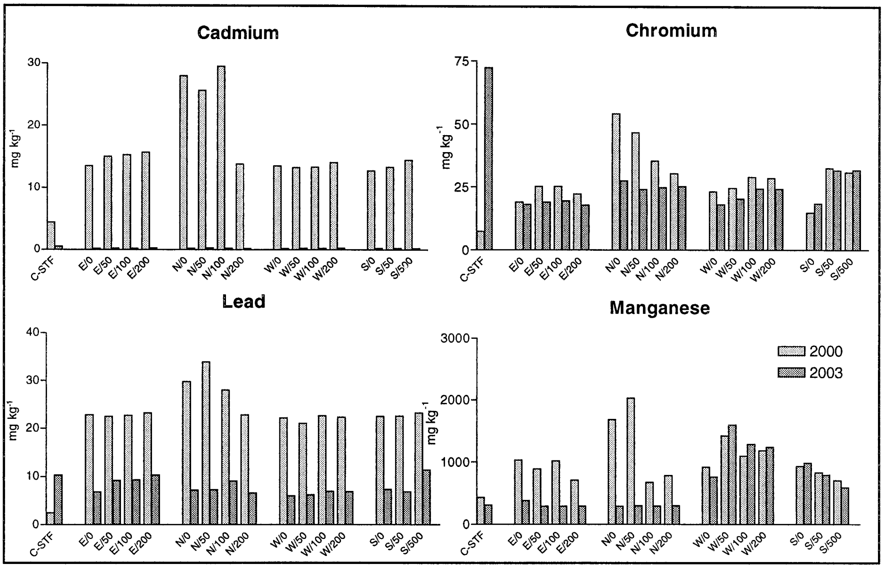

Figure 2. Spatial distribution of metal concentrations (mg kg^{-1}) in soil samples collected in the vicinity of the MLS/MWIP in 2000 and 2003.

incinerators in Spain, which revealed Cr levels in soils below 18.4 mg kg^{-1} (Schuhmacher et al., 1997; Llobet et al., 2002).

In the present study, Mn concentration decreased in relation with the results observed in 2000. However, our results are still higher than those found by Schuhmacher et al. (1997) and Llobet et al. (2002), who reported 307.6 and 234.2 mg kg^{-1}, respectively, as the highest Mn levels in soils collected in the vicinity of a municipal solid waste incinerator in Spain. Since Mn is employed in steel, aluminum and copper alloys, it can be hypothetized that these products continue being deposited in the MSL.

The maximum level of Pb for agricultural soils in São Paulo State is 200 mg kg^{-1} (CETESB, 2001). In 2000, the Pb content in soils ranged from 21.1 to 33.9 mg kg^{-1}. Three years later, Pb concentration is even lower, indicating that Pb did not represent a polluting agent at the studied site.

The significant reduction of Cd, Mn and Pb concentrations in soil is the most remarkable finding, considering the remediation actions adopted by the Municipal Government since 2000. Moreover, Recycling Programs adopted by the Ribeirão Preto Municipal Government are increasing the recycling rates of glass, paper, plastic, aluminum and steel products, retreating their disposal in the MLS. It is necessary to recognize that recycling is a very challenging issue in Brazil due the lack of education and consciousness of the population, as well as the high cost of collecting and recycling services. However, despite these obstacles, it is increasing in recent years.

The social situation of Ribeirão Preto, and in general terms in the country, is characterized by a high unemployment. It created a new economic activity, where poor families collect solid waste from trashcans. All products collected are sold to the industries and then are recycled. The social trend of informal recycling collectors may be determinant on the attenuation of metal concentration in soils around the MLS from 2000 to 2003. According to Llobet et al. (2002), a continous increase in the selective collection of the incoming waste deposited in MLS, suggests a reduction of metal products in the MSW (municipal solid waste). Consequently, it means an additional reduction in metal deposition in soil.

On the other hand, according to the reported data from Alta Mogiana Agronomic Station of Riberão Preto, since 2001 strong convective precipitations are being commonly registered during summer season in the region, with precipitations up to 159 mm per day. These heavy rains caused floods and soil erosion due the rain prevalence for more than 20 consecutive days. It could be possible that convective storms had taken away superficial soil from the area during this period. It should be taken into account that agriculture (sugar cane) is the main activity around the MLS, and it does not present a protective vegetal cover to avoid soil erosion.

A global interpretation of the above data indicates that metal levels in the soil collected in the MLS/MWIP area are being attenuated. The concentrations of metals found in the present study are similar or even lower to those previously reported in other surveys performed near MSWIs, with the exception of Mn and V (Schuhmacher et al., 1997; Meneses et al., 1999; Llobet et al., 2002). According to the current metal concentrations in soil collected near the MLS from Ribeirão Preto, the health impact of metals on the population living in the area under influence of the plant should not be of special concern. However, it is necessary to remark that control of metal levels in underground soil and water are still a worry for future surveys, considering the potential environmental impact of the MLS.

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