Bull. Environ. Contam. Toxicol. (2004) 72:157–164

DOI: 10.1007/s00128-003-0254-3

Environmental Contamination and Toxicology

Trace Metal Distribution in Surface Soil in the Area of a Municipal Solid Waste Landfill and a Medical Waste Incinerator

S. I. Segura-Muñoz,[1] A. M. M. Takayanagui,[1] T. M. B. Trevilato,[2] C. B. Santos,[3] S. E. Hering[2]

[1] Environmental Health Laboratory, Department of Maternal-Infant Nursing and Public Health, University of São Paulo at Ribeirão Preto College of Nursing, Av. Bandeirantes, 3900, CEP: 14040-902, Ribeirão Preto, São Paulo, Brazil
[2] Pediatric Laboratory-Metal Sector, General Hospital of the Faculty of Medicine at Ribeirão Preto, Pediatric Department, University of São Paulo, HC-Bloco G. Sala 219, Av. Bandeirantes, 3900, CEP: 14048-900, Ribeirão Preto, São Paulo, Brazil
[3] Statistics Area, Department of Maternal-Infant Nursing and Public Health, University of São Paulo at Ribeirão Preto College of Nursing, Av. Bandeirantes, 3900, CEP: 14040-902, Ribeirão Preto, São Paulo, Brazil

Received: 25 April 2003/Accepted: 11 September 2003

Environmental studies have prompted interest in the determination of metals in surface soil that can be considered the major recipient of pollutants (Alumaa et al., 2002). Because of their capacity to enter the food chain through soil and plants, metals are considered environmental indicators (Hamilton, 1995; Morselli et al., 2002). Therefore, special attention should be paid to the metal levels in soil in the vicinity of municipal solid waste landfills and medical waste incinerators.

In Brazil, about 228,413 ton/day of urban solid waste are generated all over the country today (IBGE, 2000) and 72% of this volume is being dumped without any previous treatment. Only 17% is going to planned landfill sites, while 11% is going to treatment facilities. In Ribeirão Preto, São Paulo State, Brazil, a municipal landfill site (MLS) for urban waste disposal integrated with a medical waste incinerator plant (MWIP) has been operating since 1989. At present, the MLS is receiving 500 ton/day of solid waste, while the MWIP is processing 9 ton/day of health services waste. This volume is generated by approximately 519,000 inhabitants. The purpose of the present study was to determine the levels of Cd, Cr, Pb, Mn, Zn, Cu and Hg in soils collected in the area of a Ribeirão Preto MLS-MWIP.

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). Duplicated surface soils were sampled in 2000 along four transects established in the north (N), east (E), west (W) and south (S) directions from the border of the MLS/MWIP, for a total of 16 sampling points (Fig. 1). Also, duplicated soil samples from the Santa Teresa Forest Ecological Station of Ribeirão Preto were collected as control samples I at six different points. This area is located 8 Km away from the MSL/MWIP, is the best preserved forest in Ribeirão Preto, and 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, Germany).

Correspondence to: S. I. Segura-Muñoz

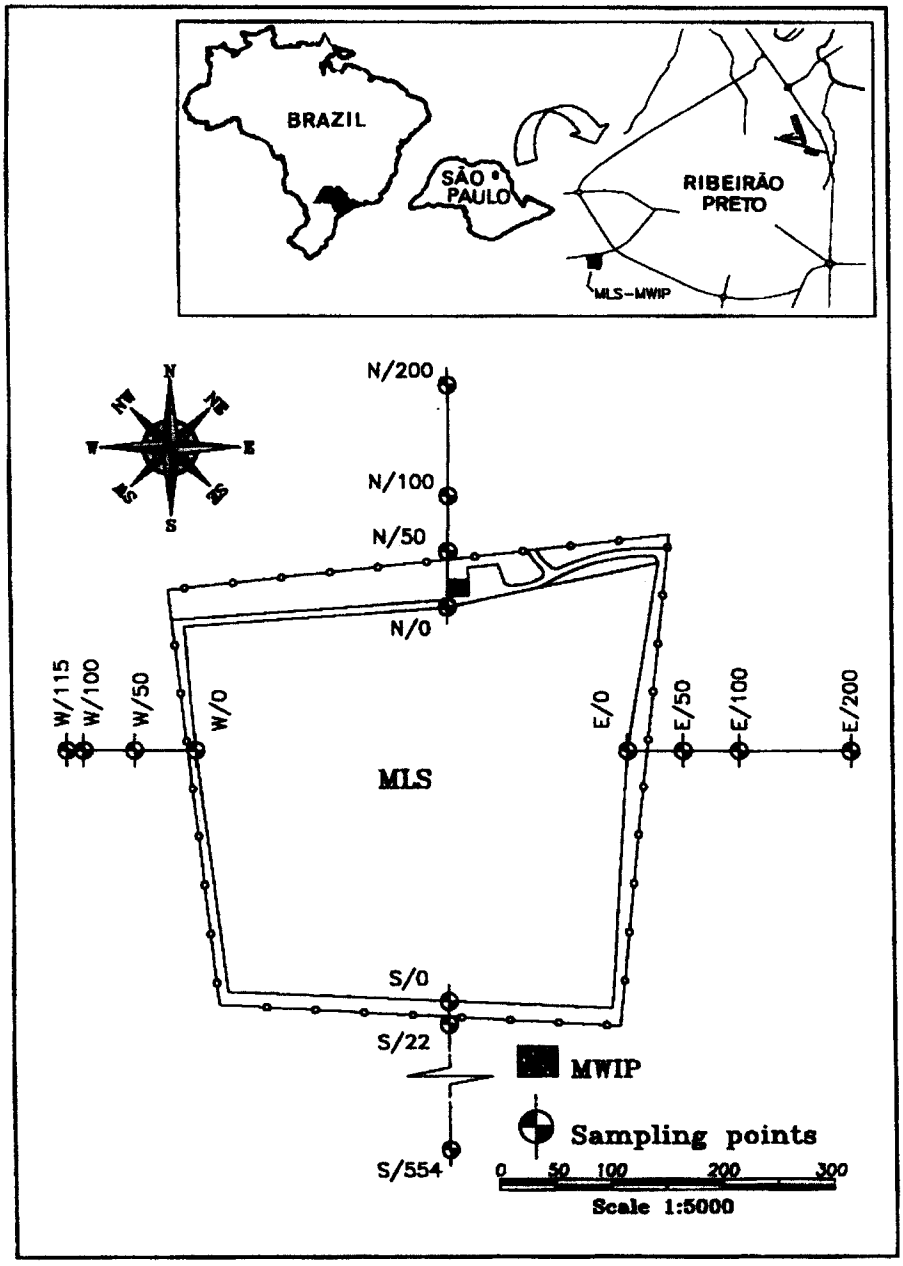

Figure 1. Location of sampling points in the area of Ribeirão Preto Municipal Landfill Site (MLS)/Medical Waste Incinerator Plant (MWIP), Ribeirão Preto, São Paulo, Brazil. Numbers are representing the distance in meters from MLS limits.

The samples were air-dried at room temperature for 2 weeks. The soils were then hand-crushed in a mortar and sieved through a 2 mm mesh screen. Soil samples were digested with aqua regia, according to the Australian Standard Method (SAA, 1997). Total Cd, Cr, Pb and Mn were measured by Graphite Furnace Atomic Absorption Spectrophotometry using an apparatus equipped with a Zeeman effect-based background corrector (Varian 640-Zeeman, Australia). Zn and Cu were analyzed by Atomic Absorption Spectrophotometry using an acetylene flame (Perkin-Elmer 380. Germany). Hg was measured by Hydryde Generation Atomic Spectrophotometry (Varian VGA-200. Australia). The accuracy of the instrumental methods and analytical procedures was checked by using certified soil samples (121-S, 127-S, 129-S, 131-S and 133-S) from Quality Control Technologies Pty. Ltd., Queensland, Australia.

Statistical analysis was performed using the Statistical Program for Social Science-SPSS (Windows version 10.0). The statistical significance of the metal concentrations from MLS samples and control samples was verified using the Mann-Whitney Rank Sum Test or Kruskal-Wallis Rank Sum Test followed by a Multiple Comparisons Test (Zar, 1999). A probability of 0.05 or less was considered to be significant. The results were compared with the Guidelines Values for Intervention Levels established for São Paulo State Soils by the São Paulo Environmental Sanitation Company (CETESB, 2001)

RESULTS AND DISCUSSION

The spatial distribution of the six metal concentrations in the soil of MLS is summarized in Fig 2, except for Hg whose concentration was below the detection limit (<0.01mg kg^{-1}) for all samples analyzed. In general, the findings allow us to conclude that the soil around the MLS area is being polluted with metals if compared with soil samples from the Santa Teresa Forest Ecological Station of Ribeirão Preto. The current metal concentrations in Santa Teresa Forest were comparable to those commonly reported in the literature for non-contaminated areas (HMSO, 1991). Results show that approximately 80% of the soils in the vicinity of the MLS contained significantly higher concentrations of total Cr and Cu when compared to the control samples ($p<0.01$). Cd levels in 73% of the soils, Pb levels in 67% and Zn and Mn levels in 53% were significantly higher than in the soil from Santa Teresa Forest ($p<0.01$).

The Cd content in soils ranged from 12.7 to 29.6 mg kg^{-1}. The Cd concentration found in soil samples makes 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). The current Cd concentrations were higher than those reported previously for soils located at a distance of 100 to 200 m from municipal solid waste incinerators in some European countries, where the Cd concentrations were between 0.03 and 0.4 mg kg^{-1} (Schuhmacher et al.,1997; Collet et al.,1998; Meneses et al., 1999). This may indicate that the municipal solid waste disposal and medical waste treatment are causing soil contamination with Cd in the area up to 200 m from the MLS. São Paulo State urban waste is

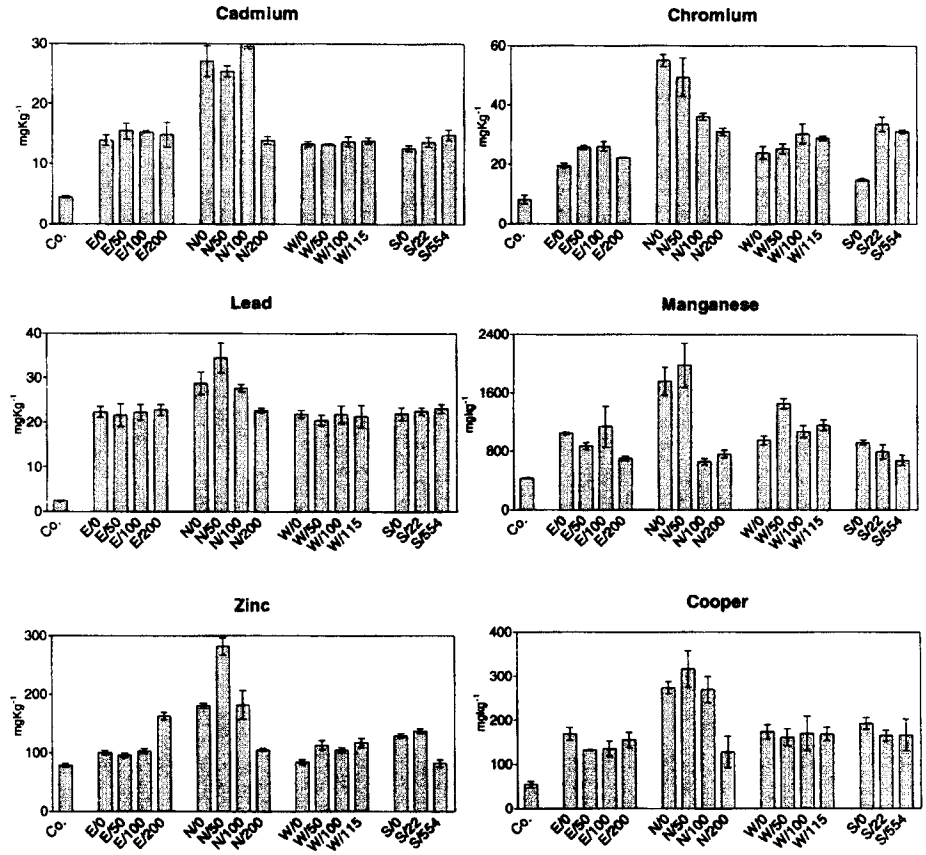

Figure 2. Metal concentration in soil samples collected in the area of Ribeirão Preto Municipal Landfill Site/Medical Waste Incinerator Plant, Ribeirão Preto, São Paulo, Brazil.

characterized by containing more than 15% of plastic material while medical waste contains more than 40%, materials that may have Cd in their composition (PRODAM, 2002). According to the Brazilian Electronic and Electric Industry Association, today Brazil produces about 800 million batteries per year, with the consumption of Ni-Cd batteries increasing over the last few years. Batteries used in domestic and urban activities represent almost 50% of the Cd present in the urban solid waste. Thus, the improper disposition of batteries may contaminate with Cd and other toxic components the soil in the vicinities of sanitary landfill sites (ABINEE, 2003).

In the present study, Mn concentration was 676 to 2032 mg kg^{-1}. In São Paulo State there are no established guidelines for Mn levels in surface soil (CETESB,

2001). Our results are higher than those obtained 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 from soils collected in the vicinity of a Municipal Solid Waste Incinerator in Spain. Mn levels up to 1085 mg kg^{-1} were also reported for soils around an incineration plant in Italy (Morselli et al., 2002). Generally, Mn has high natural concentrations and variability; however, when Mn is accumulated in surface soils over a long period of time, toxic effects on some plants are described (Kabata-Pendias & Pendias, 1992). Increased Mn levels were observed in the MLS/MWIP area compared to control samples. Since Mn is employed in steel, aluminium and copper alloys, it can be hypothetized that these kind of products are being deposited and/or incinerated in the MSL/MWIP.

Cupper showed levels between 113.5 and 299.0 mg kg^{-1}. These results are higher than those established as the maximum value of 100 mg kg^{-1} for agricultural soils in São Paulo (CETESB, 2001). The maximum Cu concentration reported by Morselli et al. (2002) in soils in the vicinity of a MSW incinerator was 35.4 mg kg^{-1}.

Chromium levels were between 14.9 and 54.2 mg kg^{-1}. These concentrations are lower than the maximum Cr concentration accepted for agricultural soil in São Paulo; which is 300 mg kg^{-1} (CETESB, 2001). However, investigations on municipal solid waste incinerators in Spain revealed Cr levels below 18.4 mg kg^{-1} (Schuhmacher et al., 1997; Llobet et al., 2002), while 94% of the samples analyzed in the present study were above that value.

The Pb content in soils ranged from 21.1 to 33.9 mg kg^{-1}, values below the maximum level of 200 mg kg^{-1} for agricultural soils in São Paulo State (CETESB, 2001). The Pb levels obtained in our study were also below 37.36 mg kg^{-1}, the mean level detected at a distance of 100-200 m from an MSW incinerator in Spain (Schuhmacher et al. 1997). Our results indicate that Pb metal did not represent a polluting agent at the site studied during the sampling time used.

The maximum Zn level was found at the N/50 sampling point (278.3 mg kg^{-1}). The recommended Zn level for agricultural soils is 500 mg kg^{-1} in São Paulo State. The concentrations of Zn found in soil samples taken from the MLS/MWIP area are comparable to those reported in the literature for non-contaminated areas (Steinbörn & Breen, 1999). However, it should be kept in mind that the worldwide mean for Zn in soil is estimated at 64 mg kg^{-1} (Kabata-Pendias & Pendias, 1992).

Metal concentrations were significantly higher ($p<0.05$) in soil collected on the North side of the MLS when compared to the other directions studied here. Specifically, the N/0, N/50 and N/100 points showed the highest concentrations. Several factors can determine this spatial distribution of metals.

The incinerator emissions can be assumed to be an important factor generating these localized higher metal levels. The MWIP has no adequate standard pollution

control system which can remove acids and heavy metals from the flue gases. Since 1998, CETESB had reported intense emissions of black smoke from the incinerator plant associated with problems in the operating conditions during combustion. It can be hypothesized that incineration is a source of the studied heavy metals in the area, considering that approximately 80% of biomedical waste is composed of items such as paper, cans, bottles and plastic materials such as vacutainer caps, plastic bags and packings (Weir, 2002). Metals such as Pb, Cd, Mn, Cr, Zn and Cu are found in these materials, and during incineration they can vaporize, forming fine fumes that enter the environment associated with the prevailing winds in the region. According to Alvarenga et al. (1986), the predominant direction of the wind in that area is to the N, with a velocity of 1.7 m/s.

Another possible explanation involves three elements. The MSW in São Paulo State is characterized by having almost 60% organic matter, 10% cellulose products, 20% plastic materials and 10% metal and glass materials (PRODAM, 2002). The metal and plastic products can subsequently be an important source of metals in the municipal solid waste disposed in the MLS. Taking into account the topographic gradient in the area, that declines gently towards the N and NW (Alvarenga et al., 1986) and the pH of the soil, between 4.8 and 5.7 (CETESB,2001), municipal solid waste degradation can generate superficial leachates, rich in metals, that can suffer a horizontal mobilization towards the North.

A global interpretation of the above data indicates that, in general terms, the natural metal composition in the soil collected in the MLS and MWIP area is being modified by the solid waste disposal and treatment processes when compared to soil from a preserved area in Ribeirão Preto. Among the metals analyzed, particular attention should be paid to Cd, Cu and Mn, elements that showed levels belonging to the *"slight contaminated soil"* and *"contaminated soil"* categories according to the HMSO-London Classification of contaminated soils (HMSO, 1991).

The current results constitute an instrument for the decision makers and public managers. At present, the authorities are discussing the possibility of retrofitting the incinerator with adequate scrubbers that remove and neutralize not only heavy metals, but also potential dioxins, furans, hydrogen chloride and nitrogen oxides or to replace the MWIP with an alternative medical waste treatment technology such as a microwave system and plasma pyrolysis. The need to improve the Municipal Waste Selective Collection and Recycling Programs already established in the city is also being discussed, with the suggestion to reduce the metals and plastic products in the incoming waste that is disposed of in the MLS and burnt in the MWIP. Certainly, future studies should determine the health impact of metals on the population living in the area under influence, taking into account that agriculture (sugar cane) is the principal activity around the MLS and metals can bioaccumulate in plants, making their way to humans through the food chain.

*Acknowledgments.*This study was financially supported by FAPESP - Fundação de Amparo à Pesquisa do Estado de São Paulo, Brazil (Grant N. 99/11064-0). The authors thank the authorities of the Municipal Solid Waste Management Department of Ribeirão Preto, São Paulo, for the collaboration and Mr. Graeme Waller from the Quality Control Technologies Pty. Ltd., in Queensland, Australia, for authorizing our participation in the Quality Control Program.

REFERENCES

ABINEE /Associação Brasileira da Indústria Eletrica e Eletrónica (2003). Site: www.reciclarepreciso.hpg.ig.com.br/pilhasbaterias.htm. Accessed in March, 2003

Alumaa P, Kirso U, Petersell V, Steinnes E (2002) Sorption of toxic heavy metals to soil. Int J Hyg Environ Health 204:375-6

Alvarenga EC, Souza A, Greco PA, Zuquete LV (1986) Estudo de Impacto Ambiental e Relatório de Impacto Ambiental do Aterro Sanitário e Incinerador (EIA-RIMA). DURSARP. Ribeirão Preto, São Paulo, p 160

CETESB (2001) Companhia de Tecnologia de Saneamento Ambiental. Relatório de Estabelecimento de Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo. Centro de Editoração da Secretaria de estado do Meio Ambiente. São Paulo, p 245

Collet RS, Oduyemi K, Lill DE (1998) An investigation of environmental levels of cadmium and lead in airbone matter and surface soils within the locality of a municipal waste incinerator. Sci Total Environ 209:157-167

Hamilton EI (1995) State of the art of trace element determinations in plant matrices: Determination of the chemical elements in plant matrices, an overview. Sci Total Environ 176:3-14

HMSO London. (1991). Protection of workers and the general public during the development of contaminated land. Health and Safety Executive Guidelines for the Classification of Contaminated Soils:20

IBGE (2000) Instituto Brasileiro de Geografia e Estatística. Pesquisa Nacional de Saneamento Básico de 2000. Site: http://www.ibge.gov.br. Accessed in April, 2002

Kabata-Pendias A., Pendias H. (1992) Trace Elements in soils and plants. 2nd edn. CRC Press, Boca Raton, Fl

Llobet JM, Schuhmacher M, Domingo JL (2002) Spatial distribution and temporal variation of metals in the vicinity of a municipal solid waste incinerator after a modernization of the flue gas cleaning systems of the facility. Sci Total Environ. 284:205-214

Meneses M, Llobet JM, Granero S, Schuhmacher M, Domingo JL (1999) Monitoring metals in the vicinity of a municipal waste incinerator: temporal variation in soils and vegetation. Sci Total Environ 226:157-164

Morselli L, Bartoli M, Brusori B, Passarini (2002) Application of an integrated environmental monitoring system to an incineration plant. Sci Total Environ 289:177-188

PRODAM. (2002) Limpeza Urbana da Prefeitura de São Paulo. Site: http://www.prodam.sp.gov.br/limpurb. Accessed in June, 2002

SAA (1997) Australian Standard. The Crescent, Homebush, NSW2140

Schuhmacher M, Meneses M, Granero S, Llobet JM, Domingo JL (1997) Trace element pollution of soils collected near a Municipal Solid waste Incinerator: Human Health Risk. Bull Environ Contam Toxicol 59:861-867

Steirbörn M, Breen J (1999) Heavy metals in soil and vegetation at Shallee Mine, Silvermines, Co, Tipperary. Biology and Environment: Proceedings of the Royal Irish Academy 99B: 37-42

Weir E (2002) Hospitals and the environment. Canadian Medical Association Journal 166: 354

Zar, J.H (1999) Biostatistical analysis. 4. ed. Prentice Hall, Upper saddle River, New Jersey, USA, p 580