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Metals in playground soils of São Paulo city, Brazil

Ana Maria G. Figueiredo^{*}, Marjorie Tocchini, Thais F. S. dos Santos

Instituto de Pesquisas Energéticas e Nucleares, IPEN – CNEN/SP, Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, SP, Brazil

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Abstract

São Paulo is a megacity, with a population of over 20 million inhabitants. Soils have an impact on human health in many ways and young children are especially vulnerable. The concentration of As, Ba, Cr and Zn, were determined in surface soil samples from playgrounds of São Paulo public parks by neutron activation analysis. The results obtained in this study indicated concentration levels higher than the values considered as reference values for soils in São Paulo. The concentrations obtained suggest an anthropogenic source and indicate a potential damage to children's wellbeing.

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1. Introduction

In urban environment soil are the natural "sink" of heavy metals from a variety of sources including industrial wastes, vehicle emissions and other activities. Studies on urban soil pollution started in the 60-70's [1-3]. There have been recent studies on chemical composition of urban soils in cities such as Palermo [4], Madrid [5], Naples [6], Hong Kong [7], Turin [8], Galway [9] and Sevilla [10]. Special attention has been devoted to studies on urban park playgrounds, in cities such as Hong Kong, Uppsala, New Orleans, Athens and Madrid [11- 15]. Trace elements in urban environments are able to exert their toxicity through dermal contact, ingestion and inhalation, as a result of the proximity of the soil to and the interaction with the inhabitants of the city [16, 17]. The presence of potentially toxic metals in high concentrations in urban soils has been recognized as an important source of human metal intake particularly in children who are more susceptible to the adverse effects of soil ingestion than adults [16].

Parks and playgrounds are where urban children spend most of their free time out of the home and are also where children most frequently come in contact with soil. Children exposed to contaminated soils, dust and air particulates may ingest a significant amount of toxic elements by putting dirty hands in their mouth [6]. The daily ingestion rates of soil by children have been calculated to be between 39 and 270 mg day⁻¹ [18].

Contaminated urban soils have been identified by several authors as a significant source of Pb exposure in children [13, 18]. Ren et al. [19], studying the soil lead exposure in children in Shenyang, China, observed that soil ingestion is an important pathway of exposure for children in that region, and that children who are 4 to 5 years old

^{*} Email corresponding author: anamaria@ipen.br

are in great risk due to soil lead exposure. De Miguel et al. [15] evaluated the risk of the exposure of children to trace elements in playgrounds in Madrid (Spain) and concluded that the highest risk is associated with ingestion of soil particles and that the trace element of most concern is arsenic the exposure to which results in a cancer risk value of $4.19 \cdot 10^{-6}$. Ng et al. [11] observed high concentrations of Zn (mean = $1883 \mu\text{g g}^{-1}$), Cu (mean = $143 \mu\text{g g}^{-1}$) and Cr (mean = $263 \mu\text{g g}^{-1}$) in playground dust of Hong Kong. Massas et al. [14] reported the concentration, distribution, and availability of heavy metals in children's playground soils of Athens and observed on site-specific cases, that metal availabilities exceeded the permissible limits, whereas the availability of Cr, Zn, Mn, Pb, and Ni generally appears high, suggesting recent pollution due to atmospheric deposition.

There has been very little research done on urban soils in São Paulo, the largest city in Latin America. In a previous study [20], high concentrations of metals such as Cr, Cu, Zn, and Pb have been observed in park soils of São Paulo. These results encouraged the authors to continue the study aiming at evaluate metal pollution in these playground soils.

2. Study Area and Sampling Strategy

The metropolitan region of São Paulo is composed of 39 municipalities, with a population of about 20 million inhabitants living in about 8000 km^2 , and strong industrial activity. The urban area is polluted by industrial emissions but, according to CETESB, the Environmental Protection Agency of the State of São Paulo, the governmental agency of air quality control, emissions from about 8.4 million motor vehicles daily are the main sources of air pollution [21]. São Paulo city has suffered a rapid and disordered growth in the last decades which lead to considerable loss of green areas. Thus, São Paulo public parks have become one of the few leisure areas for the population. Metal contamination in playgrounds are therefore of great concern to children's health.

This study presents the results obtained for the concentration levels of four potentially toxic elements (As, Ba, Cr, and Zn) in surface soil samples from the city's playgrounds in some public parks of São Paulo.

Twelve public parks of São Paulo, located in different regions of the city (downtown, residential and industrial areas), were studied. The Luz, Buenos Aires, Trianon and Aclimação Parks are located in the central region of the city, surrounded by avenues of high density traffic. The Ibirapuera Park, located in the southern region of the city, near big avenues, is by far one of the biggest and most visited parks of the city. The Rodrigo de Gásperi, Vila dos Remédios and Cidade de Toronto Parks are in the Northern region of the city, located in a less populous area. The Chico Mendes and Raul Seixas Parks are situated in the eastern region of São Paulo, a very populated area. The Carmo Park was in the early days a farm belonging to one of the city's traditional families, and is located in a green area, far from large avenues. The Alfredo Volpi Park, in the western region of the city, was part of an old tea farm and still preserves an important area of the original Atlantic Forest vegetation.

Samples of approximately 500 g of surface (1–2 cm) soil consisting of sub-samples collected in each playground were prepared. Sampling points were selected *in loco* by identifying areas where the soil was exposed due to the erosion caused by children playing and constant walking. No specific sampling design was used. The criteria observed for sampling was exposed soil at or near playground equipment such as swings, slides, etc. At each sampling site, three or four subsamples were obtained and mixed to make a bulk sample. The samples were collected by using a polyethylene dust pan and were stored in inert plastic bags for transport to the laboratory.

3. Analytical Method

The samples were dried at 40°C and sieved through plastic-only sieves into $<2 \text{ mm}$ fraction. Before and after sieving, the samples were homogenized and quartered. Samples were then grinded using an agate mortar in order to obtain a fine and homogeneous powder ($< 75 \mu\text{m}$) and analyzed for metals by Instrumental Neutron Activation Analysis (INAA). One hundred mg of each sample and of the geological reference materials basalt BE-N (ANRT) and granite GS-N (ANRT) were accurately weighed in polyethylene bags. Samples and reference materials were irradiated for 8 hours at a thermal neutron flux of $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out in gamma-ray spectrometer with a GX20190 hyperpure Ge detector (Canberra). The accuracy and precision of the results were verified by the analysis of the reference materials Soil-7 (IAEA). The results showed good accuracy (relative errors to certified values $< 5\%$ for most of elements) and good precision (relative standard deviations $< 15\%$).

4. Results and Discussion

Table 1 presents the mean values obtained for the analyzed elements in the park soils, as well as the reference values for soils in São Paulo of the Environmental Protection Agency of the State of São Paulo guidelines [22]. The Quality Reference Value (VRQ) is the concentration of an element in the soil which defines a clean soil. It is determined considering statistical interpretation of physico-chemical analysis of different kinds of soils from São Paulo State. The Prevention Value (VP) is the concentration limit of an element that causes no damage to soil and groundwater quality up to this limit. This level indicates a soil capable of maintaining its primary functions, protecting the ecological receptors and groundwater quality, and was determined based on ecological receptors assays. The Residential Intervention Value (VIR) is the concentration of an element the soil or groundwater above which there are direct or indirect potential risks to human health. This was calculated by using human health risk assessment procedures for residential exposure. These values are the available reference values for São Paulo soils. Some data from similar studies are also presented in Table 1, for comparison to playground soils of other cities all over the world. It should be pointed out that the variety of the number and depth of sampling, sample treatments, and analytical techniques may contribute to data variability. INAA provides total concentration, since there is no chemical treatment of the sample. All the other studies used acid dissolution of the sample, which does not completely destroy silicates, originating possible discrepancies.

Table 1. Mean concentration values in playground soils of São Paulo and reference values (mg kg⁻¹)

Parks	As	Ba	Cr	Zn
Aclimação	11	614	56	94
Alfredo Volpi	3.0	320	21	15
Buenos Aires	16	917	70	102
Carmo	7.9	284	46	61
Chico Mendes	13	505	57	90
Cidade Toronto	1.2	711	40	57
Ibirapuera	24	943	64	120
Luz	15	798	58	179
Raul Seixas	12	668	61	63
Rodrigo de Gásperi	1.3	873	29	70
Trianon	5.3	1022	50	93
Vila dos Remédios	5.8	544	36	34
Reference Values [22]				
Quality Reference Value (VRQ)	3.5	75	40	60
Prevention Value (VP)	15	150	75	300
Intervention Residential (VIR)	55	500	300	1000
Similar studies in other cities				
Uppsala [12]	3.4-3.11	–	25.4-37.7	78.7-111
Athens [14]	–	–	80	174
Madrid [15]	3.7-16	34-285	4.1-51	20-200

As can be observed, the studied elements presented concentration levels higher than the VRQ in most parks. The highest concentrations were obtained in the parks located in the central region of the city (Luz, Buenos Aires, Aclimação and Trianon). The Alfredo Volpi, Rodrigo de Gásperi and Cidade de Toronto Parks presented the lowest concentrations of the analyzed elements, probably due to a lower anthropogenic influence because of their history and location.

In comparison to the data from Madrid playgrounds [15], higher Ba concentrations in São Paulo playground soils were found. Ba levels exceeded the VIR in all parks except Alfredo Volpi, Chico Mendes and Carmo parks, suggesting an anthropogenic source (Fig. 1). Barium may be introduced into the environment by industrial wastes and also by vehicular emissions. Organometallic compounds containing barium and calcium have been used to reduce diesel smoke and 85-95% of the metal is emitted as particulates in vehicle exhaust. Nevertheless, the concentrations of Zn, another traffic related element, in these parks, were not as significant as those of Ba. This difference in behavior of Zn and Ba could indicate that Ba is geogenic rather than traffic-related such as may be the case of Zn.

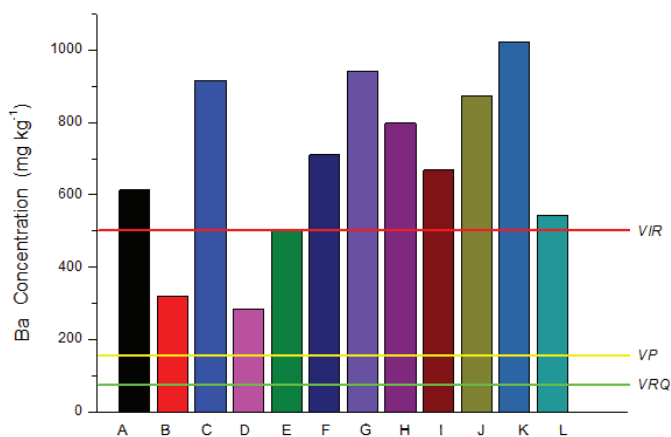


Figure 1: Ba concentration (mg kg^{-1}) in the park playgrounds and reference values. A=Aclimação; B=Alfredo Volpi; C=Buenos Aires; D=Carmo; E= Chico Mendes; F=Cidade Toronto; G= Ibirapuera; H=Luz; I=Raul Seixas; J=Rodrigo de Gásperi; K=Trianon; L= Vila dos Remédios.

Zn concentrations were above the VRQ mainly in the downtown parks (Aclimação, Luz, Buenos Aires and Trianon), area with the highest traffic intensity (Fig. 2). This metal content was significantly correlated with traffic volume, and this may indicate that its source is vehicular emissions. This was corroborated by a previous study in São Paulo city, using the bromeliad *Tillandsia usneoides* as biomonitor of metal atmospheric pollution. Zn presented high concentrations in exposure sites near dense traffic avenues (cars, buses and trucks) and were associated to vehicular sources [23]. Zn compounds are used extensively as antioxidants and as detergent/dispersant improving agents for motor oil. Tire wear, especially in the form of coarse particles, was also found as a contributing agent of Zn loading to the environment [11]. The Luz Park showed the highest Zn concentration. This park is the São Paulo city's oldest park (created in 1825) and is located just in the city centre. A positive correlation between metal concentration and the age of the park has been observed by Ljung et al. [12]. Since metals are immobile in the soil, the longer the soil is undisturbed in the urban environment, the more significant its metal content is.

The As concentrations were similar to those obtained in Madrid soils [15] and higher than those reported for Uppsala [12]. Uncontaminated soils are reported to have $<10 \text{ mg kg}^{-1}$ of As [24]. Six of the twelve studied parks presented concentration levels $> 10 \text{ mg kg}^{-1}$ and only three parks (Alfredo Volpi, Rodrigo de Gásperi e Toronto) presented As in concentration below VRQ (Fig 3). These high concentrations may be due to anthropogenic activities, since As accumulation in urban environments is most often due to fossil fuel combustion, especially coal and metal-processing industries [24]. Arsenic is also present in several products, such as pesticides. Chromated copper arsenate (CCA)-treated wood, widely used in playgrounds and other outdoor equipment, is a source of As in the soil. Non-CCA-treated playgrounds presented As concentrations in soil $<3.0 \text{ mg/kg}$ vs. mean arsenic of 19

mg/kg in CCA-treated playgrounds [25]. Inorganic arsenic is the only known carcinogen for which there is adequate evidence of carcinogenic risk by both inhalation and ingestion. According to the Preliminary Remediation Goals (PRGs) from EPA (US Environmental Protection Agency), As levels of 4.5 mg kg^{-1} may cause cancer risk of one in a million through dermal absorption [26]. Dutch Soil Federal Legislation established a trigger value for As in playground soils of 25 mg kg^{-1} that, when exceeded, requires an investigation of the contamination risk [27]. According to these criteria, the Ibirapuera park should be investigated. It should be noticed that this park is the most visited in São Paulo, receiving about 400,000 people during the weekend.

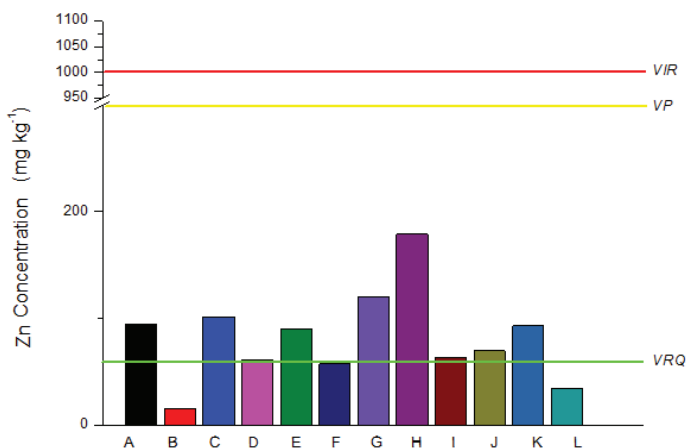


Figure 2: Zn concentration (mg kg^{-1}) in the studied park playgrounds. A=Aclimação; B=Alfredo Volpi; C=Buenos Aires; D=Carmo; E= Chico Mendes; F=Cidade Toronto; G= Ibirapuera; H=Luz; I=Raul Seixas; J=Rodrigo de Gásperi; K=Trianon; L= Vila dos Remédios.

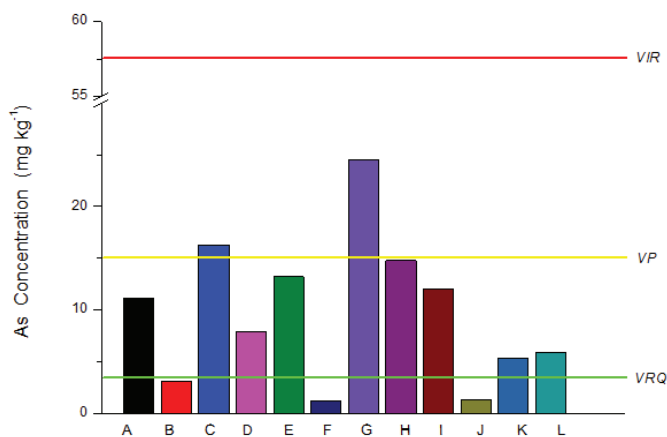


Figure 3: As concentration (mg kg^{-1}) in the studied park playgrounds and reference values. A=Aclimação; B=Alfredo Volpi; C=Buenos Aires; D=Carmo; E= Chico Mendes; F=Cidade Toronto; G= Ibirapuera; H=Luz; I=Raul Seixas; J=Rodrigo de Gásperi; K=Trianon; L= Vila dos Remédios.

Chromium and zinc presented similar concentrations to those found in Madrid and lower levels than those from Athens. Cr presented higher concentrations than VRQ in most parks, except in Rodrigo de Gásperi, Vila dos Remédios and Alfredo Volpi (Fig. 4). The presence of Cr may be associated to vehicular emissions and to industrial activities, and also as consequence of incineration of urban waste [11].

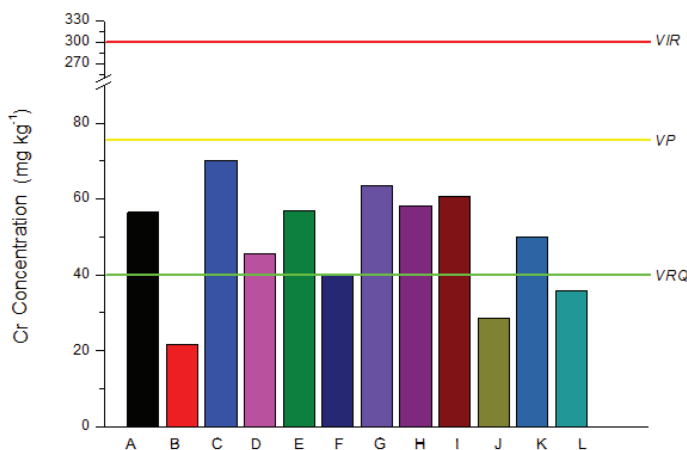


Figure 4: Cr concentration (mg kg⁻¹) in the studied park playgrounds. A=Aclimação; B=Alfredo Volpi; C=Buenos Aires; D=Carmo; E= Chico Mendes; F=Cidade Toronto; G= Ibirapuera; H=Luz; I=Raul Seixas; J=Rodrigo de Gásperi; K=Trianon; L= Vila dos Remédios.

5. Conclusions

The results obtained in this study indicated that soils of playgrounds in São Paulo public parks present higher concentration levels of As, Ba, Cr and Zn than the values considered as quality reference values for soils in São Paulo. These concentrations suggest an anthropogenic influence and indicate a potential damage to the soil quality. The results obtained in this study can contribute to provide an assessment of playground soil contamination in São Paulo.

Acknowledgments

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