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HOUSEHOLD DUST METAL LEVELS IN THE SÃO PAULO METROPOLITAN AREA

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ABSTRACT

A study about household dust is being conducted to determine the level of metal contamination in the São Paulo Metropolitan Area (SPMA). The SPMA, with 18 million inhabitants, is one of the largest urban areas of the world, with serious environmental problems, due to the great amount of industries, heavy traffic and the disordered growth of population. The pollutants originate from a multiplicity of indoor and outdoor sources. Indoor sources are originated from residual (hair, skin scales), pets, human activities, construction materials, and furnishings as well as biological material (pollen, insect parts).and outdoor pollution, usually from the urban traffic. The pollutant mixture involved in numerous physical and chemical processes and changes its characteristics with time. Its composition and concentration depend on the strengths of indoor sources, the concentration of pollutants outside and the properties of ventilation and air-conditioning systems. It is well recognized that many metals have chronic effects on humans, in particular toddlers, who are at an higher risk compared to adults because they engage in greater hand to-mouth activity and their neurological systems are still developing. The household dust samples were collected from different localities, using vacuum cleaner, and sieved up to particle size <63μm, which were then analyzed for 7 elements by X-ray fluorescence technique. The fundamental parameters method (FP) was applied and the simple pressed powder technique for sample preparation was used. The concentrations preliminary results of metals in the household dust were Cr, 18-188 μg g^{-1}; Mn, 119-369 μg g^{-1}; Fe, 372-1464 μg g^{-1}; Ni, 33-85 μg g^{-1}; Cu, 42-303 μg g^{-1}; Zn, 156-1369 μg g^{-1} and Pb, 26-160 μg g^{-1}.

1. INTRODUCTION

The worldwide population growth over the last sixty years stimulated the industries of the diverse segments to supply the necessities of the human beings. If, on the one hand, food, transport and health have evolved concerning diversities, as for quality this has not occurred. According to the American Chemical Society (CAS) [1] there are more than 31 million chemical substances (organic and inorganic) in their database and approximately 4,000 new substances are added each day. Many of them are toxic and in the norms and/or legislation absence they have been used in several industry sectors and, consequently, can interfere in the life quality and human health. This subject has been the focus of study by worldwide researchers, who have monitored the environments to establish correlations between disease and probable sources of toxic substances, mainly, in large metropolises.

Recent studies reported that the household environment is a probable potential source of toxic substances [2]. The chemical analysis carried out in household dust samples in several world regions showed worrying concentration levels of phthalates, alkylphenols, brominated flame retardants, metals and other substances [3]. These substances in the household dust come from outdoor sources such as vehicular (combustion products and pieces wear) and indoor sources (artifacts and/or household tools) caused by normal use or weather incidents, with the migration of the resulting toxic substances to the domestic environment.

São Paulo city (Brazil) is the fifth larger metropolis of the world with serious environmental and health problems like any other metropolis. In this work, the concentration levels of Cr, Mn, Fe, Ni, Cu, Zn and Pb were determined by wavelength dispersive X-ray fluorescence technique (WDXRF), with the fundamental parameters method (FP) [4] in 27 household dust samples. They were collected from the north zone, in the metropolitan area of the city. The Cluster Analysis (CA) was used to elucidate the relationship between variables and/or samples, grouping the samples in terms of their similarity. CA is the most common multivariate statistical method used in environmental studies [5]. The results were compared to other household dust samples from Birminghamand and Plymouth (UK), Sydney (Australia), Ottawa (Canada), Hong Kong (China) and Warsaw (Poland).

2. MATERIALS AND METHODS

2.1. Sampling

The sampling sites for household dust collection were according to different types of traffic volume (low and heavy traffic), of residential concentration (apartments and houses) and proximity to train station, parks, dumpsites and cemeteries. In addition, was also taken into consideration the per capita income, which was estimated to be from 2 to 20 minimum wages.

Dust samples were collected from 11 residences in the north zone of the Sao Paulo Metropolitan Area (SPMA); specifically, the neighborhoods: Freguesia do Ó (3 residences), Pirituba (5 residences) and Jaraguá (3 residences), these areas located approximately 10 ± 2 Km from each other, summing a total of 27 samples. The collections were carried out from May to December of 2006. The accumulation time for the sample was 1-4 months. Each participating householder filled a questionnaire to document the: age, size, construction characteristics, heating sources, renovation/redecoration history of the house, distance from the road, number of adult residents, children and pets, and lifestyle factors, including occupations and smoking habits.

Residents themselves collected the indoor dusts by domestic vacuum cleaner according to a protocol designed to capture all the surface dusts based on documents provided by Environmental Protection Agency (U.S.EPA) [6]. Participants were instructed to vacuum only the internal residence and all the routine surfaces, which included bare floors, rugs and wall-to-wall carpets. Following sampling, vacuum cleaner bags were sealed with filter paper and then taken to the laboratory.

2.2. Sample preparation

The samples were sieved at <63 μm particle size fraction by vibrational sifting, and stored in glass vials at ambient temperature. The household dust samples were prepared as simple pressed pellets. 2g to 3g of acid boric (H_3BO_3) were accommodated in cylindrical mold (Hidraulic press-B. Herzog, model HTP40) and pressed at 5 ton (100 Pa) for 1 minute, obtaining one base; after were added amounts 0.3-0.5g of dust sample on this base and pressed at 10 ton (203 Pa) for 1 minute; thus a 20 $\pm$ 1mm diameter and 10 $\pm$ 1mm thickness pellet was obtained.

2.3. Analytical procedure

The elemental concentrations for Cr, Mn, Fe, Ni, Cu, Zn and Pb were determined by wavelength dispersive X-ray fluorescence (WDXRF) with a RIGAKU Co. spectrometer; model RIX 3000, using the fundamental parameters method (FP) that is coupled in the equipment. This is an algorithm method that allows correcting the matrix effects such as enhancement and/or absorption. The measurement instrumental conditions such as voltage (kV), current (mA), collimators, filters, attenuator, analyze crystal, detector, 2θ positions and fixed counting time were established for each analyzed element, using high purity certified materials. The content of organic matter from the 27 household dust samples (<63μm) were determined as loss on ignition (LOI), after heating at 950±30 ^{0}C in a muffle furnace. The methodology validation was carried out using the standard reference material Domestic Sludge (SRM 2781) from NIST/USA and the statistical tests, recommended by EURACHEM/CITAC Guide.

2.4. Cluster analysis

The hierarchical cluster analysis was performed using the Ward's method and squared Euclidean. Statistical calculations were performed by using a data analysis software system STATISTICA, version 6 from StatSoft, Inc [7].

Before cluster analysis, the variables were standardized by means of z-scores; then Euclidean distances for similarities in the variables were calculated. Finally, a hierarchical clustering by applying the Ward's method was performed with the standardized data set.

3. RESULTS AND DISCUSSION

The methodology validation and uncertainty of measurement were evaluated for Cr, Mn, Fe, Ni, Cu, Zn and Pb determination in the related standard reference materials according to ISO 17025: 2005. The uncertainty of measurement was calculated as the relative standard deviation (RSD %) and Z-score values. All the elements presented a RSD value <5.0 %; exception was observed for Ni determination, which showed 5.7 % RSD value. The Cr, Mn, Fe, Ni, Cu and Pb determination presented $|Z|$ values ≤ 2.5, exception was observed for Zn determination, showing 2.6 values.

The cluster analysis applied to determine the similarity between 27 samples (cases) and 7 elements Cr, Mn, Fe, Ni, Cu, Zn and Pb (variables) as shown in Fig. 1(a), resulted in seven samples. The sample R1 grouped two samples (*n*=2); R2 grouped seven (*n*=7); R3 grouped four (*n*=4); R4 grouped three (*n*=3), R5 grouped two (*n*=2), R6 grouped four (*n*=4) and R7 grouped five (*n*=5) as shown in Fig. 1(b).

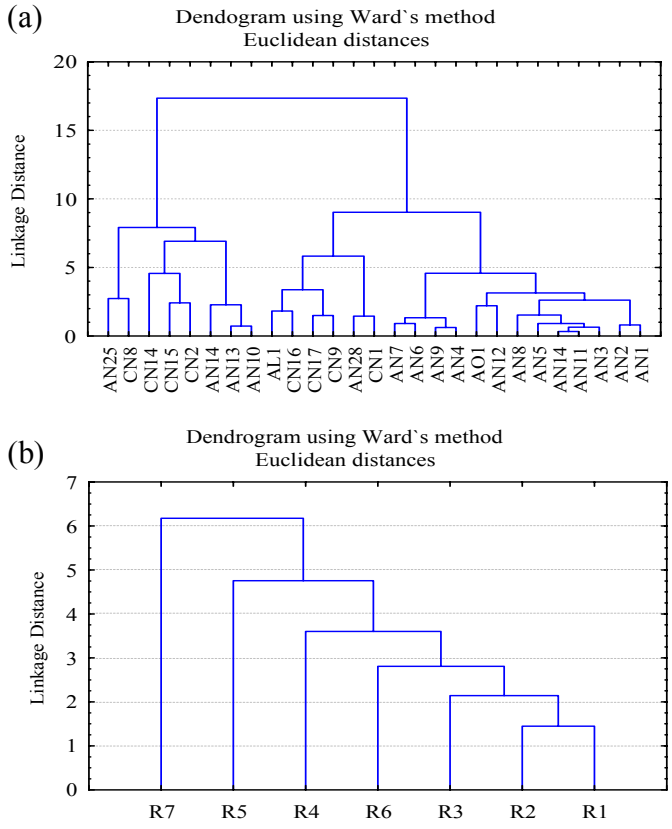

Figure 1.Cluster Analysis for the 27 samples and 7 variables

In Table 1 the mean concentration values of the metals Cr, Mn, Fe, Ni, Cu, Zn and Pb for seven samples after the cluster analysis from São Paulo and for other locations are presented.

Table 1. Mean concentration values of metals for different locations (in μg g^{-1})

Locations	Element								
	Particle size	Preparation method	Cr	Mn	Fe	Ni	Cu	Zn	Pb
SPMA-R1 (*n=2*)			87±7	149±16	829±96	48±5	116±1	1369±148	86±5
SPMA-R2 (*n=7*)			89±1	195±32	951±14	57±114	184±1	1082±133	62±6
SPMA-R3 (*n=4*)			71±26	142±17	736±70	37±5	149±37	780±97	26±31
SPMA-R4 (*n=3*)	<63μm	WDXRF	188±37	223±24	1083±117	74±14	175±6	1140±178	93±5
SPMA-R5 (*n=2*)			18±26	119±52	372±98	33±8	42±1	156±49	31±44
SPMA-R6 (*n=4*)			52±65	268±11	1182±74	50±18	121±17	461±175	61±26
SPMA-R7 (*n=5*)			93±31	369±21	1464±99	85±34	303±281	751±49	160±95
B'ham, W.Mid, Plym., W. Devon UK[2] (*n*=32)	63μm	HCl/ HNO_3	–	578±262	9450±3840	56.5±20	339±163	666±240	181±104
Sydney. Australia[8] (*n*=82)	<100μm	HNO_3	83.6±71.2	76.1±80.8	5850±15600	27.2±62.4	147±170	657±1140	389±1890
Ottawa. Canada[9] (*n*=50)	100-250μm	HNO_3/ HF	86.7±191.8	269.3±407.3	14135±21575	62.9±116.4	206.08±488.96	716.9±1460.8	405.56±1311.92
Hong Kong. China[10] (*n*=151)	<250μm	HNO_3/ H_2SO_4/ $HClO_4$	_	216.2	_	_	310.8	11408.8	157.4
Warsaw. Poland[11] (*n*=27)	23-63μm	EDXRF	102±37	_	_	54±68	136±48	1230±487	169±66

SPMA (São Paulo Metropolitan Area), [2]Turner et al. (2006); [8]Chattopadhyay et al. (2003); [9]Rasmussen et al. (2001); [10]Tong et al. (2000); [11]Lisiewicz et al. (2000). The arithmetic mean of metal concentrations (in μg g^{-1}) is given in all cases with the exception of the Hong Kong data where a median value is reported.

The comparison of the results from São Paulo and other locations are shown in Fig. 2.
The results for Cr and Ni elements in household dust from the samples R4 and R7 located in São Paulo (Brazil) were higher (188±37 μg g^{-1} and 85±34 μg g^{-1}, respectively) in comparison with other cities. This may be attributed to the distance between the residences and the roads, soil type, traffic density and carpet and rug wear in accordance with the reports of worldwide researchers.

Other factors also attributed are: the dusts were collected in the autumn, season of the year when the pollutants were in suspension for longer, furthermore, the residences which contained these samples were near the avenues with heavy traffic density, generating particles that were tracked into the dwellings on shoes and clothes and the proximity to a train station and a dumpsite. The results for Pb (sample R7, 160±95 μg g^{-1}) and Zn (samples R1 and R4, 1369±148 and 1140±178 μg g^{-1}, respectively) were very similar to those in Warsaw (169±66 and 1230±487 μg g^{-1}, respectively). This may be attributed to the fact that, in these two studies, sampling and sample preparation techniques were identical. The most probable sources of contamination by Pb and Zn elements in domestic dust of Warsaw were attributed to the intense vehicular traffic in the city, releasing many pollutants such as Zn, widely used as antirust in detergent additives for lubricating oils and to prevent corrosion of galvanized vehicular parts. It is also prevent window sills, which are covered with a Zn anticorrosive layer together with a Pb-containing solder. In the case of São Paulo city, a probable explanation for the formation of such particles may be the heavy vehicular traffic and the proximity to a dumpsite.

The level of Mn in São Paulo city (sample R7, 369±21 μg g^{-1}) was similar to that in Ottawa (269.3±407.3 μg g^{-1}). In this city, the results were attributed to the use of lead-based paints, solders and the plumbing of its old houses. The type of heating (electrical, by gas or oil) was also found to influence the indoor metal dust concentration. In São Paulo, the results could be attributed again to vehicular traffic and the dumpsite; moreover, the samples were collected in the period of winter and in accordance with a report published by Environmental Protection Agency of the State of São Paulo (CETESB) the pollution during the 2006 winter was the worst in the last 10 years. Between May and September, there were 49 days with pollution above the acceptable indices and, dry time, few rains or winds made the pollutants dispersion difficult. The result for Cu in São Paulo (sample R7, 303±281 μg g^{-1}) was similar to that in the UK (339±163 μg g^{-1}), this result being attributed to the type of ventilation used by inhabitants, which were by means of opened windows, thus facilitating the external environment metal transport into the residences. The concentration of Fe element in household dust within the SPMA was smaller than that in other cities.

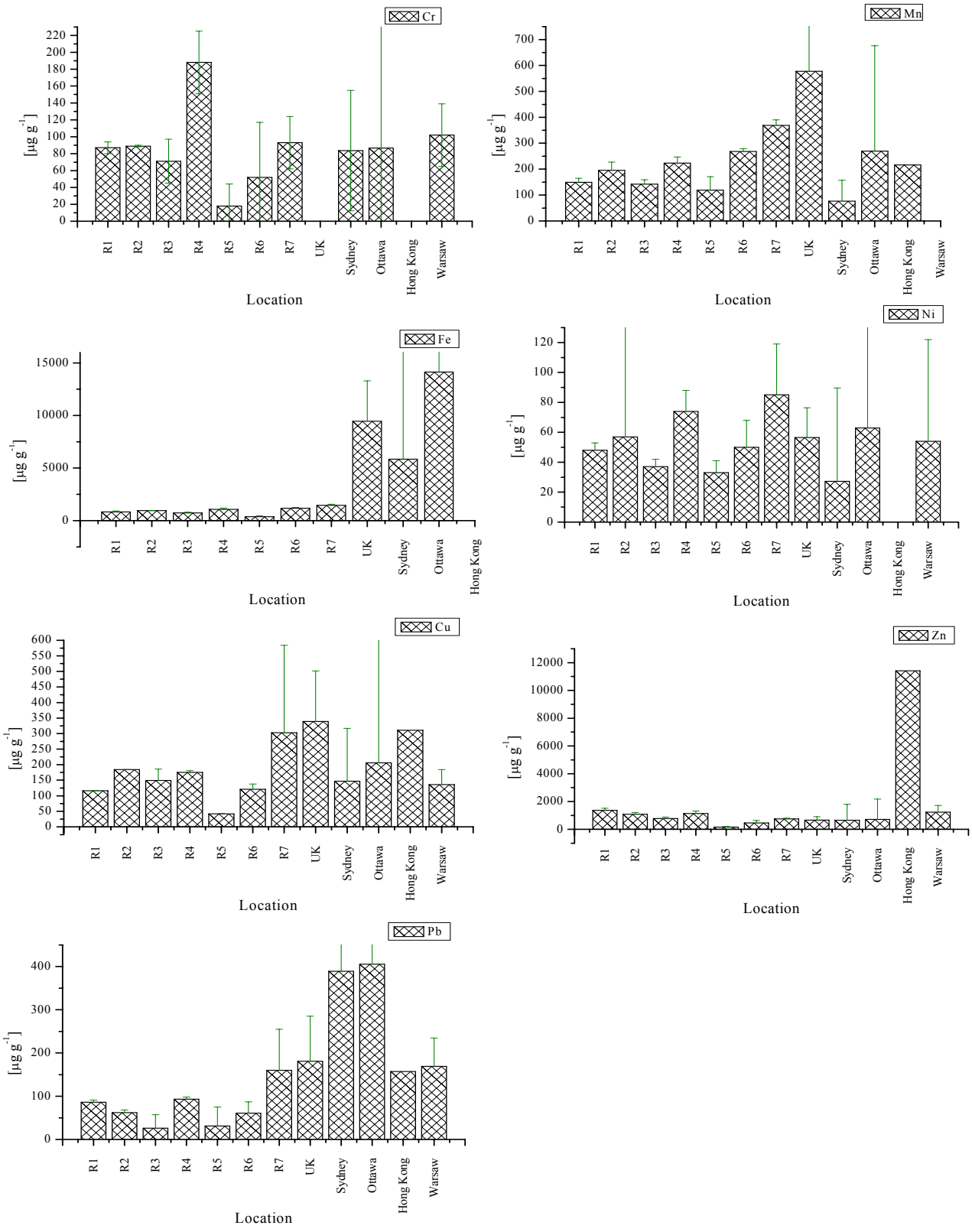

Figure 2. Average concentrations of seven metals in São Paulo and other locations

3. CONCLUSIONS

The concentrations of Cr and Ni metals in household dust, within the São Paulo metropolitan area, were generally higher than those of other cities around the world, but for the Fe this has not occurred, it was lower. Comparisons with earlier studies have revealed that the household dust Mn, Cu, Zn and Pb levels were similar and that the source of this contamination is primarily motor vehicle emissions, but also generated particles from train stations and dumpsites. The dwellings themselves, in the city of São Paulo, may pose a health hazard to human beings because of the potential effect of the content of toxic metals registered in household dust. This warning has been raised by other studies, concerning household dust in big cities.

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