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Elemental Composition of $PM_{2.5}$ in Araraquara City (Southeast Brazil) during Seasons with and without Sugar Cane Burning

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Abstract

Particulate matter with an aerodynamic diameter below 2.5 μm ($PM_{2.5}$), present in polluted air, has been associated with a large spectrum of health impairments, mainly because of its deep deposition into the lungs. Araraquara City (Southeast Brazil) is surrounded by sugar-cane plantations, which are burned to facilitate the harvesting; this process causes environmental pollution due to the large amounts of soot that are released into the atmosphere. In this work, the elemental composition of $PM_{2.5}$ was studied in two scenarios, namely in sugar-cane harvesting (HV) and in non-harvesting (NHV) seasons. The sampling strategy included one campaign in each season. $PM_{2.5}$ was collected using a dichotomous sampler (10 L·min^{-1}, 24 h) with PTFE filters. Information concerning the bulk elemental concentration was provided by energy-dispersive X-ray fluorescence. Enrichment factor analysis indicated that S, Cl, K, Cr, Ni, Cu, Zn, As, Cd and Pb were highly enriched relative to their crustal ratios (to Al). Principal component analysis was used to get some insight about the sources of the elements. Principal component 1 (PC1) explained 30.5% of data variance. The elements that had high loading (>0.7) were: S, Cr, As, and Pb; these are associated with combustion of fossil fuels. In principal component 2 (PC2), Cl, Cu, Zn, and Cd showed high loadings;

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these elements are associated with biomass burning. The Ni concentration found is three times larger than the threshold of risk for lung cancer, as recommended by the World Health Organization.

Keywords

Sugar-Cane Burning, $PM_{2.5}$, Individual Particle Analysis, EDXRF, Cluster Analysis, Principal Components Analysis

1. Introduction

Araraquara City, located in the central area of São Paulo State (Brazil), has 222,000 inhabitants and it is surrounded by sugar-cane plantations (49,000 hectares of total cultivated area, in the crop year 2013/2014) [1]. In the harvest season, from May to November, each year, the crops are burned to facilitate the process of manual harvesting. Burning protects the workers from the sharp leaves (because of biogenic silica naturally found in grasses) and snakes, and increases the sugar content by weight due to water evaporation [2]. This process causes environmental pollution from the large amounts of soot released into the atmosphere [3] [4].

Humans are exposed to various chemicals, through various routes, and from several sources which are ubiquitous in the environment; these sources are linked to from natural and anthropogenic activities [5] [6]. Airborne particulate matter with diameters smaller than 2.5 micrometers ($PM_{2.5}$) has a large atmospheric residence time, enough to interact with the human body, and it may reach the bronchi and alveoli [7]. Metals contained in airborne particulate matter may bind to tissues of the lungs during the breathing process causing health risks for short-term effects (premature mortality, hospital admissions) and long-term or cumulative health effects, such as morbidity, lung cancer, cardiovascular, and cardiopulmonary diseases [8]. Anthropogenic burning processes such as engine motor exhaust (fossil fuels) and agricultural burning processes (at sugarcane harvesting, for example) release metals into atmosphere above natural levels [9]-[11]. Airborne particulate from the streets contributes mostly in quantities of oxides of Al, Si, Ca, Ti, Fe and others, depending on the study area [12]. Because of this, several studies involving the determination of elements in particulate matter have been published. Some of these studies have been conducted in Brazil. Ref. [13] evaluated the presence of metals in different fractions of atmospheric dust at three different sites in Salvador City (NE, Brazil). The authors found Fe, Zn and Cu in higher levels, whose sources were attributed to mining activities and vehicular traffic. Godoi *et al*. [11] determined 16 elements in total particulate matter (Araraquara City, SE, Brazil) for a week in August 2004 and identified the presence of three main groups. The first group, including Al, Si, Ti, Fe and Ca was attributed to soil aerosol particles. The second group was represented by P, S and Cl, indicating the presence of bioorganic aerosol components. The third group was characterized by the presence of Cr, Cu, Mn, Ni, Pb, V and Zn. Cu, Mn and Zn are essential elements that are absorbed by sugar cane (*Saccharum officinarum* L.) [14] and can be released from the burning of leaves into the atmosphere. Ref. [15] investigated the presence of water-soluble inorganic ions and metals from total airborne particulate matter in three cities of São Paulo State (São Paulo, Araraquara and Piracicaba). The highest concentrations for NO_3^-, SO_4^{2-}, and K^+ were found in Araraquara City and the authors attributed them to motor vehicle exhaust emission and biomass burning. In all papers about sugarcane burning, the sampling was done only in the harvesting season. Chemical composition of aerosol particles from emissions of vegetation fires in the Amazon [16] and cerrado [17] points to some elements such as K, Cl, Zn as responsible for the variability of the data set, indicating that the source is biomass burning.

Several statistical tools and models have been used to determine the sources of PM, when elemental composition is the input data of choice [18]. The most used statistical tools, for this propose, have been multivariate statistical analysis, like hierarchical cluster analysis (HCA) and principal component analysis (PCA) [12] [19] [20].

We have studied the polycyclic aromatic hydrocarbons (PAHs) composition of atmospheric particulate matter over Araraquara City [3] [4] and the PAHs data (PM_{10} and $PM_{2.5}$) showed a high positive correlation to sugarcane burning, indicating an increased cancer risk and mutagenicity of PM. Additionally we have done an initial study on the elemental composition of TSP (Total Suspended Particle) from Araraquara City [11] in the sugarcane burning season; the results pointed out a strong contribution with sugarcane burning for some elements (P, S, Cl, Cu, Zn). The main focus of our studies is environmental health, and thus this work presents the data obtained for the elemental composition for $PM_{2.5}$ in both sugarcane seasons (harvesting and non-harvesting), aiming to investigate the inorganic contribution to this PM that is important for human health concern.

2. Experimental

2.1. Sampling

Sampling was conducted by a dichotomous sampler type "Havard", operated with a flow of 10 $L \cdot min^{-1}$. Each filter (PTFE, 37 mm, 2 μm in pore size, Pall Corporation, New York, NY, USA) was exposed for 24 h. Samples were taken in two different seasons: 10 samples corresponding to the months of January and February 2009 (non-harvest) and 10 samples corresponding to the months of May and June 2009 (harvest). The sampler was placed at a height of 2 m (664 m above sea level) at the Institute of Chemistry of Universidade Estadual Paulista (UNESP, 21˚48'20.57"S and 48˚11'30.44"W), in a suburban area of Araraquara City. The closest sugar-cane fields are approximately 5 km distant (**Figure 1**).

2.2. Elemental Analysis

The $PM_{2.5}$ elemental analysis was investigated by X-ray fluorescence using an energy-dispersive spectrometer PANalytical, model Epsilon 5 HE-P-EDXRF, equipped with an X-ray tube of 600 W as excitation source, and a three-dimensional geometry, defined by three orthogonal axes. The measurements were performed on this equipment with three-dimensional geometry of polarization with 13 secondary targets (W, CeO_2, CsI, Ag, Mo, Zr, KBr, Ge, Co, Fe, Ti, CaF_2, Al) and two Barkla targets (Al_2O_3 and B_4C). The characteristic X-ray radiation was detected by a Ge detector (PAN 32) with a width at half maximum resolution of 165 eV, performing non-destructive quantitative analysis of elements from Al up to U. To evaluate the accuracy and precision of data generated by EDXRF, certified reference material of the National Institute of Standards and Technology (NIST) (SRM 2783—particulate material on filter) was used.

2.3. Statistical Analysis

HCA and PCA were performed using Statistica 7.0 software [21]. For HCA, we used standardized data matrices and the Ward method where the Euclidean distance was applied. The numbers of principal components (PCs) extracted were analyzed according to the Kaiser criterion [22]. This criterion retains only factors with eigenvalues > 1 of the complete data set of elemental concentrations.

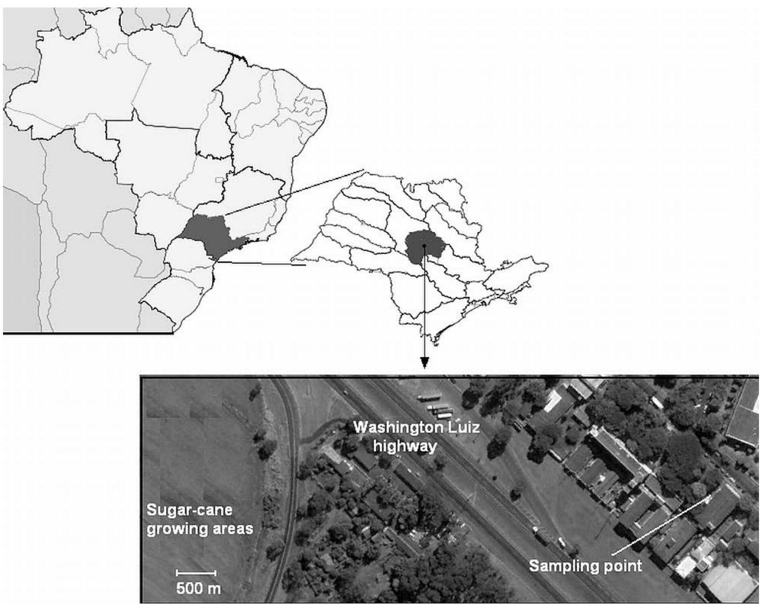


Figure 1. Sampling location in relation to area of burning sugar cane.

2.4. Enrichment Factors (EF)

To assess the contribution of anthropogenic versus crustal sources, we calculated enrichment factors (EF). The EF calculation is done using the concentration of an element found in the airborne particulate material, relating it with an already established pattern of concentration for this element in nature [23]. Thus, it is possible to distinguish whether an analyte is natural or anthropogenic [23] [24].

Several elements for the crustal enrichment factor are being reported in the literature such as Al, Fe, Sc, Si, and Ti [23] [25], of which Al is used in the majority of the studies [23]. Elements with enrichment factor values above a threshold of 4 are considered enriched [26].

3. Results and Discussion

To evaluate the precision and accuracy of the EDXRF technique, certified reference material of NIST 2783 was used; these results (including limits of detection) are presented in **Table 1**.

The results obtained by EDXRF analysis for each filter, expressed in $\mu g \cdot cm^{-2}$ were as multiplied by the filter area (8.00 cm^2) and divided by the air sampling volume (in m^3).

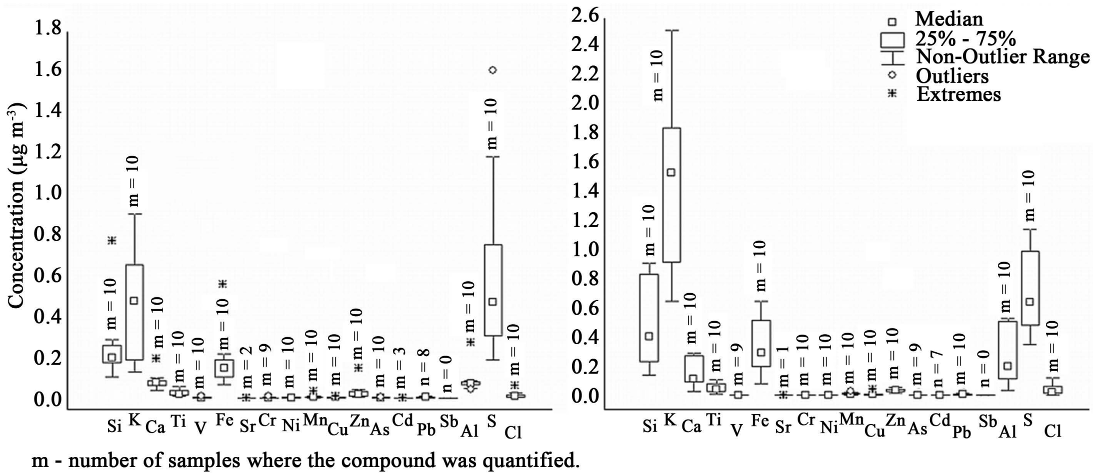
Table 2 and **Figure 2** show elements concentrations in non-harvest and harvest seasons.

It is observed in **Figure 2**, e.g., that K has a profile of variation in different concentration in both seasons, with non-harvest and harvest of the sugar-cane. K has been reported as emitted from biomass burning [11] [15]. The elements that showed enrichment factor > 10 were: S, Cl, K, Cr, Ni, Cu, Zn, Cd, and Pb, indicating that the source is anthropogenic. The predominant wind direction is not a relevant datum for this study, because the sampling site is surrounded by sugar-cane plantations at a distance of 5 km at the most. The sugar-cane burning events occur randomly in the fields, and therefore on all the sampling days, there was burning in all directions from the sampling site [3].

Table 1. Evaluation of precision and accuracy of EDXRF for a sample of certified reference material NIST 2783 (airborne particulate matter) (n = 6, $p = 0.95$).

Elements	Certified values ($\mu g \cdot cm^{-2}$)	Found values ($\mu g \cdot cm^{-2}$)	Limit of detection ($ng \cdot m^{-3}$)
Al	2.33 ± 0.05	2.8 ± 0.4	0.04
Si	Not certified (reference value, 5.9 ± 0.2)	6.4 ± 0.2	0.03
S	Not certified (reference value, 0.11 ± 0.03)	0.14 ± 0.04	0.01
Cl	ND	0.26 ± 0.03	0.006
K	0.53 ± 0.05	0.53 ± 0.01	0.003
Ca	1.3 ± 0.2	1.35 ± 0.03	0.003
Ti	0.15 ± 0.02	0.15 ± 0.02	0.002
Fe	2.7 ± 0.2	2.73 ± 0.04	0.02
Zn	0.18 ± 0.01	0.18 ± 0.01	0.06
V	0.005 ± 0.001	0.002 ± 0.002	0.04
Cr	0.014 ± 0.003	0.015 ± 0.003	0.01
Mn	0.032 ± 0.001	0.035 ± 0.003	0.02
Ni	0.007 ± 0.001	0.005 ± 0.002	0.04
Cu	0.040 ± 0.004	0.044 ± 0.003	0.01
As	0.0012 ± 0.0001	<LOD	ND
Pb	0.03 ± 0.01	0.02 ± 0.01	0.02

ND = not detected; LOD = limits of detection.



(a) (b)

Figure 2. Boxplot of Whiskers relating the concentrations found at seasons of the various elements of the non-harvest (a) and harvest (b), n = 10 in each season. The point in the box is the median, the box represents 25% - 75% percentiles and the whiskers are the minimum and the maximum.

Table 2. The mean, median, minimum and maximum of elemental concentrations (in μg·m^{-3}) in non-harvest and harvest season.

Element	Non-harvest season (μg·m^{-3})				Harvest season (μg·m^{-3})			
	Mean	Median	Minimum	Maximum	Mean	Median	Minimum	Maximum
Si	0.2509	0.1941	0.1021	0.7647	0.4759	0.4001	0.1376	0.9001
K	0.4452	0.4713	0.1253	0.8955	1.4595	1.5123	0.6400	2.4841
Ca	0.0821	0.0758	0.0367	0.1920	0.1479	0.1150	0.0299	0.2915
Ti	0.0255	0.0198	0.0078	0.0555	0.0474	0.0403	0.0112	0.1052
V	0.0023	0.0010	0.0002	0.0080	0.0011	0.0008	<LOD	0.0024
Fe	0.1684	0.1438	0.0674	0.4700	0.3281	0.2863	0.0828	0.6390
Sr	-	-	<LOD	0.0002	-	-	<LOD	0.0003
Cr	0.0017	0.0008	<LOD	0.0073	0.0025	0.0024	0.0005	0.0049
Ni	0.0022	0.0014	0.0002	0.0061	0.0012	0.0012	0.0003	0.0021
Mn	0.0074	0.0051	0.0023	0.0305	0.0129	0.0106	0.0042	0.0267
Cu	0.0033	0.0028	0.0014	0.0082	0.0096	0.0063	0.0016	0.0386
Zn	0.0331	0.0209	0.0069	0.1447	0.0333	0.0324	0.0173	0.0531
As	0.0023	0.0017	0.0005	0.0055	0.0022	0.0025	<LOD	0.0039
Cd	0.0002	<LOD	<LOD	0.0015	0.0003	0.0003	<LOD	0.0009
Pb	0.0038	0.0027	<LOD	0.0092	0.0077	0.0067	0.0003	0.0166
Sb	-	-	<LOD	<LOD	-	-	<LOD	<LOD
Al	0.0865	0.0690	0.0415	0.2693	0.2582	0.1990	0.0380	0.5251
S	0.6278	0.4666	0.1873	1.5901	0.7120	0.6308	0.3476	1.1281
Cl	0.0138	0.0082	0.0027	0.0600	0.0373	0.0241	0.0029	0.1190

ND = not detected; LOD = limits of detection.

HCA showed three distinct grouping for samples (**Figure 3**). Groups 1 and 3 (G1 and G3) are mainly samples collected during the harvest season, while the Group 2 (G2) refers to samples collected during the non-harvest, with the exception of two samples (S275 and S279).

The Groups E1 and E2 are characterized by S, Cl, Cr, Cu, Mn, Ni, Pb, V and Zn, where Zn and Cu are essential elements present in the fluid movement of higher plants [11] and can be released through the sugarcane burning process. Sulfur (S) can be associated with fossil fuel burning or with particulate emission from vehicle tires. Chlorine is frequently associated to the waste incineration process of material containing plastics (mainly PVC) and chloride salts [27]; however in Araraquara there is only one solid waste incinerator located around 20 km away from the sampling point. Thus this source of Cl was considered not important to explain Cl concentration in the analyzed sample. The E3 group was represented mainly by Al, Si, Ti, Fe and Ca, which is the particulate matter from the soil [11].

In PCA analysis, there were four components, which account for 74% of the data variability. Four PCs were selected according to the Kaiser criterion (eigenvalue > 1). **Table 3** shows the values of the loadings on the PCs and % of total variance.

The PC1 corresponding to samples G2 (non-harvest season), indicated that it is mainly associated with emissions from burning fossil fuels and particulate matter from vehicle tire wear, because it has high loads for S (0.743), As (0.720) and Pb (0.824). Vehicle tires contain S and As compounds (As_2S_3) and other sulfides (PbS and CuS) [28]. PC2, corresponding to samples G1 (harvest season), indicates an association with biomass burning. It has a high loading value for Cl (0.754), Cd (0.602), Zn (0.433) and Cu (0.465). The element Cl is an indicator of the presence of bioinorganic compounds in the aerosol and Zn and Cu are essential elements present in the fluids of higher plants [11].

PC3 and PC4 reflect a complex pattern of pollution that can originate from various sources such as vegetation burning (K), and industrial emission in Araraquara, which is responsible for emitting about 3.2 ton of particulate matter in the year 2009 [29].

The meteorological parameters (temperature and rainfall) were entered in multivariate analysis, and a low correlation (<0.16) was observed with the chemical species analyzed. Ref. [12] introduced meteorological parameters in the multivariate analysis; the correlation between chemical species was not altered.

Comparing the results of harvest for the elements with greater EF obtained in this work with Godoi *et al*. [11] (**Table 4**) in the same locality and also during the harvest season, a significant difference (T-test, $\alpha = 0.05$) was found for the elements Ni, Zn and Cl. The 2009 values were below the 2004 values for these elements. As described earlier, Cl is a marker of bioinorganic aerosol and Zn is an essential element for higher plants. This decrease in concentration may be related to the reduction of burning straw cane sugar due to increased mechanization of harvesting [30]. The number of fire foci in Brazil for the month of August 2004, sampling period by Ref. [11] in 2004 was 38,000 [31] while in the period of June 2009 (sample period in this study) the number of foci totaled less than 5% (1850 foci) compared with the period of Godoi *et al*. [11].

Table 3. Loading values with total variance (%) of their PCs.

Variable	PC1 (30.5%)	PC2 (17.7%)	PC3 (14.3%)	PC4 (11.6%)
K	**0.597**	0.125	−0.009	**0.493**
Cr	**0.719**	−0.095	−0.072	**−0.603**
Ni	0.202	−0.316	**0.736**	**0.467**
Cu	**0.443**	**0.465**	−0.397	0.325
Zn	0.120	**0.433**	**0.605**	−0.366
As	**0.720**	−0.371	−0.193	−0.157
Cd	0.347	**0.602**	0.277	−0.199
Pb	**0.824**	−0.007	−0.299	0.094
S	**0.743**	−0.416	0.379	0.022
Cl	0.231	**0.754**	0.088	0.143

Loading values greater than 0.4 are in bold.

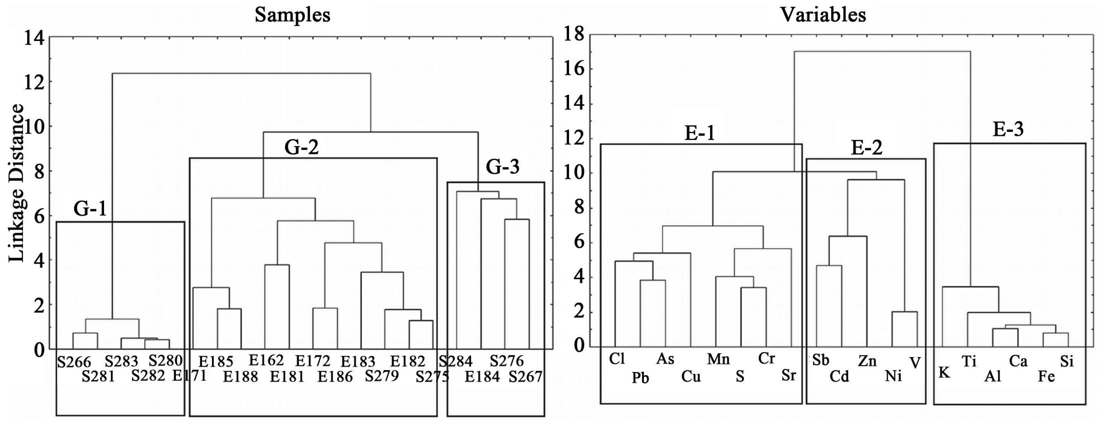


Figure 3. Hierarchical cluster analysis of the samples: G1: Group 1, G2: Group 2, and G3: Group 3; and variables: E1: Elements 1, E2: Elements 2 and E3: Elements 3.

Table 4. Comparison of the values obtained in this work with Godoi *et al.* [11].

Element-period	N[a]	Confidence interval (−95%)	Confidence interval (+95%)	Median ($\mu g \cdot m^{-3}$)	*p* value[b]
K-2004	9	0.9343	1.2324	1.1000	0.09
K-2009	10	1.0270	1.8920	1.5123	
Cr-2004	9	*	0.0184	0.0000	0.57
Cr-2009	10	0.0015	0.0034	0.0024	
Ni-2004	9	0.0029	0.0149	0.0100	**0.006**
Ni-2009	10	0.0008	0.0017	0.0012	
Cu-2004	9	0.0044	0.0112	0.0100	0.63
Cu-2009	10	0.0021	0.0171	0.0063	
Zn-2004	9	0.0430	0.0592	0.0500	**0.003**
Zn-2009	10	0.0248	0.0418	0.0324	
Pb-2004	9	0.0044	0.0112	0.0100	0.96
Pb-2009	10	0.0042	0.0112	0.0067	
S-2004	9	0.4021	0.8535	0.5500	0.53
S-2009	10	0.5093	0.9148	0.6308	
Cl-2004	9	0.0904	0.2363	0.1300	**0.001**
Cl-2009	10	0.0128	0.0617	0.0241	

N: number of samples; [b]t-test with $\alpha = 0.05$; *Values less than zero were omitted.

The World Health Organization apud Quitério [12] recommends maximum values for several elements concerning lung cancer risk factors: for e.g. Pb (500 $ng \cdot m^{-3}$), Cd (5 $ng \cdot m^{-3}$), Ni (0.38 $ng \cdot m^{-3}$) and Cr (1100 $ng \cdot m^{-3}$) in ambient air in order to avoid, prevent or reduce harmful effects on human health [12]. In this study the median concentrations found for Pb, Cd, Ni, and Cr in $PM_{2.5}$ were 6.7, 0.6, 1.20 and 2.4 $ng \cdot m^{-3}$, respectively. The values were below the established limit for all elements with the only exception of Ni, which showed a value three times higher than that recommended by WHO.

When comparing the present results with the data obtained in 2004, a decrease was observed in the concentration of Cl and Zn, whose occurrence may be due to the reduction of foci in the Araraquara region.

4. Conclusions

$PM_{2.5}$ showed different elemental compositions both in relation to qualitative or quantitative profiles. Our data pointed out that Cl, Cu, and Zn were the elements enriched in the sugar cane burning season. Additionally, data comparison between 2004 and 2009 samples, demonstrated diminishing concentration of elements which was coherent with the lower number of burning foci in São Paulo State, this fact was observed in studies of PAHs in $PM_{2.5}$ developed by this research group.

In Brazil, there are no laws that set limits for the concentration of metals/elements in airborne particulate matter. The results for Cr, Cd, and Pb were below the level recommended by the World Health Organization (WHO), but the Ni concentrations were three times larger than the threshold of risk of lung cancer. The data suggest a worrying scenario for human exposure to elemental concentrations in cities surrounded by sugar cane plantations, where the burning process is widely used. On the other hand, K, the most abundant element in sugarcane burning season, although it is not considered as a toxic element, can cause inflammation of lung tissue; this may be a theme of concern.

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References

[1] INPE (2015) Monitoring of Cane Sugar. http://www.dsr.inpe.br/laf/canasat/dados/SP_2013-14.xls

[2] Zamperlini, G.C.M., Santiago-Silva, M. and Vilegas, W. (2000) Solid-Phase Extraction of Sugar-Cane Soot Extract for Analysis by Gas Chromatography with Flame Ionisation and Mass Spectrometric Detection. *Journal of Chromatography A*, **889**, 281-286. http://dx.doi.org/10.1016/S0021-9673(00)00291-0

[3] Andrade, S.J., Cristale, J., Silva, F.S., Zocolo, G.J. and Marchi, M.R.R. (2010) Contribution of Sugar-Cane Harvesting Season to Atmospheric Contamination by Polycyclic Aromatic Hydrocarbons (PAHs) in Araraquara City, Southeast Brazil. *Atmospheric Environment*, **44**, 2913-2919. http://dx.doi.org/10.1016/j.atmosenv.2010.04.026

[4] Silva, F.S., Cristale, J., Andre, P.A., Saldiva, P.H.N. and Marchi, M.R.R. (2010) $PM_{2.5}$ and PM_{10}: The Influence of Sugar-Cane Burning on Potential Cancer Risk. *Atmospheric Environment*, **44**, 5133-5138. http://dx.doi.org/10.1016/j.atmosenv.2010.09.001

[5] Zheng, N., Liu, J., Wang, Q. and Liang, Z. (2010) Heavy Metals Exposure of Children from Stairway and Sidewalk Dust in the Smelting District, Northeast of China. *Atmospheric Environment*, **44**, 3239-3245. http://dx.doi.org/10.1016/j.atmosenv.2010.06.002

[6] Brito, J.M., Belotti, L., Toledo, A.C., Antonangelo, L., Silva, F.S., Alvim, D.S., Andre, P.A., Saldiva, P.H.N. and Rivero, D.H.R.F. (2010) Acute Cardiovascular and Inflammatory Toxicity Induced by Inhalation of Diesel and Biodiesel Exhaust Particles. *Toxicological Sciences*, **116**, 67-78. http://dx.doi.org/10.1093/toxsci/kfq107

[7] Fahmy, B., Ding, L., You, D., Lomnicki, S., Dellinger, B. and Cormier, S.A. (2010) *In Vitro* and *in Vivo* Assessment of Pulmonary Risk Associated with Exposure to Combustion Generated Fine Particles. *Environmental Toxicology and Pharmacology*, **29**, 173-182. http://dx.doi.org/10.1016/j.etap.2009.12.007

[8] Valavanidis, A., Fiotakis, K. and Vlachogianni, T. (2008) Airborne Particulate Matter and Human Health: Toxicological Assessment and Importance of Size and Composition of Particles for Oxidative Damage and Carcinogenic Mechanisms. *Journal of Environmental Science and Health, Part C*, **26**, 339-362. http://dx.doi.org/10.1080/10590500802494538

[9] Mihucz, V.G., Szigeti, T., Dunster, C., Giannoni, M., Kluizenaar, Y., Cattaneo, A., Mandin, C., Bartzis, J.G., Lucarelli, F., Kelly, F.J. and Záray, G. (2015) An Integrated Approach for the Chemical Characterization and Oxidative Potential Assessment of Indoor $PM_{2.5}$. *Microchemical Journal*, **119**, 22-29. http://dx.doi.org/10.1016/j.microc.2014.10.006

[10] Kovacevik, B., Wagner, A., Boman, J., Laursen, J. and Pettersson, J.B.C. (2011) Elemental Composition of Fine Particulate Matter ($PM_{2.5}$) in Skopje, FYR of Macedonia. *X-Ray Spectrometry*, **40**, 280-288. http://dx.doi.org/10.1002/xrs.1337

[11] Godoi, R.H.M., Godoi, A.F.L., Worobiec, A., Andrade, S.J., de Hoog, J., Santiago-Silva, M.R. and Van Grieken, R. (2004) Characterisation of Sugar Cane Combustion Particles in Araraquara Region, Southeast Brazil. *Microchimica Acta*, **145**, 53-56. http://dx.doi.org/10.1007/s00604-003-0126-x

[12] Quiterio, S.L., Silva, C.R.S., Arbilla, G. and Escaleira, V. (2004) Metals in Airborne Particulate Matter in the Industrial District of Santa Cruz, Rio de Janeiro, in an Annual Period. *Atmospheric Environment*, **38**, 321-331. http://dx.doi.org/10.1016/j.atmosenv.2003.09.017

[13] Pereira, P.A.P., Lopes, W.A., Carvalho, L.S., Rocha, G.O., Bahia, N.C., Loyola, J., Quiterio, S.L., Escaleira, V., Arbilla, G. and Andrade, J.B. (2007) Atmospheric Concentrations and Dry Deposition Fluxes of Particulate Trace Metals in Salvador, Bahia, Brazil. *Atmospheric Environment*, **41**, 7837-7850. http://dx.doi.org/10.1016/j.atmosenv.2007.06.013

[14] Bowen, J.E. (1969) Absorption of Copper, Zinc, and Manganese by Sugarcane Leaf Tissue. *Plant Physiology*, **44**, 255-261. http://dx.doi.org/10.1104/pp.44.2.255

[15] Vasconcellos, P.C., Balasubramanian, R., Bruns, R.E., Sanchez-Ccoyllo, O., Andrade, M.F. and Flues, M. (2007) Water-Soluble Ions and Trace Metals in Airborne Particles over Urban Areas of the State of São Paulo, Brazil: Influences of Local Sources and Long Range Transport. *Water, Air, & Soil Pollution*, **186**, 63-73. http://dx.doi.org/10.1007/s11270-007-9465-2

[16] Artaxo, P., Fernandes, E.T., Martins, J.V., Yamasoe, M.A., Hobbs, P.V., Maenhaut, W., Longo, K.M. and Castanho, A. (1998) Large-Scale Aerosol Source Apportionment in Amazonia. *Journal of Geophysical Research*, **103**, 31837-31847. http://dx.doi.org/10.1029/98JD02346

[17] Yamasoe, M.A., Artaxo, P., Miguel, A.H. and Allen, A.G. (2000) Chemical Composition of Aerosol Particles from Direct Emissions of Vegetation Fires in the Amazon Basin: Water-Soluble Species and Trace Elements. *Atmospheric Environment*, **34**, 1641-1653. http://dx.doi.org/10.1016/S1352-2310(99)00329-5

[18] Yatkin, S. and Bayram, A. (2007) Elemental Composition and Sources of Particulate Matter in the Ambient Air of a Metropolitan City. *Atmospheric Research*, **85**, 126-139. http://dx.doi.org/10.1016/j.atmosres.2006.12.002

[19] Brokamp, C., Rao, M.B., Fan, Z. and Ryan, P.H. (2015) Does the Elemental Composition of Indoor and Outdoor $PM_{2.5}$ Accurately Represent the Elemental Composition of Personal $PM_{2.5}$? *Atmospheric Environment*, **101**, 226-234. http://dx.doi.org/10.1016/j.atmosenv.2014.11.022

[20] Vallius, M., Janssen, N.A.H., Heinrich, J., Hoek, G., Ruuskanen, J., Cyrys, J., Van Grieken, R., Hartog, J.J., Kreyling, W.G. and Pekkanen, J. (2005) Sources and Elemental Composition of Ambient $PM_{2.5}$ in Three European Cities. *Science of the Total Environment*, **337**, 147-162. http://dx.doi.org/10.1016/j.scitotenv.2004.06.018

[21] (2009) Statistica 7.0. StatSoft Inc., Tulsa, USA.

[22] Stevens, J.P. (2002) Applied Multivariate Statistics for the Social Sciences. 4th Edition, Lawrence Erlbaum, Mahwah.

[23] Hoornaert, S., Godoi, R.H.M. and Van Grieken, R. (2004) Elemental and Single Particle Aerosol Characterisation at a Background Station in Kazakhstan. *Journal of Atmospheric Chemistry*, **48**, 301-315. http://dx.doi.org/10.1023/B:JOCH.0000044432.74476.b0

[24] Maenhaut, W., Cornille, P., Pacyna, J.M. and Vitols, V. (1989) Trace Element Composition and Origin of the Atmospheric Aerosol in the Norwegian Arctic. *Atmospheric Environment*, **23**, 2551-2569. http://dx.doi.org/10.1016/0004-6981(89)90266-7

[25] Van Malderen, H., Van Grieken, R., Bufetov, N.V. and Koutzenogii, K.P. (1996) Chemical Characterization of Individual Aerosol Particles above Lake Baikal, Siberia. *Environmental Science & Technology*, **30**, 312-321. http://dx.doi.org/10.1021/es950402k

[26] Duce, R., Hoffman, G., Ray, B., Fletcher, I., Wallace, G., Fasching, J., Piotrowicz, S., Walsh, P., Hoffman, E., Miller, J. and Heffter, J. (1976) Trace Metals in the Marine Atmosphere: Sources and Fluxes. Lexington Books, Lexington.

[27] Avigo Jr., D., Godoi, A.F.L., Janissek, P.R., Makarovska, Y., Krata, A., Potgieter-Vermaak, S., Alfoldy, B., Van Grieken, R. and Godoi, R.H.M. (2008) Particulate Matter Analysis at Elementary Schools in Curitiba, Brazil. *Analytical and Bioanalytical Chemistry*, **391**, 1459-1468. http://dx.doi.org/10.1007/s00216-008-2031-y

[28] Monteiro, L.P.C. and Mainier, F.B. (2008) Queima de pneus inservíveis em fornos de clínquer. *Engevista*, **10**, 52-58.

[29] CETESB (2009) Report on Air Quality in the State of São Paulo, Brazil. http://www.cetesb.sp.gov.br/ar/qualidade-do-ar/31-publicacoes-e-relatorios

[30] Van Den Wall Bake, J.D., Junginger, M., Faaij, A., Poot, T. and Walter, A. (2009) Explaining the Experience Curve: Cost Reductions of Brazilian Ethanol from Sugarcane. *Biomass and Bioenergy*, **33**, 644-658. http://dx.doi.org/10.1016/j.biombioe.2008.10.006

[31] Monitoring of Foci (2010). http://sigma.cptec.inpe.br/queimadas/queimamensaltotal1.html?id=mm#