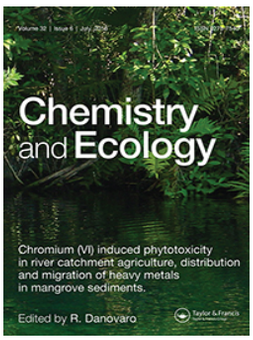

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Simultaneous determination of Cd, Pb, and Cu in atmospheric particulate matter from different regions of the city of Presidente Prudente, Sao Paulo, Brazil

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ABSTRACT

This article explores the assessment of atmospheric deposition, from the analysis of the sampling methods, the analytical procedures for chemical characterisation of pollutants, and the main results from the scientific literature. Atmospheric particulate matter (PM) was collected in four regions of the city of Presidente Prudente (Sao Paulo State, Brazil) characterised by heavy traffic flows and high population density. The Cd, Pb, and Cu metals were determined in samples using differential pulse anodic stripping voltammetry. The PM was collected every fortnight using passive sampling, over a total period of two years. A comparative study between the element deposition fluxes in four sampling sites was performed. The relative contribution of the quantitative descriptors to divergence among the analysis by Tocher grouping method was also studied.

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Metal deposition flux; atmospheric particulate; Tocher method

1. Introduction

Atmospheric particulate matter (PM) is a complex mixture of solid and/or liquid substances suspended in an atmospheric environmental. Atmospheric particles range in diameter from a few nanometres to tens of micrometres, and contain a myriad of chemical species. The principle types of directly emitted particles are associated with soil-related particles and elemental carbon particles from the combustion of fossil fuels and biomass materials.[1] The atmospheric particulate can influence physicochemical processes related to climate, precipitation patterns, radiative transfer, and mainly the population health.[2] Several studies have established a strong correlation between exposure of the fine particles with increase of the rates of mortality, morbidity, respiratory, and cardiovascular problems.[1–7]

From the toxicological perspective, some of the metals most toxic to humans include cadmium, lead, nickel, antimony, chromium, and tin, which have been widely studied due to their use in industry.[8–10] Although in many regions the levels of these metals are low, they can nevertheless accumulate in the food chain and the environment. The metals are not degraded naturally and their interaction with other substances increases

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the risk of their persistence in the environment. The effect of pollution by atmospheric particulates can result in bioaccumulation in living organisms including humans, its effects take for long periods even after their emission.[11,12]

The city of Presidente Prudente, where this work was conducted, is located in the west of Sao Paulo State, 587 km from the capital. The municipality occupies an area of 562 km^2 and has a population of around 207,000 inhabitants. The main point sources of pollution in Presidente Prudente include a tannery (currently inactive), plastics industries, a hospital waste incinerator (currently inactive), and sugar mills producing sugar and ethanol. In this region, there has been major expansion in cultivation of sugarcane and installation of the associated processing plants, together with agricultural modernisation and growth in the service sector. The advantageous location of Presidente Prudente, especially in terms of transport links, has resulted in substantial economic growth in the region. The expansion of the city generated a diversification of industry, with significant contributions from the civil construction, chemical, and metallurgy sectors.

Although the literature contains many reports concerning atmospheric particulate pollutants, there is very little information available for the study region. This is important information, given the rapid pace of development and the advance of agro-industry in the region. The present work therefore presents an evaluation of the sources and deposition fluxes of cadmium, lead, and copper present in atmospheric PM at four locations in Presidente Prudente. This study contributes to an understanding of the toxic metals in atmospheric PM in regions of rapid environmental and societal change.

2. Experimental

2.1. Study area

The climate of Presidente Prudente is characterised as humid tropical, with an annual average temperature of 23.6°C. The winter months are cooler, with low precipitation, and the summer is hot with high precipitation rates. The region is located within the basin of the Paraná River, and the geology consists of igneous and sedimentary rocks with a high frequency of geological faults and geothermal sources.[13,14] At the study area, the prevailing winds are from the east quadrant (E, SE, NE), representing about 60% of the average operating time and frequency. The prevailing winds from the E (NE and SE) are associated with the Tropical Atlantic anticyclone, where temperatures are high, with low humidity and average speeds. These winds provide a reasonable dispersion of pollutant fumes and odours. Conversely, the W and NW winds are those with the lowest frequencies (6.6% and 7.6%) and duration (4.4% and 4.6%). These winds are associated with Tropical Continental Mass of low atmospheric pressure.

The samples were collected at four sites in the city. Site 1 was located at the meteorological station of UNESP, in the neighbourhood of Jardim Marupiara (22°07′12.06″ S, 51° 24′30.6″ W). Site 2 was at the city's main bus station (22°07′52.33″ S, 51°23′16.80″ W). Site 3 was established at 9th July Plaza central square (22°07′22.49″ S, 51°23′17.89″ W). Site 4 was at a health post in the Vila Real district (22°08′01.09″ S, 51°26′50.46″ W). The sampling sites are shown in Figure 1. The sites at the bus station and the central square were close to the city centre, while the UNESP (2.400 m) and Vila Real (5.600 m) sites were more distant and were exposed to less atmospheric pollution derived from local

Figure 1. Locations of sampling atmospheric PM sites in Presidente Prudente. Site 1: Meteorological station at FCT-UNESP; Site 2: Central bus station; Site 3: Central square (9th July Plaza); Site 4: Vila Real health post. Scale: 800 m. Source: Google Earth.

anthropogenic activities. Constant emission sources during the study period included road vehicles and civil construction works. The characteristics of the sampling sites are provided in Table 1.

The atmospheric PM was collected onto filters using a passive sampler-air system (Figure 2) developed by the Electroanalytical and Sensors Research Group (GPES). At all sites, the samplers were positioned 1.6 m above ground level and sampling was conducted continuously between March 2011 and April 2013, using fortnightly collection periods. Blank filters were included in all collections. The filters with atmospheric PM were rescued fortnightly and new filters were added during the collections.

2.2. Analytical procedures

The PM mass was determined by weighing the filters on an analytical balance (precision scale 0.0001 g), before and after each sample collection. After of the final weighing, the filter papers with PM were calcined in a muffle furnace at 250°C and then decomposed

Table 1. Sampling locations in the city of Presidente Prudente, Sao Paulo State, Brazil.

Site number	Location	Characteristics
1	Meteorological station of the São Paulo State University	Intermediate traffic flow (high flows at certain times), near residential areas
2	Central bus station	High traffic flow and high population density
3	Central square	High population density, high light-duty and heavy-duty vehicle flow, commercial activities
4	Vila Real	Residential neighbourhood with commercial activities and constant vehicle flow

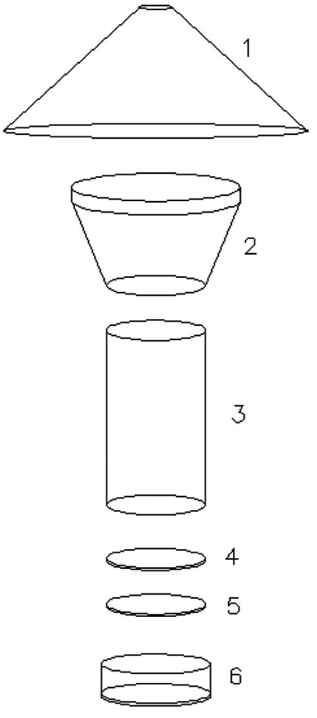

Figure 2. Components of the passive sampler-air. (1) Protective cover; (2) polypropylene funnel; (3) PVC tube; (4) filter paper; (5) polypropylene ring, and (6) PVC base.

for 24 h with 25 mL of HNO_3 (65%, v/v). The samples were subsequently placed in a block digester for 5 h at 102°C. The product of the digestion was transferred into a 50 mL volumetric flask containing sufficient $NaNO_3$ (1.0 mol L^{-1}) to maintain the ionic strength in 0.1 mol L^{-1} after completion of the volume with deionised water. The thermogravimetric analysis was conducted in order to confirm that no metal was lost during the calcination step (this procedure is described in Figure SM1 in the Supplementary Material).

The particular advantages of the voltammetric approach in analysis for metals are high sensitivity, good precision, and accuracy and the possibility of simultaneous determination of different trace metals in the same sample. Measurements were performed using 797 VA Computrace (Metrohm, Switzerland) with 8 hanging mercury drop electrode (drop size 4) as a working electrode. The concentrations of Cd, Pb, and Cu were determined by the multiple standard additions method, employing differential pulse voltammetry with anodic stripping. The measurements were performed in a glass electrochemical cell containing three electrodes: mercury working electrode, an Ag/AgCl (3 mol L^{-1} KCl) reference electrode, and a platinum counter-electrode. The analyses were performed in the potential range from −0.8 to 0.15 V (vs. Ag/AgCl), using a concentration interval of 0.2–1.4 µmol L^{-1}. The sample volume was 4.0 mL and the pre-concentration time was 150 s (at −1.2 V vs. Ag/AgCl). Analytical curves were constructed for Cd, Pb, and Cu using the multiple standard additions procedure (Figure 3).

A total of 48 samples were collected over fortnightly periods at each sampling site (total period of 2 years). Spatial trends in the deposition rates of the metals were investigated

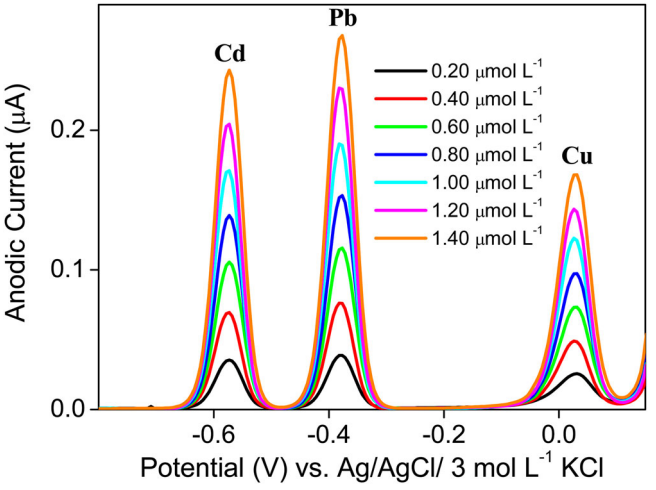

Figure 3. Differential pulse voltammograms for analysis of cadmium, lead, and copper in different concentrations.

using multivariate statistical techniques (canonical analysis and the Tocher grouping method, employing average Euclidean distances) performed using SAS software.

3. Results and discussion

Figure 4 illustrates the profiles of metal concentration in the PM samples in four sampling sites. For all studied elements, the standard deviation values were elevated with variations from ±17.26 μg m^{-2} day^{-1} for deposition flux of Cu (Site 1) to ±53.56 μg m^{-2} day^{-1} for deposition flux of Pb (Site 1). Such variability is considered normal in atmospheric studies,[15–17] given the diversity of sources of PM, as well as different particle sizes

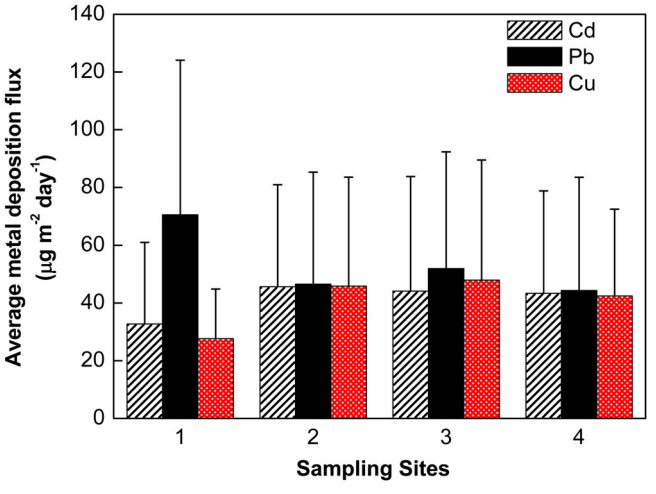

Figure 4. Average deposition fluxes of Cd, Pb, and Cu at the four sampling sites ($n = 48$ analysis per site) during two years.

and local meteorological factors. The average deposition fluxes ranged from 27.59 μg m^{-2} day^{-1} of Cu on Site 1 to 47.93 μg m^{-2} day^{-1} of Cu on Site 3. The average deposition fluxes of the three metals were similar in the Sites 2–4. However, the deposition of Pb was higher on Site 1, indicating greater environmental contamination by this metal during the study period.

The Pearson correlation coefficients obtained for Cd, Pb, and Cu at the four sampling sites are shown in Table 2. The positive correlation between the deposition fluxes of Cd and Pb on Site 1 ($r = 0.4080$) was indicative of similar trends in the deposition fluxes of these two metals. In the Site 2, the significant correlations were obtained between the deposition fluxes of Cd and Pb ($r = 0.7387$) and Cd and Cu ($r = 0.4252$). The correlation on Site 3 was observed between the fluxes of Cd and Pb ($r = 0.5222$) and Cd and Cu ($r = 0.3140$). As found for the other sites, correlation between the deposition of Cd and Pb ($r = 0.6802$) was also observed for Site 4.

Highly significant positive correlations obtained among the deposition fluxes of metals make us to believe that these elements have a common origin. Although the identification of the absolute source of emission was not feasible, the main emissions in the study region include soil dust resuspension and the road transport. In addition, during the sampling period, there were many civil construction sites in operation in the central urban region (Sites 2 and 3). Similar emissions were observed on Site 4, where deposits of sand and gravel were found in the region. In metropolitan areas, the production and use of cement is often one of the most important sources of metals including mercury, lead, cadmium, arsenic, antimony, and chromium, as well as other toxic substances such as dioxins.[18] Another source of cadmium and lead is tobacco smoke, and observations (by both the research team and local workers) indicated a high frequency of smokers at all the sites. The city centre locations were also affected by maintenance work on older buildings, resulting in the release of paint dusts containing metal oxides.

The elevated deposition flux of Pb on Site 1 was unexpected, once the lowest deposition fluxes of Cu and Cd were observed in the same site. Nonetheless, many studies have demonstrated the importance of monitoring the concentrations of atmospheric lead in urban and industrial regions, and have shown that deposition fluxes of the

Table 2. Pearson correlation coefficient matrix for Cd, Pb, and Cu at four sites.

	Cd	Pb	Cu
Site 1			
Cd	1		
Pb	0.4080*	1	
Cu	−0.1891	−0.1281	1
Site 2			
Cd	1		
Pb	0.7387*	1	
Cu	0.4252*	0.1870	1
Site 3			
Cd	1		
Pb	0.5222*	1	
Cu	0.3140**	0.1971	1
Site 4			
Cd	1		
Pb	0.6802*	1	
Cu	−0.1179	−0.1931	1

*Significant at a 1% level of probability.
**Significant at a 5% level of probability.

Table 3. Comparative study of lead deposition fluxes.

Location	[Pb] (μg m^{-2} day^{-1})	Ref.
Goiânia	6.7 ± 6.4	[19]
Australia	34,100 ± 18,800	[20]
Pearl River Delta	12.7 ± 6.72	[21]
North Sea	3.20 ± 6.4	[22]
Tokyo Bay	27.1 ± 5.5	[23]
Presidente Prudente	70.54 ± 53.56	This work

element can vary greatly on both local and regional scales. Table 3 provides a comparison of lead deposition fluxes measured in different locations, including industrial, urban, maritime, and rural regions.

The value of lead obtained in the city of Goiânia (Brazil) [19] corresponds to 90.5% inferior to the overall average for Presidente Prudente. In the study of Alphen (1999), high levels of lead in Australia (Port Pirie) were attributed to the presence of one of the largest lead foundries in the south of the country.[20] These differences reflect the substantial spatial variability in levels of particulate pollutants and the important contributions of local and regional sources of metal emissions to the atmosphere. Sakata et al. [23] studied dry deposition fluxes of lead during by two years at three sites in the Tokyo Bay area. The authors suggest that large particles from sources in the coastal regions contribute largely to the wet and dry depositions of trace elements to the bay, suggesting the importance of river and effluent discharges. In contrast, the region studied here lies another 100 km of a watershed (Paraná River).

3.1. Multivariate analysis

SAS computer program was used for the analysis following the procedures of average linkage clustering analysis method. In this type of analysis, there is grouping of the sites according to their degree of similarity (Figure 5). On the program two groups were

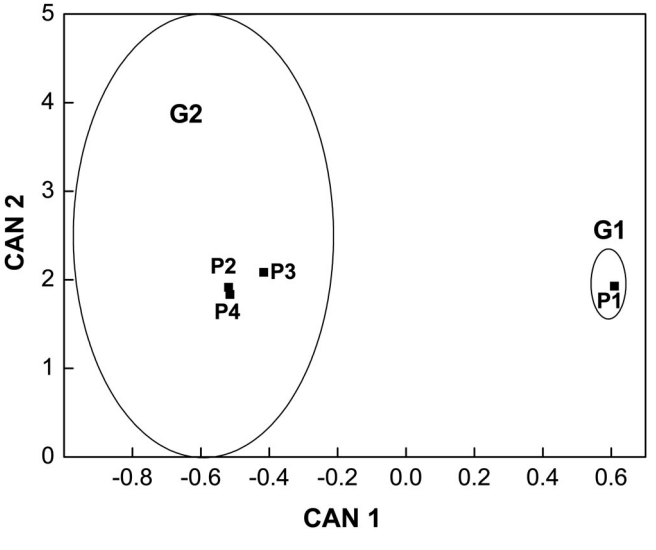

Figure 5. Canonical analysis for Cd, Pb, and Cu present in atmospheric PM collected in four sampling sites.

identified. The first concentrates only the Site 1 and the second concentrates the Sites 2–4. This provided clear evidence of the existence of distinct emission sources on Site 1. The results of the statistical analysis showed that this difference was mostly due to spatial variation in the deposition flux of Pb.

One of the unusual aspects of Site 1 was its proximity to geological faults emitting radon gas and its daughter atoms. Lead is the final stable product of the decay of radon, and is therefore more persistent in the environment compared to the other elements of the series. The fact that the geological faults were confined to the region of Site 1 strongly suggests that these were the source of enhanced emissions of lead at this location.

There have been previous reports in the literature concerning the occurrence of pollution due to the proximity to geological faults. Examples include urban areas in the city of Goiânia (in the central Brazilian state of Goiás) that are located close to geological faults and geothermal sources.[24,25] Nonetheless, despite similarities in terms of geology, the lead deposition fluxes in Goiânia were around 10 times lower than found for Presidente Prudente. This difference can be explained by the fact that in Presidente Prudente, the sampler was installed directly above one of the region's existing geological faults, while in Goiania the samples were collected at a greater distance from the fault, resulting in dilution during atmospheric transport.[19]

4. Conclusions

The deposition rates of Pb, Cd, and Cu on sites of the city centre and farther area were similar. Significant positive correlations, especially between Cd and Pb, were indicative of similar emission sources associated with emissions from vehicles, civil construction works, and the stripping of paint from older buildings.

Multivariate analysis enabled segregation of the sampling sites into two groups, according to the similarities in the metal deposition rates.

Group 1 is only an area where higher deposition of Pb was identified. Group 2 consists of the central bus station, the central square and the more distant location from the city centre.

The distinct behaviour of the lead deposition in one of the study sites was related to the proximity of the location in geologic fault areas and consequently the emission of radon. Further work will be needed to confirm this source of lead, as well as to quantify the relative magnitudes of other sources of the three metals at the different locations in Presidente Prudente.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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