

Article

Characterization of Fine Particulate Matter Emitted from the Resuspension of Road and Pavement Dust in the Metropolitan Area of São Paulo, Brazil

Ivan Gregorio Hetem and Maria de Fatima Andrade *

Atmospheric Science Department, Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo, São Paulo 05508-090, Brazil; ivanhetem@hotmail.com

* Correspondence: mftandra@model.iag.usp.br; Tel.: +55-11-3091-4706; Fax: +55-11-3091-4714

Academic Editor: Armin Sorooshian

Received: 20 October 2015; Accepted: 15 January 2016; Published: 23 February 2016

Abstract: Many studies have been performed in order to characterize the sources of airborne particles in the Metropolitan Area of São Paulo (MASP), in Brazil. Those studies have been based on receptor modeling and most of the uncertainties in their results are related to the emission profile of the resuspended road dust particles. In this study, we analyzed the composition of resuspended road dust particles in different environments: local streets, paved roads inside traffic tunnels, and high traffic streets. We analyzed the samples to quantify the concentrations of trace elements and black carbon. On the basis of that analysis, we developed emission profiles of the resuspended road dust that are representative of the different types of urban pavement in the MASP. This study is important given the international efforts in improving emissions factors with local characteristics, mainly in South America and other regions for which there is a lack of related information. This work presents emission profiles derived from resuspended road dust samples that are representative of the different types of urban pavement in the Metropolitan Area of São Paulo.

Keywords: atmospheric aerosols; road dust resuspension; enrichment factor; urban road dust profile; pavement resuspension

1. Introduction

Airborne particles that originate specifically from vehicle emissions are known to cause a variety of deleterious health effects, such as cardiorespiratory diseases and intrauterine mortality [1,2]. The particles emitted by vehicles can originate from exhaust and non-exhaust emissions. Non-exhaust particles comprise those generated from brake and tire wear; road surface abrasion; and corrosion. The resuspended road dust identified in the source apportionment of the atmospheric aerosol is composed of particles originating from the abrasion of different pavements, including bare soil and asphalt. In urban areas, road surfaces are contaminated by the deposition of pollutants from anthropogenic sources, mainly vehicle emissions. The resuspension of urban road dust affects not only the concentration of particulate matter (PM) smaller than 10 microns (PM_{10}) but also that of fine particles—those smaller than 2.5 microns ($PM_{2.5}$). It has been estimated that urban road dust resuspension is responsible for 8% of the total $PM_{2.5}$ concentration in the Metropolitan Area of São Paulo (MASP), in southeastern Brazil, [3]. Pant and Harrison [4] presented a review of road traffic emissions of particulate matter. The authors concluded that road traffic can make a significant contribution to airborne concentrations of particulate matter, and that the particles arise not only from engine exhaust but also from the abrasion of tires, of the road surface, and of brake components. The particles arising from dust emissions can be classified as urban dust, which is comprised of soluble

inorganics, carbonaceous compounds, and inert species (including metals). Some compounds derive from the composition of the soil itself, whereas others are derived from the deposition on the soil of particles and gases emitted by anthropogenic sources. Abbasi [5] performed experiments simulating different tires and driving patterns, as well as testing the brake system, to determine the mass and composition of the particles produced. Although most of those particles are in the coarse fraction of particulate matter, the abrasion process can generate the fine fraction (PM_{2.5}). Studies performed in road tunnels in the MASP showed a large contribution of metals that are not known to be emitted during the exhaust process: Ba, Cd, and Sb, from brake wear [6]; and Zn, Sr, Co, and W from tire wear [7,8]. Studies have shown that a significant proportion of the coarse fraction of particulate matter is road dust produced by the vehicles traveling over paved or unpaved roads [9].

In the MASP, there has long been a need to quantify the contributions that vehicle emissions make to the total concentration of particulate matter, differentiating between that coming from exhaust and that generated by the mechanical process of road dust resuspension. It has been a challenge to determine the contribution of each of these sources to the PM_{2.5} concentration using trace-elements because of the difficulty in finding element characteristics of one specific source. Determining the contribution that vehicle emissions make to the concentration of particles in the atmosphere of the MASP has been the theme of many studies. Many authors have evaluated the role that urban sources play in determining the concentration of pollutants, mainly particulate matter. In studies applying multivariate analysis, specifically factor analysis, Ynoue and Andrade [10] and Sanchez-Ccoyllo *et al.* [11], considering the elements Fe, Al, Si, and Ti as tracers of road dust, found that the proportion of resuspended road dust in the PM_{2.5} varied from 15% to 25%. These trace elements are also emitted by other processes, such as the mechanical action of tires on road surfaces, evaporation, and fuel combustion. To distinguish between particles derived from exhaust and those derived from mechanical abrasion, we analyzed samples of urban road dust from inside and just outside road tunnels. These analyses were performed in the context of a more comprehensive project that had the objective of evaluating the emission factors of gaseous and particulate emissions by vehicles. In that project, the emission factors of pollutants were determined using measurements taken inside and outside road tunnels. Tunnel measurements were taken in order to characterize the true nature of the vehicle fleet in the MASP. In one tunnel study, Pérez-Martínez *et al.* [12] showed that the emission factors of regulated pollutants were higher than those presented in official reports (CETESB, 2014). The authors compared their data with those of analyses performed under the same conditions in 2004 [11,13]. The CO and nitrogen oxide (NO_x) emission factors reported by Pérez-Martínez *et al.* [12] for light-duty vehicles in 2011 were both significantly (2.2 times) lower than those reported by Martins *et al.* [13] for light-duty vehicles in 2004, whereas they were five times and 2.5 times lower for CO and NO_x, respectively, from heavy-duty vehicles. Analyzing the number and mass size distribution of particles, Pérez-Martínez *et al.* [12] calculated the PM_{2.5} emission factor to be 20 mg/km for light-duty vehicles and 277 mg/km for heavy-duty vehicles, showing the great contribution of diesel to the emission of fine particles. The authors also showed that black carbon accounted for 40% of the PM_{2.5} diesel emissions, compared with 50% in 2004 [13]. The decreases in the emission factors were due to the implementation of a program for controlling vehicle emissions in Brazil. Although the vehicle fleet in the MASP has increased from 4 million in 2004 to almost 8 million in 2011, total emissions have decreased [11–14]. Brito *et al.* [15] showed that the burning of diesel by heavy-duty vehicles produced particles that were more numerous and for which the mean geometric diameter was smaller than that reported for particles produced by light-duty vehicles: the average particle count found for light-duty vehicles was 73,000 cm⁻³ with an average diameter of 48 nm, compared with 366,000 cm⁻³, with an average diameter of 39 nm, for heavy-duty vehicles.

Quantification of the contributions that road dust and vehicle emissions make to the concentration of particulate matter is a major step in developing a road dust profile for the urban area of the MASP. The objective is to distinguish, within the PM_{2.5} fraction, between the metals and black carbon that originate from the exhaust process and those that originate from the resuspension of dust from paved roads. The same approach was applied by [16], who presented an analysis of the enrichment factors

of atmospheric particulate pollutants at the roadside, calculating the contribution that each different source made to the total particle concentration.

In this study, we attempted to provide emission profiles for road dust contaminated by vehicle emissions in the MASP. We present the composition of particles collected on a local street near an air quality monitoring station, as well as inside and outside two road tunnels. These data are a rich resource for the characterization of urban dust profiles that are highly influenced by vehicle emissions. The road dust resuspension source profile will be used in receptor modeling studies in the MASP and can also be a reference for other urban areas that are particularly affected by vehicle emissions.

2. Material and Methods

2.1. Sample Collection

Road dust samples were collected in bags at five different sites: inside and just outside the Jânio Quadros road tunnel (JQ_i and JQ_o, respectively; 23°35'S, 46°41'W), where only light-duty and small diesel utility vehicles are allowed to travel; inside and just outside the Rodoanel road tunnel (RA_i and RA_o, respectively; 23°27'S, 46°47'W), which is part of the beltway running outside the main area of the city, with a significant contribution by heavy-duty vehicles, mainly trucks; and on a local street, traveled by a mix of light- and heavy-duty vehicles, with a significant contribution by buses, near the Institute of Astronomy, Geophysics, and Atmospheric Sciences (IAG; 23°33'S, 46°44'W), which is on the main campus of the University of São Paulo, within the MASP.

Light-duty vehicles consist of those running on gasohol, ethanol, or diesel, with a gross weight of less than 3900 kg. In Brazil, most of the light-duty vehicles run on gasohol and ethanol. Passenger cars are not allowed to use diesel as fuel. Heavy-duty vehicles in Brazil consist of diesel vehicles with a gross weight of more than 3900 kg. The collection of samples inside and outside tunnels was part of a project to determine the emission factors of vehicles [12]. The JQ_i/JQ_o and RA_i/RA_o samples were collected in May and June 2011, respectively. Table 1 provides details of the sampling sites. Samples were collected by broom sweeping paved roads at five different spots, 10 m apart, collectively representing one site. The samples were collected in plastic bags, totaling 200 g of material per site.

Table 1. Characteristics of the roadways sampled.

| Characteristic | JQ | RA | IAG |
|----------------------|------------------|------------------|------------------|
| Location | 23°35'S; 46°41'W | 23°27'S; 46°47'W | 23°33'S; 46°44'W |
| LDVs per hour, mean | 2356 | 1511 | 140 |
| H DVs per hour, mean | 18 | 634 | 32 |
| Hierarchy | Arterial | Freeway | Local |

JQ, Jânio Quadros (road tunnel, inside and outside measurements); RA, Rodoanel (road tunnel, inside and outside measurements); IAG, Institute of Astronomy, Geophysics, and Atmospheric Sciences (local street); LDVs, light-duty vehicles; HDVs, heavy-duty vehicles.

2.2. Sample Preparation

The samples were stored in bags at 4 °C until use, and the material in each bag was manually sieved. The structure of the resuspension chamber and dichotomous sampler are illustrated in Figure 1, together with the protocol for the procedure. After being sieved, each sample was transferred to a resuspension chamber belonging to the São Paulo State Environmental Protection Agency. The chamber consists of a virtual impactor (dichotomous sampler; Sierra-Andersen, Smyrna, GA, USA), coupled to a stainless steel vat (Figure 1). The vat is cylindrical, with a diameter of 40 cm and a height of 100 cm. The dichotomous sampler uses a PM₁₀ inlet operating at 16.7 L/min to provide the D₅₀ particle size cutoff at 10 microns in diameter. The virtual impactor is located after the inlet, and there are two separate flow controllers that maintain the fine particle air flux at 15.0 L/min and the coarse particle air flux at 1.6 L/min.

We inserted 100 mg of the dust sample in the vat and then scattered it with filtered laboratory compressed air. Using laboratory procedures, we determined that, after 3 min of scattering, the volume

within the vat was homogeneously filled with the dust particles. The dust was collected on 37-mm Teflon-membrane filters. Each filter was exposed to four resuspension cycles, and samples from each site were collected on four filters, corresponding to one sample for each resuspension cycle. Each filter sampled a total of 0.4 m^3 of air. The elemental analysis was performed in the fine mode fraction ($\text{PM}_{2.5}$), which is the focus of this study.

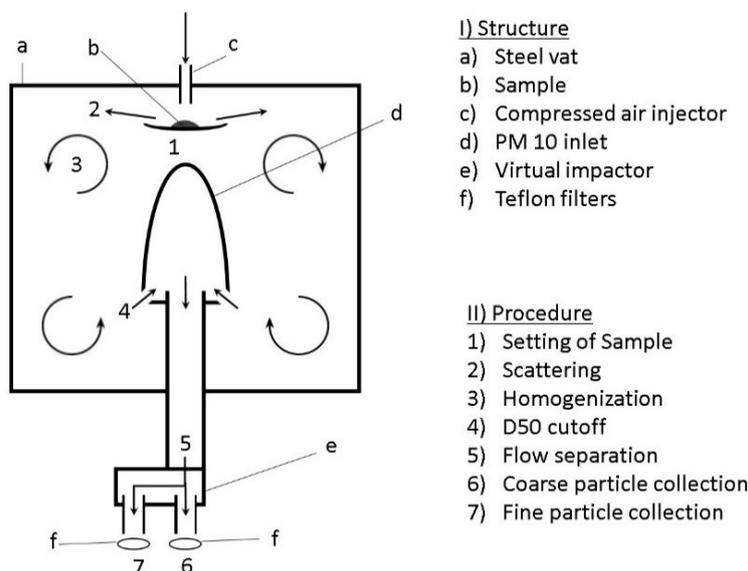


Figure 1. Structure of the resuspension chamber, including the dichotomous sampler, and the procedure for collecting the material on the filters.

3. Analysis

The speciated emission inventory for road dust was constructed based on the material deposited on the filters. Although the particles may be shattered, the material deposited on the membrane filters retains the characteristics of the road dust that were generated by the abrasion of tires and wind on the road at the sampling site.

For the evaluation of the mass deposited on the filters, we submitted the samples to gravimetric analysis using a balance with a resolution of $1 \mu\text{g}$ (Mettler-Toledo MX-5). The filters were stored for 48 h in a temperature- and humidity-controlled environment ($24 \text{ }^\circ\text{C}$; 40% relative humidity). To quantify the accumulated mass, each filter was weighed before and after sampling. Measurements were corrected by subtracting the fluctuation observed on a set of blank filters. Ten blank filters were used for each set of samples. Concentrations of black carbon were evaluated through reflectance analysis of each filter with a smoke stain reflectometer (model 43; Diffusion Systems Ltd., London, UK). In brief, the filters were exposed to known amounts of visible light and a sensor registered the reflected fraction, thus inferring the superficial concentration of light-absorbing material, which can be classified as equivalent black carbon (BC_{eq}), as described by Bond *et al.* [17]. The material deposited on the filters was also submitted to analysis in an energy-dispersive X-ray fluorescence spectrometer (Epsilon 5; PANalytical, Almelo, The Netherlands). The spectrometer has three-dimensional, polarizing geometry with a supercritical water anode X-ray tube, up to 15 secondary targets as the polarizing scatterers. Details of the methodology for analyzing the trace-elements using this setup were described previously [15]. The typical detection limits for X-ray fluorescence analysis can be found elsewhere [18].

Data Processing Analysis

The profiles, composed of the mean concentrations for each element and for each sampling site, were defined as representing distinct sources. We then compared those sources with each other

by calculating the coefficient of divergence (COD). The COD, as presented by [19], was defined as a measure of the data point spread between the road dust resuspension data sets and was applied to help determine whether any two profiles could be considered similar. The COD was calculated through the use of the following expression:

$$COD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (1)$$

where j and k represent two source profiles; p is the number of investigated components; and x_{ij} and x_{ik} represent the average mass concentrations of a compound i for the profiles j and k , respectively. The sources j and k can be considered similar if the COD_{jk} is close to zero and significantly different if the COD_{jk} is close to 1. In this analysis, we considered the following compounds: BCe, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, Cd, Sb and Pb. Following the example set by [20], we excluded elements that accounted for less than 0.001% of the total mass, which resulted in the exclusion of As. According to those authors, a COD above the threshold of 0.3 indicates that the profiles were different from each other, whereas COD values that were mostly lower than or near 0.3 indicate that the profiles are mostly similar to each other and can be substituted for each other.

4. Results and Discussion

Table 2 shows the composition of the road dust samples collected from each of the sampling sites according to their order of importance in explaining the mass concentration. The trace elements Al_2O_3 , SiO_2 , $CaCO_3$, K_2O , Fe_2O_3 and ZnO were considered to be oxides and collectively accounted for an average of 60% of the total mass, the main contributors being black carbon and the oxides Al, Si, Fe and Ca. The tunnel profiles present some remarkable differences: at the JQ site, Fe was a major contributor, accounting for 10% of the mass concentration; and at the RA site, the contribution of BCe was ten times higher inside the tunnel than outside of it.

Some elements, such as Na and P, were not considered to be in the oxidized state due to the uncertainties in the composition. The unexplained portion of the mass was due to components not measured in the samples, mainly water and organic compounds. In atmospheric samples, Ynoue and Andrade [10] demonstrated that organic material accounted for approximately 50% of the mass and black carbon (measured by optical reflectance) accounted for 30%, and they also showed that sulfate is present in the form of $(NH_4)_2SO_4$. Those authors showed that, within the explained fraction, crustal elements were the most abundant species, and that oxides of aluminum and silicon explained more than 10% and 20% of the mass, respectively. The compounds BCe, Na, $(NH_4)_2SO_4$, Cl, CuO, ZnO, As, Se, Br, Sb and Pb were more abundant in samples from inside the tunnels, whereas MgO, Al_2O_3 , SiO_2 , TiO and Rb were more abundant in samples from outside of the tunnels, as well as in those from the IAG site.

Compounds such as BCe and sulfur are characteristic of vehicle emissions in São Paulo, mainly from heavy-duty vehicles. This is similar to the situation in other parts of the world where policies to control diesel exhaust (mandatory use of diesel particle filters, for instance) have not been implemented. Strict regulations on diesel emissions, involving the mandatory use of retrofit systems, have been put in place only in recent years. One important program to control pollutant emissions from the light-duty fleet was the implementation of policies mandating the use of three-way catalysts, although the catalysts may also produce ammonia under reducing conditions. Typically, Cu and Zn are used as tracers of gasoline and ethanol emissions, respectively. Silva *et al.*, [21], analyzing PM_{10} collected from ethanol and gasohol exhaust emissions in a dynamometer study performed with the fuels consumed in São Paulo, found different groups of metal elements in gasohol exhaust: Mn, Pt, Ni, Cu, Pb, Cr and Zn. Copper is added as an antioxidant, and Zn is associated with the use of additives and lubricants, as found also by Morawska and Zhang [22].

Within the road tunnels, vehicle emissions are the dominant sources. Some elements, such as Al, Si and Ti, are mostly associated with road dust composition. Outside-tunnel samples were rich in

those elements, because the outdoor pavement is more likely to have a dust component, due to soil transport mechanisms, than is the pavement within the tunnels. It is of note that diesel fuel contains Si and emissions of Si are therefore also associated with the burning of diesel [23,24].

Table 2. Composition of the road dust as a percentage of the total mass of the resuspended material collected on the Teflon filters in the resuspension chamber.

| Compound | IAG | RA_i | RA_o | JQ_i | JQ_o |
|---|----------------|----------------|----------------|----------------|-----------------|
| BCe | 1.96 ± 0.39 | 10.75 ± 4.3 | 1.52 ± 0.17 | 3.99 ± 1.99 | 1.04 ± 0.19 |
| Al ₂ O ₃ | 32.22 ± 6.44 | 19.27 ± 7.71 | 32.57 ± 3.58 | 13.99 ± 7 | 32.76 ± 5.9 |
| SiO ₂ | 33.41 ± 6.68 | 12.53 ± 5.01 | 30.68 ± 3.37 | 19.52 ± 9.76 | 29.36 ± 5.29 |
| Fe ₂ O ₃ | 4.54 ± 0.91 | 3.76 ± 1.5 | 6.18 ± 0.68 | 9.74 ± 4.87 | 4.75 ± 0.85 |
| K ₂ O | 2.15 ± 0.43 | 1.41 ± 0.56 | 1.78 ± 0.2 | 1.55 ± 0.78 | 1.32 ± 0.24 |
| CaCO ₃ | 2.85 ± 0.57 | 6.27 ± 2.51 | 3.98 ± 0.44 | 8.78 ± 4.39 | 7.77 ± 1.4 |
| MgO | 2.34 ± 0.47 | 1.11 ± 0.44 | 2.23 ± 0.24 | 1.97 ± 0.98 | 2.29 ± 0.41 |
| (NH ₄) ₂ SO ₄ | 1.68 ± 0.34 | 10.99 ± 4.4 | 1.51 ± 0.17 | 6.77 ± 3.39 | 1.14 ± 0.21 |
| Na | 0.34 ± 0.07 | 0.73 ± 0.29 | 0.27 ± 0.03 | 0.7 ± 0.35 | 0.2 ± 0.04 |
| TiO | 0.61 ± 0.12 | 0.23 ± 0.09 | 0.57 ± 0.06 | 0.43 ± 0.22 | 0.65 ± 0.12 |
| ZnO | 0.11 ± 0.02 | 0.44 ± 0.18 | 0.2 ± 0.02 | 0.73 ± 0.36 | 0.13 ± 0.02 |
| MnO ₂ | 0.07 ± 0.01 | 0.11 ± 0.05 | 0.12 ± 0.01 | 0.16 ± 0.08 | 0.06 ± 0.01 |
| P | 0.06 ± 0.01 | 0.26 ± 0.11 | 0.44 ± 0.05 | 0.14 ± 0.07 | 0.04 ± 0.01 |
| Cl | 0.06 ± 0.01 | 0.74 ± 0.3 | 0.19 ± 0.02 | 0.53 ± 0.27 | 0.02 ± 0.004 |
| CuO | 0.04 ± 0.01 | 0.23 ± 0.09 | 0.06 ± 0.01 | 0.28 ± 0.14 | 0.05 ± 0.01 |
| V ₂ O ₅ | 0.01 ± 0.002 | -- | 0.02 ± 0.002 | 0.02 ± 0.011 | 0.01 ± 0.002 |
| Cr | -- | -- | 0.05 ± 0.005 | 0.04 ± 0.018 | 0.03 ± 0.005 |
| NiO | 0.01 ± 0.002 | 0.04 ± 0.016 | 0.03 ± 0.004 | 0.01 ± 0.006 | 0.02 ± 0.003 |
| Rb | 0.01 ± 0.002 | -- | 0.01 ± 0.001 | 0.004 ± 0.002 | 0.01 ± 0.001 |
| Sr | 0.02 ± 0.004 | 0.02 ± 0.007 | 0.03 ± 0.004 | 0.06 ± 0.032 | 0.02 ± 0.004 |
| Cd | 0.01 ± 0.001 | -- | 0.01 ± 0.001 | 0.02 ± 0.011 | 0.01 ± 0.001 |
| Sb | 0.01 ± 0.003 | 0.08 ± 0.033 | 0.01 ± 0.001 | 0.1 ± 0.048 | 0.02 ± 0.004 |
| Pb | 0.03 ± 0.005 | 0.07 ± 0.028 | 0.01 ± 0.001 | 0.05 ± 0.026 | 0.01 ± 0.002 |
| As | 0.001 ± 0.0002 | 0.01 ± 0.0041 | 0.002 ± 0.0003 | 0.009 ± 0.0047 | 0.0004 ± 0.0001 |
| Se | 0.002 ± 0.0005 | 0.03 ± 0.01 | -- | 0.01 ± 0.01 | 0.003 ± 0.001 |
| Br | 0.001 ± 0.0003 | 0.005 ± 0.0021 | 0.001 ± 0.0001 | 0.005 ± 0.0027 | 0.002 ± 0.0003 |

Values are expressed as average ± standard deviation. JQ_i and JQ_o, respectively, inside and outside the Jânio Quadros Tunnel (traveled primarily by light-duty and small, diesel-powered utility vehicles); RA_i and RA_o, respectively, inside and outside the Rodoanel Tunnel (traveled by a significant number of heavy-duty vehicles); and IAG, Institute of Astronomy, Geophysics, and Atmospheric Sciences (local street traveled by a mix of light- and heavy-duty vehicles).

The COD results, shown in Table 3, present another form of grouping to these profiles. To define which groups could be considered similar and could be substitutes for each other, being considered representative of the resuspended road dust, we used the classification system devised by Kong *et al.* [20]. According to the COD values, the pairings between the IAG, JQ_o, and RA_o sites show that they are similar, even though they were collected from roadways that were quite different (hierarchy-wise) and in distinct areas of the MASP. This result is relevant, given that different sampling sites show the same profile for pavement dust emission. Previous studies applying principal component analysis to fine particle concentrations in various capital cities in Brazil, including São Paulo [3], have shown that it is very difficult to distinguish among road dust resuspension, vehicle exhaust, and the different urban sources. This was the motivation to improve the knowledge of resuspended road dust in order to subtract this source from the database before performing the receptor model analysis.

Table 3. Coefficient of divergence values for the different profiles analyzed, considering a similarity threshold of 0.3, as proposed by Kong *et al.* [20].

| Site | RA_i | RA_o | JQ_i | JQ_o |
|------|-------|--------------|--------------|--------------|
| IAG | 0.557 | 0.340 | 0.533 | 0.305 |
| RA_i | X | 0.450 | 0.279 | 0.555 |
| RA_o | X | X | 0.414 | 0.321 |
| JQ_i | X | X | X | 0.501 |

Profile pairings with a COD below (or near) 0.3 are similar, whereas pairings with a COD above 0.3 are different. RA_i and RA_o, respectively, inside and outside the Rodoanel Tunnel (traveled by a significant number of heavy-duty vehicles); JQ_i and JQ_o, respectively, inside and outside the Jânio Quadros Tunnel (traveled primarily by light-duty and small, diesel-powered utility vehicles); and IAG, Institute of Astronomy, Geophysics, and Atmospheric Sciences (local street traveled by a mix of light- and heavy-duty vehicles).

The pairing of the profiles from inside the tunnels (RA_i and JQ_i) also resulted in COD values < 0.3, and those profiles are therefore also similar, despite the differences shown in Table 2, and could represent the dust profile inside traffic tunnels in São Paulo [19,20,25,26]. The pairings of the respective in- and outside-tunnel profiles for both tunnels resulted in COD values > 0.3. The concentrations of fine particles were higher in the in-tunnel samples than in the outside-tunnel samples, which also differed in composition, despite being collected from roadways traveled by the same types of vehicles. The profiles derived from in-tunnel samples are different from those derived from outside-tunnel samples, including those collected at the IAG site. The compounds presenting the highest contribution to the mass concentration were black carbon, Ca and Pb. Pairings of the mismatched profiles RA_o-JQ_i and RA_i-JQ_o resulted in COD values > 0.3, as did pairings of the IAG profile with both in-tunnel profiles, emphasizing how distinct they are. Considering the results obtained with the COD analysis, it was possible to establish a representative profile for road dust resuspension by using the average values for the JQ_o, RA_o and IAG samples, as presented in Table 4.

In the samples collected from the three outside-tunnel sites, we observed high contributions of the crustal elements Al₂O₃, SiO₂, Fe₂O₃, K₂O, CaCO₃ and MgO (Table 4). These compounds are also important tracers for tires, break wear and pavement abrasion which are the main sources of road dust [8,9].

In future multivariate analyses, that profile will likely be used as a standard road dust resuspension profile for the MASP. The contribution of BCe to that profile was one order of magnitude less than was its contribution to the in-tunnel profile. The profile encountered here was compared with data found for other urban sites in the United States and Spain. In its emissions profile database (SPECIATE 4.0), the United States Environmental Protection Agency (EPA) presented a composite of five paved road dust profiles from the cities of San Antonio and Laredo, Texas (BVPVRD01, BVPVRD02, BVPVRD03, BVPVRD04 and BVPVRD05). Amato *et al.* [27] analyzed road dust at different sites in Spain and compiled a profile for an urban site in the city of Seville. Table 4 compares the urban profile for the MASP (derived from the present study), the EPA composite urban profile, and the urban profile for Seville.

Comparing the profiles obtained for the fine fraction of resuspended road dust in urban areas, we can see that the MASP profile presents more aluminum and iron and less calcium than do the profiles obtained in the United States and Spain. The contributions of S, Na, P and Mg in the MASP were similar to those reported for Spain, whereas the contributions of K, Mn, Zn and Cu were similar to those reported for the United States. Although comparable for some species, the MASP sites had their own characteristics, demonstrating the need to expand the current road dust emission profiles. That would lead to better identification of this source and the evaluation of its contribution to the concentration of fine particulate matter.

Table 4. Profile of resuspended road dust from the three outside-tunnel sites evaluated in Brazil, together with comparable profiles for cities in Texas and for the city of Seville, Spain.

| Compound/Element | Urban Resuspended Road Dust Profiles | | |
|------------------|--------------------------------------|------------------------------|------------------------------|
| | Brazil | United States | Spain |
| | % of Total PM _{2.5} | % of Total PM _{2.5} | % of Total PM _{2.5} |
| BCe | 1.50 ± 0.16 | 2.54 ± 0.28 | 5.3 ± 2.1 |
| Si | 10.37 ± 1.72 | 19.13 ± 2.10 | -- |
| Al | 8.61 ± 1.42 | 6.81 ± 0.75 | 2.1 ± 0.6 |
| Fe | 5.15 ± 0.82 | 2.63 ± 0.29 | 2.5 ± 0.5 |
| Ca | 2.81 ± 0.47 | 30.11 ± 3.30 | 11.2 ± 3.1 |
| Mg | 1.38 ± 0.23 | 0.54 ± 0.06 | 1.9 ± 1.3 |
| K | 1.32 ± 0.22 | 1.42 ± 0.16 | 0.7 ± 0.2 |
| Ti | 0.61 ± 0.10 | 0.31 ± 0.03 | 1.6 ± 0.3 |
| S | 0.35 ± 0.06 | 3.04 ± 0.33 | 0.4 ± 0.1 |
| Na | 0.27 ± 0.04 | 0.02 ± 0.002 | 0.3 ± 0.1 |
| P | 0.18 ± 0.02 | 0.28 ± 0.03 | 0.1 ± 0.0 |
| Zn | 0.14 ± 0.02 | 0.22 ± 0.02 | 1.3 ± 0.3 |
| Mn | 0.07 ± 0.01 | 0.05 ± 0.01 | 0.37 ± 0.13 |
| Cu | 0.04 ± 0.01 | 0.03 ± 0.003 | 0.77 ± 0.27 |
| Cl | 0.04 ± 0.005 | 0.15 ± 0.02 | 0.9 ± 1.5 |
| Cr | 0.03 ± 0.002 | 0.02 ± 0.002 | 0.145 ± 0.061 |
| Sr | 0.0254 ± 0.0040 | 0.1537 ± 0.0169 | -- |
| Pb | 0.0158 ± 0.0027 | -- | -- |
| Sb | 0.0118 ± 0.0020 | -- | -- |
| Ni | 0.0113 ± 0.0016 | 0.0090 ± 0.0010 | -- |
| V | 0.01 ± 0.001 | 0.02 ± 0.002 | 0.0057 ± 0.001 |

Values are expressed as average ± standard deviation. Data for the United States (five sites within the cities of San Antonio and Laredo, Texas) were obtained from the SPECIATE 4.0 emissions profile database of the United States Environmental Protection Agency. Data for Spain (an urban site in the city of Seville) were obtained from Amato *et al.* [27].

5. Conclusions

Here, we have presented the inorganic composition of the fine (PM_{2.5}) fraction of resuspended road dust. The road dust samples were collected from (inside and outside) two tunnels and from one suburban street. The profiles defined here are representative of the inorganic fraction of resuspended urban road dust in the MASP. Our study was part of an initiative to provide more information regarding emission profiles in cities in South America. These profiles are important to the estimation of the sources responsible for particulate air pollution. We demonstrated that the profiles inside the tunnels were different from those outside the tunnels, as well as from that defined for the local street. We also found that the outside-tunnel profiles were similar and can be substitutes for each other. Therefore, the average profile for resuspended urban dust might be useful in quantifying the contribution of other vehicle emissions, including exhaust emissions. The in-tunnel profiles will improve the identification of this source of fine particulate matter. The profile found here provides important information for the identification of compounds in the fine fraction of particulate matter originating from the resuspension of road dust and from vehicle exhaust. This profile can be used in receptor model studies to estimate the impact that resuspended dust has on the fine particle mass concentration. Our results can be valuable for studies analyzing the toxicity of the PM content of road dust in urban areas that are especially affected by vehicle emissions.

Acknowledgments: The authors thank the Research Program on Global Climate Change of the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, São Paulo Research Foundation) for the financial support provided (Grant No. 2008/58104-8, NUANCE project). This study was also supported by the Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, National Council for Scientific and Technological Development) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Office

for the Advancement of Higher Education). We are also grateful to the São Paulo State Companhia de Tecnologia de Saneamento Ambiental (CETESB, Environmental Protection Agency) for providing logistical support.

Author Contributions: Ivan Hetem conceived the experimental setup and Maria de Fatima Andrade with Ivan Hetem analysed the data.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Saiki, M.; Santos, J.O.; Alves, E.R.; Genezini, F.A.; Marcelli, M.P.; Saldiva, P.H.N. Correlation study of air pollution and cardio-respiratory diseases through NAA of an atmospheric pollutant biomonitor. *J. Radioanal. Nucl. Chem.* **2014**, *299*, 773–779. [[CrossRef](#)]
2. Loomis, D.; Pereira, L.A.; Conceição, G.M.; Arcas, R.M.; Kishi, H.S.; Singer, J.M.; Böhm, G.M.; Saldiva, P.H.N. Association Between Air Pollution and Intrauterine Mortality in São Paulo, Brazil. *Environ. Health Perspect.* **1998**, *106*, 325–329.
3. Andrade, M.F.; Miranda, R.M.; Fornaro, A.; Kerr, A.; Oyama, B.; André, P.A.; Saldiva, P.H. Vehicle emissions and PM_{2.5} mass concentrations in six Brazilian cities. *Air Qual. Atmos. Health* **2012**, *5*, 79–88. [[CrossRef](#)] [[PubMed](#)]
4. Pant, P.; Harrison, R. Estimation of the contribution of road traffic emissions to particulate matter concentration from field measurements: A review. *Atmos. Environ.* **2013**, *77*, 78–97. [[CrossRef](#)]
5. Abbasi, S. Technical note: Experiences of studying airborne wear particles from road and rail transport. *Aerosol Air Qual. Res.* **2013**, *13*, 1161–1169. [[CrossRef](#)]
6. Grieshop, A.P.; Lipsky, E.M.; Pekney, N.J.; Takahama, S.; Robinson, A.L. Fine particle emission factors from vehicles in a highway tunnel: Effects of fleet composition and season. *Atmos. Environ.* **2006**, *40*, 287–298. [[CrossRef](#)]
7. Apeageyi, E.; Bank, M.S.; Spengler, J.D. Distribution of heavy metals in road dust along an urban-rural gradient in Massachusetts. *Atmos. Environ.* **2011**, *45*, 2310–2323. [[CrossRef](#)]
8. Wählén, P.; Berkowicz, R.; Palmgren, F. Characterization of traffic-generated particulate matter in Copenhagen. *Atmos. Environ.* **2006**, *40*, 2151–2159. [[CrossRef](#)]
9. Kupiainen, K.J.; Tervahattu, H.; Räisänen, M.; Mäkelä, T.; Aurela, M.; Hillamo, R. Size and composition of airborne particles from pavement wear, tires, and traction sanding. *Environ. Sci. Technol.* **2005**, *39*, 699–706. [[CrossRef](#)] [[PubMed](#)]
10. Ynoue, R.Y.; Andrade, M.F. Size resolved mass balance of aerosol particles over São Paulo Metropolitan Area, Brazil. *J. Aerosol Sci. Technol.* **2004**, *38*, 52–62. [[CrossRef](#)]
11. Sánchez-Ccoyllo, O.R.; Ynoue, R.Y.; Martins, L.D.; Astolfo, R.; Miranda, R.M.; Freitas, E.D.; Borges, A.S.; Fornaro, A.; Freitas, H.; Moreira, A.; *et al.* Vehicular particulate matter emissions in road tunnels in Sao Paulo, Brazil. *Environ. Monit. Assess.* **2009**, *149*, 241–249. [[CrossRef](#)] [[PubMed](#)]
12. Pérez-Martínez, P.J.; Miranda, R.M.; Nogueira, T.; Guardani, M.L.; Fornaro, A.; Ynoue, R.; Andrade, M.F. Emission factors of air pollutants from vehicles measured inside road tunnels in São Paulo: Case study comparison. *Int. J. Environ. Sci. Tech.* **2014**, *11*, 2155–2168. [[CrossRef](#)]
13. Martins, L.D.; Andrade, M.F.; Freitas, E.D.; Pretto, A.; Gatti, L.V.; Albuquerque, E.L.; Tomaz, E.; Guardani, M.L.; Martins, M.; Junior, O.M.A. Emission factors for gas-powered vehicles traveling through road tunnels in Sao Paulo, Brazil. *Environ. Sci. Technol.* **2006**, *40*, 6722–6729. [[CrossRef](#)] [[PubMed](#)]
14. São Paulo State Companhia de Tecnologia de Saneamento Ambiental. *Qualidade Do Ar No Estado De São Paulo 2013*; Série Relatórios; CETESB Report: Sao Paulo, Brazil, 2014.
15. Brito, J.; Rizzo, L.V.; Herckes, P.; Vasconcellos, P.C.; Caumo, S.E.S.; Fornaro, A.; Ynoue, R.Y.; Artaxo, P.; Andrade, M.F. Physical-chemical characterisation of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area. *Atmos. Chem. Phys.* **2013**, *13*, 12199–12213. [[CrossRef](#)]
16. Amato, F.; Viana, M.; Richard, A.; Furger, M.; Prevot, A.S.H.; Nava, S.; Lucarelli, F.; Bukoviwecki, N.; Alastuey, A.; Reche, C.; *et al.* Size and time-resolved roadside enrichment of atmospheric particulate pollutants. *Atmos. Chem. Phys.* **2011**, *11*, 2917–2931. [[CrossRef](#)]
17. Bond, T.C.; Doherty, S.J.; Fahey, D.W.; Forster, P.M.; Berntsen, T.; DeAngelo, B.J.; Flanner, M.G.; Ghan, S.; Krächer, B.; Koch, D.; *et al.* Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res. Atmos.* **2013**, *118*, 5380–5552. [[CrossRef](#)]

18. Spolnik, Z.; Belikov, K.; van Meel, K.; Adriaenssens, E.; de Roeck, F.; van Grieken, R. Optimization of measurement conditions of an energy dispersive X-ray fluorescence spectrometer with high-energy polarized beam excitation for analysis of aerosol filters. *Appl. Spectrosc.* **2005**, *59*, 1465–1469. [[CrossRef](#)] [[PubMed](#)]
19. Wongphatarakul, V.; Friedlander, S.K.; Pinto, J.P. A comparative study of PM_{2.5} ambient aerosol chemical databases. *Environ. Sci. Technol.* **1998**, *32*, 3926–3934. [[CrossRef](#)]
20. Kong, S. Similarities and Differences in PM_{2.5}, PM₁₀ and TSP Chemical Profiles of Fugitive Dust Sources in a Coastal Oilfield City in China. *Aerosol Air Qual. Res.* **2014**, *14*. [[CrossRef](#)]
21. Silva, M.F.; Assunção, J.V.; Andrade, M.F.; Pesquero, C.R. Characterization of Metal and Trace Element Contents of Particulate Matter (PM₁₀) Emitted by Vehicles Running on Brazilian Fuels—Hydrated Ethanol and Gasoline with 22% of Anhydrous Ethanol. *J. Toxicol. Environ. Health A* **2010**, *73*, 901–909. [[CrossRef](#)] [[PubMed](#)]
22. Morawska, L.; Zhang, J.J. Combustion sources of particles. 1. Health relevance and source signatures. *Chemosphere* **2002**, *49*, 1045–1058. [[CrossRef](#)]
23. Taylor, D. Fuel Oils, Lubricant Oils and Their Treatment. In *Introduction to Marine Engineering*; Butterworth-Heinemann: Oxford, UK, 1996; pp. 150–162. Available online: <http://books.google.com/> (accessed on 20 October 2015).
24. Giordano, S.; Adamo, P.; Spagnuolo, V.; Vaglieco, B.M. Instrumental and bio-monitoring of heavy metal and nanoparticle emissions from diesel engine exhaust in controlled environment. *J. Environ. Sci.* **2010**, *22*, 1357–1363. [[CrossRef](#)]
25. Feng, Y.C.; Xue, Y.H.; Chen, X.H.; Wu, J.H.; Zhu, T.; Bai, Z.P. Source apportionment of Ambient Total Suspended Particulates and Coarse Particulate Matter in Urban Areas of Jiaozuo, China. *J. Air Waste Manag. Assoc.* **2007**, *57*, 561–575. [[CrossRef](#)] [[PubMed](#)]
26. Kong, S.F.; Shi, J.W.; Lu, B.; Qiu, W.G.; Zhang, B.S.; Peng, Y.; Zhang, B.W.; Bai, Z.P. Characteristic of PAHs with PM₁₀ Fraction for Ashes from Coke Production, Iron Smelt, Heating Station and Power Plant Stacks in Liaoning Province, China. *Atmos. Environ.* **2011**, *45*, 3777–3785. [[CrossRef](#)]
27. Amato, F.; Alastuey, A.; de la Rosa, J.; Gonzalez Castanedo, Y.; Sánchez de la Campa, A.M.; Pandolfi, M.; Lozano, A.; Contreras González, J.; Querol, X. Trends of road dust emissions contributions on ambient air particulate levels at rural, urban and industrial sites in southern Spain. *Atmos. Chem. Phys.* **2014**, *14*, 3533–3544. [[CrossRef](#)]



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons by Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).