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Analysis of atmospheric aerosol (PM_{2.5}) in Recife city, Brazil

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Several studies indicate that mortality and morbidity can be well correlated to atmospheric aerosol concentrations with aerodynamic diameter less than 2.5 μm (PM_{2.5}). In this work the PM_{2.5} at Recife city was analyzed as part of a main research project (INAIRA) to evaluate the air pollution impact on human health in six Brazilian metropolitan areas. The average concentration, for 309 samples (24-hr), from June 2007 to July 2008, was 7.3 $\mu\text{g}/\text{m}^3$, with an average of 1.1 $\mu\text{g}/\text{m}^3$ of black carbon. The elemental concentrations of samples were obtained by x-ray fluorescence. The concentrations were then used for characterizing the aerosol, and also were employed for receptor modelling to identify the major local sources of PM_{2.5}. Positive matrix factorization analysis indicated six main factors, with four being associated to soil dust, vehicles and sea spray, metallurgical activities, and biomass burning, while for a chlorine factor, and others related to S, Ca, Br, and Na, we could make no specific source association. Principal component analysis also indicated six dominant factors, with some specific characteristics. Four factors were associated to soil dust, vehicles, biomass burning, and sea spray, while for the two others, a chlorine- and copper-related factor and a nickel-related factor, it was not possible to do a specific source association. The association of the factors to the likely sources was possible thanks to meteorological analysis and sources information. Each model, although giving similar results, showed factors' peculiarities, especially for source apportionment. The observed PM_{2.5} concentration levels were acceptable, notwithstanding the high urbanization of the metropolitan area, probably due to favorable conditions for air pollution dispersion. More than a valuable historical register, these results should be very important for the next analysis, which will correlate health data, PM_{2.5} levels, and sources contributions in the context of the six studied Brazilian metropolises.

Implications: The analysis of fine particulate matter (PM_{2.5}) in Recife city, Brazil, gave a significant picture of the local concentration and composition of this pollutant, which exhibits robust associations to adverse human health effects. Data from 1 year of sampling evaluated the seasonal variability and its connections with weather patterns. Source apportionment in this metropolitan area was obtained based in a combination of receptor models: principal component analysis (PCA)/chemical mass balance (CMB) and positive matrix factorization (PMF). These results give guidelines for local air pollution control actions, providing significant information for a health study in the context of establishing a new national air pollution protocol based on Brazilian cities data.

Introduction

Several studies have been done to analyze air pollutants and their effects on human health. The present one takes part of "INAIRA" (the Brazilian acronym for "National Institute of Integrated Environmental Risk Analysis"), a project sponsored by the Ministry of Science and Technology (MCT), National Council of Research (CNPq), and São Paulo Research Foundation (FAPESP), designed to evaluate the automotive sources contribution to the PM_{2.5} atmospheric concentrations, and its impacts to human health in six Brazilian metropolitan areas: São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Porto

Alegre, and Recife. The first results, presenting average concentrations for all cities and the characteristics of samplings, were presented in Miranda et al. (2010).

Various studies indicate that mortality and morbidity are well correlated to the PM_{2.5} concentrations (e.g., Anderson et al., 2011; Pope and Dockery, 2006; Pope et al., 2009). Nevertheless, this type of evaluation is not straightforward, due to several other factors, specifically those related to meteorological variables and quality of living in the urban areas, that could also impart damage to human health. In this collection of metropolises a high amplitude of values is covered for several characteristics, from geographic positioning and climatic dynamic, to economical and

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social parameters. The study performed for Recife provided elements, for the next steps of the project, to distinguish between air pollution and other factors that could impact human health.

Recife has 1.55 million inhabitants, being the main city of a metropolitan area (RMR) with 3.69 million people, and capital of the state of Pernambuco. Its shoreline has beautiful beaches and the city is crossed by big rivers, like the Beberibe and the Capibaribe with their tributaries, some islands, and several bridge connections, thus giving its nickname of “Brazilian Venice.” Among the other 14 cities of the RMR, the neighboring city of Olinda is recognized by UNESCO as a World Heritage Site, because of its historical and cultural value. Besides those qualifiers, the RMR has an important economical regional role, and due to the natural propitious attributes of the coastal area, it is an important commercial port. Since the European occupation of the region, in the sixteenth century, the sugarcane crops occupied the area’s fertile lands for the sugar industry. In the last decade this intensive farming supplied also the engines that produce ethanol for fueling vehicles. In both cases, the cane that burning, preceding harvesting, imparts a significant environmental impact. In the last decade there has been also a regional increase of industrial activities and of the vehicular fleet.

Until recently, just a few studies about the local air pollution, not related to this project, have been done. More than 30 years ago Van Greken et al. (1982) conducted a pioneering and dense work, analyzing the total suspended particulate matter (TSP) and its size distribution. They identified a restricted number of sources (mainly soil dust and sea spray) due to the sampling characteristics and to the limitations of the available analytical tools. Conference communications show a few other studies, like heavy metals identification in the TSP collected in the local environmental control stations during the year of 1991 (Florêncio et al., 1997), or the identification of some chemical elements, by neutron activation analysis, in extracts of bromeliads obtained in two local forestry reserves (Santos et al., 2011), and a study of the black carbon concentration variability as a function of rainfall for this project (Picolo et al., 2010).

The present study evaluated the concentrations of chemical elements, black carbon, and total mass of $PM_{2.5}$ samples, from June 2007 to July 2008. This database enabled the use of positive matrix factorization (PMF) and principal component analysis (PCA) and enabled us to obtain absolute factors used in a chemical mass balance (CMB) source apportionment (all referenced in the Methodology section). Confronting the results of these methodologies and using meteorological data as well as local sources mapping, the main source of $PM_{2.5}$ impacting the samples could be identified. A previous analysis for the identification of sources in the context of INAIRA, for six Brazilian capitals, including Recife, was performed and the results were presented in Andrade et al. (2012). The analysis was undertaken with fewer samples and it was not possible to identify the same number of sources.

The Recife city area is characterized as under a regional shoreline meteorological system with favorable conditions for air pollution dispersion, especially considering the sampling point. The measured $PM_{2.5}$ concentration levels in the sampling station did not exceeded the World Health Organization (WHO) Guidelines (WHO, 2005) during the experiment, notwithstanding the high state of regional urbanization. The results obtained in this work

represent a valuable historical register, and will be very important for the main project, which has the objective of correlating health data, $PM_{2.5}$ levels, and sources responsibility, in the context of six important Brazilian metropolises.

Methodology

Figure 1 shows the Recife metropolitan area, including some potential sources with appreciable magnitude and the sampling station, settled in the campus of the Federal University of Pernambuco (UFPE), at $8^{\circ}2.93' S$; $34^{\circ}56.77' W$, at an altitude of 15 m amsl. The sampling period was from June 2007 to July 2008, providing 309 samples of 24 hr each.

The $PM_{2.5}$ was collected on 37-mm polycarbonate filters (0.4 μm pore size) using Harvard samplers with a flow rate of 10.0 L/min (Marple and Willeke, 1976; Marple et al., 1987). The filters were weighted before and after sampling using a balance with a precision of 1 μg , after at least a 24-hr equilibration period inside the weighing room (humidity and temperature controlled: $45 \pm 5\%$ relative humidity [RH] and $22 \pm 1^{\circ} C$, respectively; Gatti and Kerr, 2008), and submitted to a system to eliminate accumulated electrical charges. The volumes to calculate concentrations were given by a volume integrator.

The filters were analysed by energy-dispersive x-ray fluorescence (XRF-ED) for the determination of the concentrations of the elements with atomic number (Z) greater than or equal to 11 (Na). Black carbon (BC) concentrations were obtained by light reflectance. Since this BC measurement depends on the standard used for calibration and on the specific PM composition being analyzed (Baumgardner et al., 2012; Quincey et al., 2011), these data were corrected using an intercalibration between our reflectometer and thermal/optical transmittance (TOT) equipment (U.S. Environmental Protection Agency [EPA], 2012).

Three receptor models were used to identify and estimate the sources impact in the study area: positive matrix factorization (PMF), principal components analysis (PCA) with the determination of absolute factors, and chemical mass balance (CMB).

PMF (Paatero, 1997) enables the obtaining of a set of p factors, searching the best solution for the equations relating the data base matrix x , with the factor profiles f and the amount of mass g the factor contributed in each sample:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where i and j identify the sample and the chemical species, respectively, and e_{ij} is the residual. The numerical process (Norris et al., 2008) solves a least-square problem, minimizing the Q function:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (2)$$

where u_{ij} is the uncertainty of the observed x_{ij} .

In this methodology, the determination of u_{ij} is an important issue, since each data x_{ij} is inversely weighed by this value,

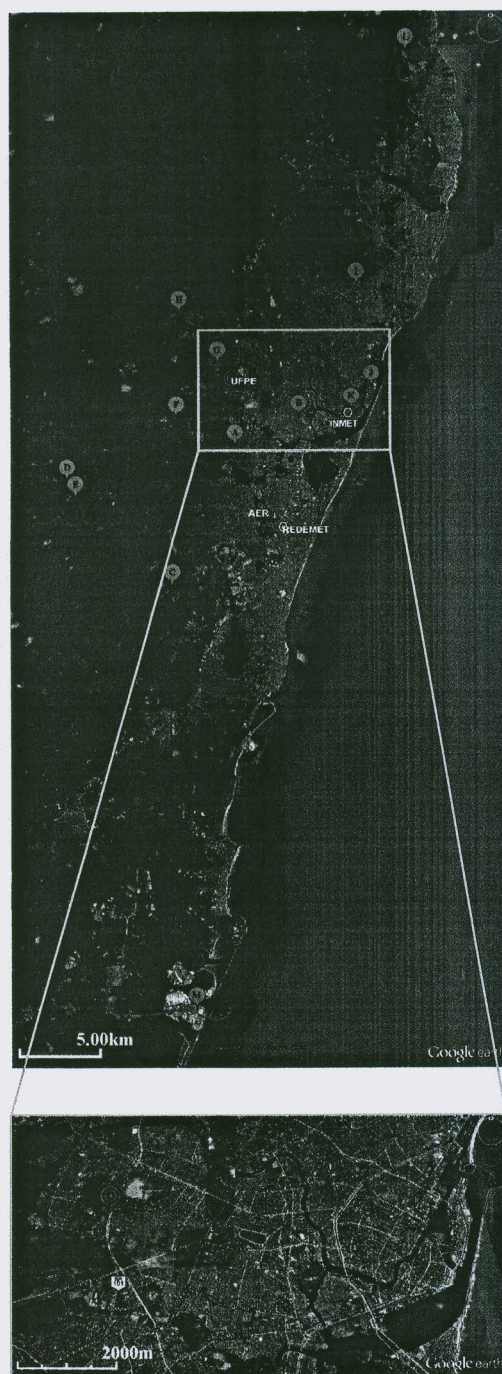


Figure 1. Map of Recife. UFPE: sampling station of $PM_{2.5}$ ($8^{\circ}2.93' S$, $34^{\circ}56.77' W$, and 15 m amsl). INMET, meteorological station of the National Institute of Meteorology; AER, Weather Station—Airport of Guararapes (REDEMET). (A) Metallurgy, (B) chemical industry, (C) landfill, (D) alcohol plant, (E) sugarcane crop, (F) steel mill, (G) thermoplastic, (H) metallurgy, (I) landfill, (J) port, (K) central commerce area, (L) cement plant, (M) industrial area and port. The detail shows a magnification of the area around the sampling site with the road system and port. (Images from Google Earth: Image©2013DigitalGlobe – DATA SIO, NOAA, US Navy, NGA, GEBCO, and for detail, Image©2013TerraMetrics, Image©2013MapLink, Image©2013DigitalGlobe.)

impacting the g and f determination. Polissar et al. (1998) used the analytical uncertainty plus LD/3 (1/3 of the limit of detection [LD]) as the total uncertainty of each element, reducing the weight of the elements that were harder to detect. Nevertheless, the uncertainty for analytical methods like XRF-ED has an LD bias because of the background subtraction when integrating the characteristic x-ray peak for each element. Therefore, we opted for not increasing the LD weights beyond this limit. Otherwise, the u_{ij} used were a combination (square root of the squared values sum) of the uncertainties due to the analytical method and the general 8% uncertainty associated to the $PM_{2.5}$ sampling process itself (using the result for paired sampling obtained for Harvard samplers by Dionisio et al. [2010]). Doing so, there is a reduction in the range of weights values for the elements more precisely determined by the analytical method, smoothing their role in the f and g determination. Finally, a few missing values, for a few elements [Mg (7.4%), Al (2.3%), Cl (1.6%), S and K (0.65%), Na and Ca (0.32%)], were filled with LD/2 (half the limit of detection), considering equally probable any concentration value between 0 and LD, and adopting (5/6)LD as their analytical method uncertainty (Polissar et al. 1998).

The concentration matrix (missing values filled) was also used for PCA, a well-known methodology (e.g., Johnson and Wincherm, 1982) that seeks the least number (p) of factors (F_k) explaining well the common variance of a database x , in general normalized by its average (μ_i) and standard deviation (σ_{ii}); therefore:

$$z_i = l_{i1} F_1 + l_{i2} F_2 + \dots + l_{ip} F_p + e_i \quad (3)$$

where l_{ik} is the factor loading, e_i is the residual, and z_i the normalized database variable,

$$z_i = \frac{x_i - \mu_i}{\sqrt{\sigma_{ii}^2}} \quad (4)$$

which makes the factor loadings be the correlation between the variable and the factor.

The factors were rotated to maximize the variance of its squared loadings (Varimax), given the rotated loadings l'_{ij} , used also to calculate f_{ij} , the absolute factors profile (Keiding, 1986):

$$f_{ij} = \frac{\sigma_{xi} l'_{ij}}{\sigma_{PM} l'_{PMj}} \quad (5)$$

where σ_{xi} and σ_{PM} are the standard deviation for x_i and mass concentration, respectively, and l'_{PMj} is the rotated mass concentration loading in the factor j .

CMB is a well-established receptor model, used to evaluate sources participation in the collected samples, assuming that

$$x_i = \sum_{j=1}^p f_{ij} S_j \quad (6)$$

The f_{ij} must be known and the numerical solution is obtained by weighted least squares. With the U.S. EPA software CMB 8.2 (Coulter, 2004), we evaluated the source apportionment in the collected $PM_{2.5}$, using either the sources identified with the

absolute factors obtained by PCA, or source profiles from the literature (SPECIATE, for instance, from U.S. EPA [2011]).

Results and Discussion

Figure 2 shows the mass concentrations obtained for $PM_{2.5}$ during the sampling period. The average concentration for the sampling period was $7.4 \mu\text{g}/\text{m}^3$. Averaging the concentrations month by month (from July 1, 2007, to June 30, 2008), the annual monthly average concentration was $7.3 \mu\text{g}/\text{m}^3$, and no daily concentration exceeds $25 \mu\text{g}/\text{m}^3$, following the WHO guidelines for this pollutant (WHO, 2005). Notwithstanding the high state of urbanization of the metropolitan area, the $PM_{2.5}$ concentrations were acceptable for this period in the sampling station. This most likely is due to the general circulation in the local and to the regional shoreline meteorological system, both favorable to air pollution dispersion.

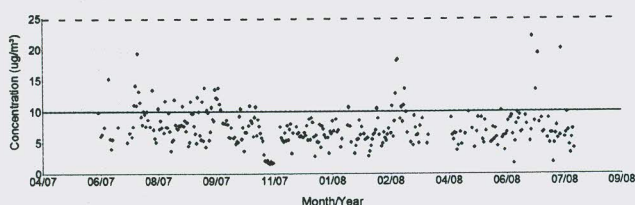


Figure 2. Daily concentration of $PM_{2.5}$ for the sampling period. The continuous and the dashed lines show the WHO guidelines for $PM_{2.5}$ (annual concentrations of $10 \mu\text{g}/\text{m}^3$, and daily concentrations not exceeding $25 \mu\text{g}/\text{m}^3$ in more than 1% of the samples).

$PM_{2.5}$ and BC concentrations were reported for this Recife database in previous works (Andrade et al., 2012; Miranda et al., 2010), registering values higher than that shown here (Table 1) for BC: $1.9 \mu\text{g}/\text{m}^3$ for a global average, or $1.3 \mu\text{g}/\text{m}^3$ and $2.7 \mu\text{g}/\text{m}^3$ for BC in summer and winter periods, respectively. There is a small difference in the number of samples selected, since in this work we are taking only those simultaneously analyzed by XRF and reflectance. However, the main difference was in the methodology adopted after those publications. We used an intercalibration with TOT, as described in the Methodology section, while the previous work calibrated the reflectometer with standard filters coated with a reference BC.

The BC concentrations are presented in Figure 3. A seasonal trend can be observed in Figures 2 and 3 for the total mass and BC, respectively. The Recife region has two climatic seasons: summer or dry (October to March), and winter or rainy (April to September). The higher concentration levels occurred during the winter period. Although such a result is often expected, it was not obvious for that region, close to the Equator and with the rainy period, propitious to PM removal, occurring during the winter. Figures 4a and 4b show the rainfall distribution during sampling periods, during winter and summer, respectively, making it clear that the winter has a higher precipitation level than summer, and that the last period had 2.6 times more dry days than the first. Otherwise, the wind speed distribution for winter (Figure 5a) indicates lower intensities than in summer (Figure 5b), with 8 times more hours of calm winds, which could explain the higher concentration levels in the winter. The decrease in the wind intensity reduces the air pollution dispersion, while the higher

Table 1. Average concentrations and standard deviation for chemical elements, BC, and total $MP_{2.5}$ (309 samples)

Element	All period ($\mu\text{g}/\text{m}^3$)		Winter ($\mu\text{g}/\text{m}^3$)		Summer ($\mu\text{g}/\text{m}^3$)	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Na	0.294	0.089	0.281	0.078	0.307	0.098
Mg	0.114	0.039	0.108	0.044	0.120	0.033
Al	0.063	0.097	0.040	0.029	0.09	0.13
Si	0.127	0.235	0.078	0.058	0.18	0.32
S	0.18	0.11	0.139	0.064	0.23	0.12
Cl	0.09	0.14	0.14	0.18	0.040	0.057
K	0.123	0.097	0.120	0.094	0.126	0.099
Ca	0.052	0.039	0.049	0.043	0.055	0.035
Ti	0.0042	0.0052	0.0031	0.0014	0.0053	0.0071
Cr	0.00212	0.00054	0.00219	0.00059	0.00205	0.00048
Mn	0.0030	0.0025	0.0037	0.0030	0.0023	0.0015
Fe	0.070	0.061	0.077	0.056	0.062	0.064
Ni	0.00376	0.00058	0.00378	0.00062	0.00373	0.00053
Cu	0.0031	0.0027	0.0040	0.0034	0.0022	0.0010
Zn	0.017	0.022	0.024	0.027	0.011	0.013
Br	0.0043	0.0024	0.0041	0.0023	0.0044	0.0025
Er	0.0054	0.0015	0.0050	0.0015	0.0059	0.0014
Pb	0.0095	0.0037	0.0104	0.0044	0.0085	0.0025
BC	1.07	0.47	1.30	0.44	0.84	0.38
Total mass	7.4	3.0	7.8	3.2	6.9	2.8

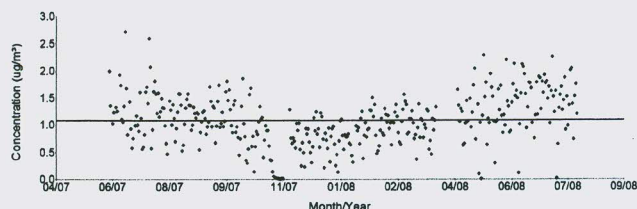


Figure 3. Daily concentration of black carbon, for the sampling period. The continuous line shows the mean.

insolation in summer has an opposite action, due to the increase of wind speed, of turbulence, and of the mixing layer height. From the wind direction point of view, an opposite behavior would be expected. The prevalent wind direction is from the south to east quarter for both seasons (Figures 6a and 6b). Nevertheless, there is an increase of more easterly wind frequencies in summer, probably due to the intensification of the solar radiation and the corresponding intensification of the regional sea breeze circulation pattern (from the east). Easterly wind intensifies the air pollution transport from the downtown zone, an important source of PM, to the sampling point (Figure 1). Anyway, the prevailing effect observed was the lowering of $PM_{2.5}$ concentrations during summer.

Average concentrations, and respective standard deviations, of elements, black carbon, and total mass for the 309 samples are presented in Table 1. Winter (rainy) and summer (dry) periods are highlighted.

Analyzing the database by PMF, six factors were identified and associated to regional sources (Table 2): (1) metallurgy, (2) CI sources, (3) Na/S/Ca/Br source, (4) soil dust, (5) biomass burning, and (6) vehicles and sea spray.

In Table 3 are presented the rotated loadings (VARIMAX method) obtained for the six factors extracted by PCA analysis, using the same database. In Table 4 are presented the absolute factors obtained using the PCA loadings calculated as presented in eq 5. The elements are grouped following the intensity of the loadings for each factor (the high loading values in each factor are bold marked). In the last line below the factor number is the percentage of database variance explained by each factor. The six factors explained 78.5% of the total database variance. The source association for each factor is also indicated in the table, and followed the connection between the chemical elements in the sources and the high loaded element in the factor. Therefore, the association of the first factor with soil dust is straightforward, in the same way as the fifth is related to the sea spray. The second factor was associated to

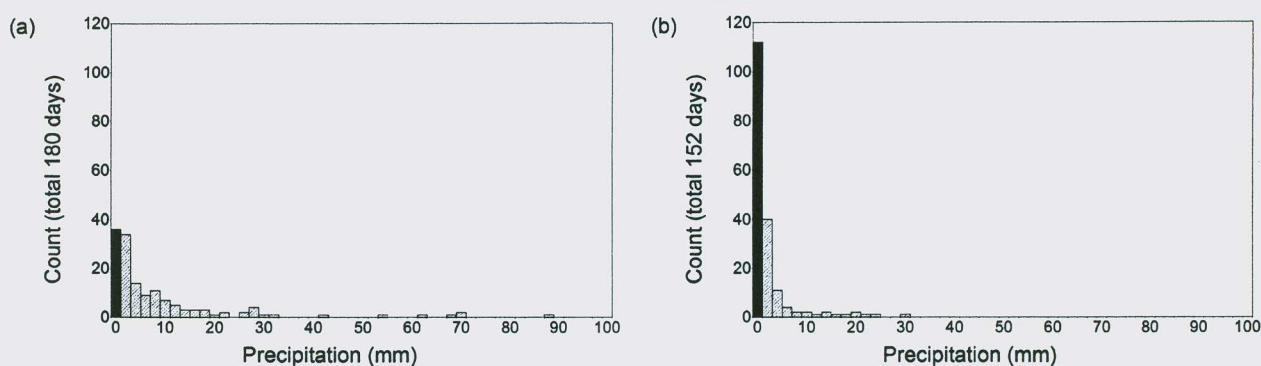


Figure 4. Rainfall amount distribution during the sampling period [database from INMET meteorological station at Recife, INMET (2007)]: (a) winter; (b) summer. The black column indicates days without precipitation.

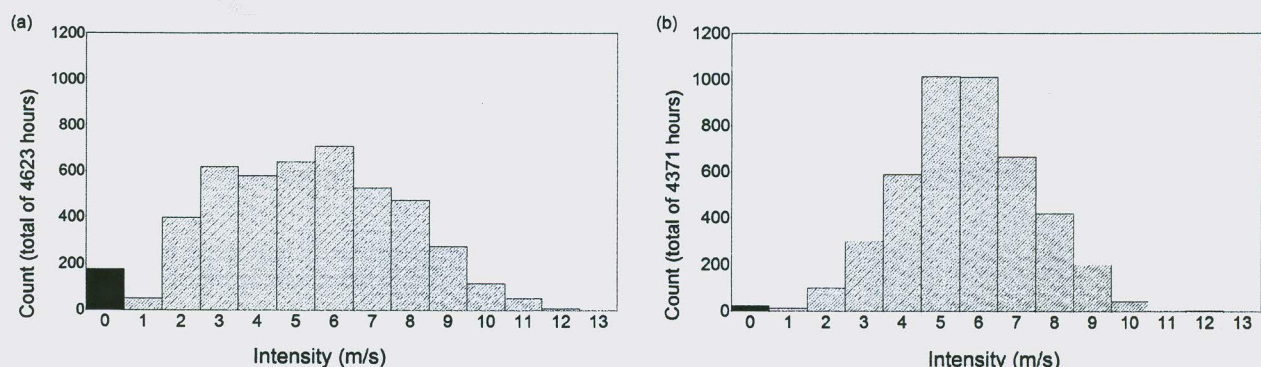


Figure 5. Wind intensity distribution [database from REDEMET meteorological station at Recife (REDEMET, 2012)]: (a) winter; (b) summer. The black column indicates hours with calm winds (speed < 0.5 m/s).

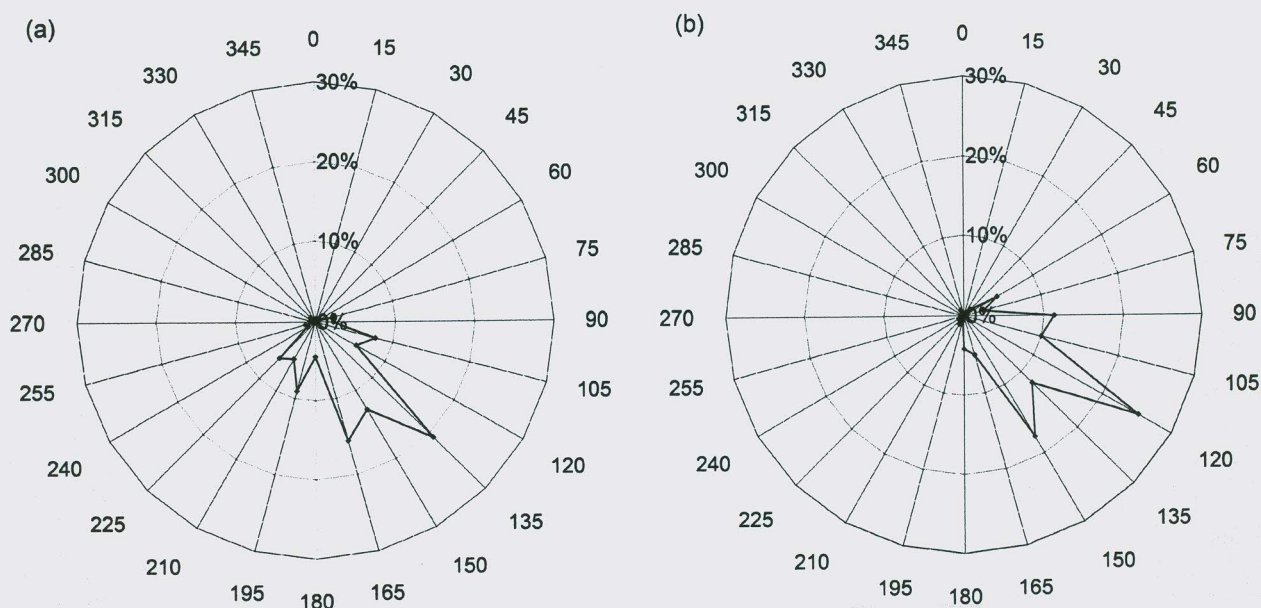


Figure 6. Wind direction frequency [database from REDEMET meteorological station at Recife (REDEMET, 2012)]: (a) winter; (b) summer.

Table 2. PMF analysis indicating the percentage of each element in the extracted six factors, with the predominant elements on each factor boldfaced

Element	Factor 1, Metallurgy	Factor 2, Chlorine	Factor 3, Na/S/Ca/Br	Factor 4, Soil	Factor 5, Biomass burning	Factor 6, Vehicles + sea spray
Total mass	3.8%	5.7%	9.1%	9.2%	27.5%	44.7%
BC	12.2%	0.4%	0.0%	4.9%	22.0%	60.5%
Na	4.5%	7.4%	40.4%	0.0%	9.6%	38.1%
Mg	0.0%	3.2%	27.0%	6.1%	8.6%	55.1%
Al	2.9%	0.0%	11.8%	73.5%	5.9%	5.9%
Si	0.8%	4.5%	4.9%	88.1%	1.7%	0.0%
S	11.7%	0.3%	64.5%	10.1%	13.4%	0.0%
Cl	0.0%	86.7%	0.8%	0.9%	2.2%	9.4%
K	8.9%	4.1%	12.3%	14.4%	60.3%	0.0%
Ca	13.9%	15.0%	47.5%	20.1%	1.2%	2.2%
Ti	5.0%	2.0%	18.5%	51.9%	3.0%	19.6%
Cr	14.3%	3.0%	20.8%	5.8%	10.8%	45.4%
Mn	49.1%	0.8%	0.7%	11.2%	11.9%	26.3%
Fe	50.1%	2.8%	11.8%	25.9%	0.0%	9.5%
Ni	6.1%	4.0%	24.0%	2.7%	12.8%	50.4%
Cu	20.7%	19.0%	9.6%	0.7%	21.2%	28.8%
Zn	90.2%	0.0%	0.0%	0.0%	9.8%	0.0%
Br	0.0%	0.0%	38.9%	0.0%	29.5%	31.6%
Pb	27.9%	0.6%	12.1%	3.0%	18.0%	38.4%

vehicles emission mainly due to the presence of Pb (and also BC); in Brazil leaded gasoline has been banned for a long time, but in this case Pb is a geological residue in the petroleum or contamination in the production process (Gioia et al., 2010). K in the third factor indicates the association with biomass burning. We are not secure about the four and six factors'

association, but they could be attributed specially to industrial activity. An integrated source discussion will be done after the CMB results.

Equation 6 may be solved using several source arrangements to obtain a local source apportionment. However, a mathematically adequate blend of sources is not necessarily compatible

Table 3. Main rotated factors loadings, with the six factors explaining 78.5% of the total database variance

Element	Factor 1, Soil	Factor 2, Vehicle	Factor 3, Biomass burning	Factor 4, Chlorine	Factor 5, Sea spray	Factor 6, Nickel
Si	0.976	0.067	0.051	−0.043	0.018	−0.077
Ti	0.967	0.081	0.088	−0.050	0.018	−0.056
Al	0.963	0.053	0.047	−0.107	0.022	−0.080
Fe	0.668	0.652	0.046	0.066	−0.078	−0.110
Ca	0.596	0.049	0.263	0.474	−0.190	−0.031
Zn	−0.043	0.903	−0.044	0.052	−0.116	−0.167
Mn	0.194	0.846	0.000	0.091	−0.126	−0.172
Pb	−0.029	0.803	0.098	0.054	−0.179	0.130
Cr	0.163	0.551	−0.027	0.040	0.212	0.195
BC	0.098	0.491	0.321	0.344	−0.285	−0.062
Br	−0.101	−0.099	0.869	−0.023	0.020	0.066
S	0.404	0.073	0.773	−0.133	0.074	−0.150
K	0.464	0.294	0.624	0.225	−0.207	0.083
Cl	−0.074	−0.056	−0.092	0.917	0.034	0.002
Cu	−0.083	0.284	0.059	0.709	0.041	0.138
Mg	0.078	−0.172	−0.071	−0.059	0.802	0.236
Na	−0.300	−0.118	0.524	0.278	0.584	−0.127
Ni	−0.198	−0.051	−0.002	0.116	0.176	0.889
Total mass	0.391	0.280	0.537	0.490	−0.222	0.085
Percent of variance explained	23.1	18.3	13.3	11.2	7.1	5.6

Table 4. Absolute factors (fraction of the total mass)

Element	Absolute factors				
	1 Soil	2 Vehicle	3 Biomass Burning	4 Chlorine	6 Nickel
Na			0.029	0.017	
Mg	0.0026	—	—	—	0.036
Al	0.080	0.0062	0.0028	—	—
Si	0.19	0.019	0.0074	—	—
S	0.037	0.0094	0.051	—	—
Cl	—	—	—	0.090	0.0014
K	0.038	0.034	0.037	0.015	0.032
Ca	0.020	0.0023	0.0063	0.012	—
Ti	0.0043	0.00050	0.00028	—	—
Cr	0.000080	0.00035	—	0.000010	0.00041
Mn	0.00041	0.0025	—	0.00015	—
Fe	0.035	0.047	0.0017	0.0027	—
Ni	—	—	—	0.000050	0.0020
Cu	—	0.00091	0.00010	0.0013	0.0015
Zn	—	0.024	—	0.00079	—
Br	—	—	0.0013	—	0.00061
Pb	—	0.0035	0.00022	0.00013	0.0019
BC	0.032	0.22	0.076	0.090	—

with the local observed reality. PMF and PCA may show what should be expected, and PCA does that by grouping the correlated elements. But the selections provided by PCA and PMF are sensitive, among others, to the defined number of factors, or to the elements turned on or off, and, in the case of PMF, to the uncertainty set up. An integrated use of these models, with their peculiarities, besides the knowledge of local environmental characteristics (sources, wind transport and other meteorological factors, for instance), could provide a more balanced evaluation of the local sources and respective impacts.

Table 5 groups the source apportionment results for PMF and PCA/CMB in the average concentrations (general, winter, and summer). We did not have local sources profiles to be used in CMB. We tried to use vehicular profiles recently obtained inside tunnels at, or around, São Paulo city in Brazil (not published yet) and U.S. EPA profiles organized by SPECIATE (U.S. EPA, 2011): sea spray, biomass burning, steel mill, and cement plant (there is one factory 22 km NNE of the sampling point, and another 37 km SSW). From the several combinations possible, the best results come when considering only the five sources obtained by absolute PCA (Table 4), and only the sea spray component was not extracted because of its anticorrelation with total mass concentration.

The sources profiles extracted by receptor models express the transformations of the aerosol in its trajectory from the emission until the receptor. But they also show some sources blending, depending on wind transport and the sampling station positioning, and yet, long sampling period, like a 24-hr cycle, averages sources specificities that otherwise could help sources' discrimination. It is not surprising, therefore, that PMF mixed vehicles and sea spray, since the most frequent wind, from the east-southeast, brings together the urban and the sea particles. The model attributed 40 to 54% of the sampled mass to that source, being the summer value higher than winter one. This result is

consistent with the easterly deviation of the wind, transporting more of the harbor and vehicular emissions from downtown and from a highway placed beside the UFPE campus. These values seem to be more adequate than the CMB/PCA (9 to 20%), considering the dimension of the local vehicular fleet (400,000 units, being 17,000 heavy duty vehicles). The higher value obtained by PMF for this source probably is not due to the adjunct sea spray, present prevalently in the coarse PM. Both methods identified a source highly loaded with Cl, probably because it comes from more than one source. There are industries of plastics, sea spray, and biomass burning, for instance, and the sugar and alcohol production. This factor is lower in the summer, and one possible explanation is connected to Cl depletion in salt-containing particles. The intensification of solar radiation during the summer can increase the production of sulfuric and nitric acid due to photochemical reactions. Both acids could react with Cl from NaCl-containing particles, forming gaseous HCl and reducing the Cl concentration in the PM_{2.5} (McInnes, 1994). The biomass burning source, characterized by K and Br (and some correlation with BC), could have expressive participation of the sugarcane thatch burning, before harvesting, and wood burning for cooking. This factor was well defined and apportioned an expressive mass amount in both models, although for summer the PMF estimated much less mass than PCA/CMB. The source soil dust also was well defined in both models, and in this case no severe discrepancy was observed in the seasonal values. The increase of soil dust fraction during summer is coherent with the rain reduction and higher wind speed, facilitating dust resuspension in this period. The Ni source discriminated by PCA/CMB may be connected to metallurgical activities in the area (Figure 1).

Taking the 20 samples with higher concentrations, only 4 days were in the dry period (summer), and for 3 of them the dominant source was soil dust, being related to reported intense

Table 5. PCA/CMB and PMF estimative of the contribution of factors/sources for average concentrations, for all samples, winter period samples, and summer period samples

	All	Uncertainty	Winter	Unc.	Summer	Unc.
PCA/CMB factor contribution						
1 Soil	9.9%	1.3%	4.3%	0.9%	16.1%	1.7%
3 Biomass burning	40.3%	5.4%	32.2%	4.4%	48.2%	6.2%
4 Chlorine	18.9%	2.5%	28.9%	3.4%	8.0%	1.3%
2 Vehicle	14.6%	1.7%	20.0%	1.9%	9.1%	1.4%
6 Nickel	16.3%	5.7%	14.5%	5.4%	18.7%	6.0%
Percent mass explained	76.9%		75.6%		80.1%	
PMF factor contribution						
4 Soil	9.2%	1.2%	8.4%	0.6%	11.5%	2.4%
5 Biomass burning	27.5%	1.6%	30.4%	2.7%	18.4%	1.4%
2 Chlorine	5.7%	0.6%	11.1%	1.3%	0.0%	0.0%
1 Metallurgy	3.8%	0.3%	6.4%	0.6%	12.2%	1.2%
6 Vehicles + sea spray	44.6%	1.2%	38.8%	1.6%	53.9%	2.1%
3 Na/S/Ca/Br	9.1%	0.3%	5.0%	0.3%	3.9%	0.2%
Percent mass explained	100%		100%		100%	

Note: PMF considers 100% of the mass explained with the extracted factors.

NW to N winds (a rare wind direction in the region). In the 16 other days, in the wintertime, soil dust had a reduced participation and the impact was fractionated among the other sources, and in the more intense concentrations the prevalent wind came from the south.

It is important to point out some differences between the receptor modeling results shown here and those obtained in a previous work dealing with results of the six Brazilian capitals studied in the main project INAIRA (Andrade et al., 2012). That study considered a global view of the six capitals, and approximately half of the database had been submitted to XRF analysis (148 samples in the case of Recife). The present work went deeply into the study of Recife, analyzing all samples with an increased LD for the elements with $Z < 14$ (reanalyzing the first 148 samples to avoid any analytical disruption), using an intercalibration for BC, and articulated absolute PCA/CMB with PMF to improve the sources identification analysis, considering, otherwise, more extensively the meteorological parameters. The first work identified that the average $PM_{2.5}$ source apportionment gave 8% for light vehicles, 8% for crustal, 29% for heavy-duty vehicles, and 24% for sea spray. We could observe that crustal was very similar, and if we sum all contribution from vehicles, this result do not diverge substantially from that obtained by PMF analysis performed here. The use of the double number of samples and better LD for elements with low Z provided the inclusion of Na, Mg, and Al, not used before. Therefore, in the present work it was possible to increase the number of factors and to distinguish, also, biomass burning and industrial contributions, although the sea spray could not be separated from vehicles.

Conclusion

The use of PCA/CMB and PMF receptor models provided a study of the impact of the principal sources acting in the area of Recife, considering the seasonal peculiarities. The models showed some difference in the results, but for soil dust and biomass burning they were similar (a participation between 5 to 17% and between 18 to 47%, respectively). PCA/CMB estimated a participation of 9 to 20% of vehicles to the $PM_{2.5}$, less realistic than PMF (40 to 54%), although it mixed sea spray in this factor, while PCA/CMB did not. Both models showed a factor highly identified with chlorine, which could come from more than one source, and other factors with different structures that could be related to metallurgical activities.

The $PM_{2.5}$ concentration levels in the sampling site, during the period of this experiment, remained within the WHO guidelines, notwithstanding the high state of urbanization of the metropolitan area. Probably this could be related to the general wind circulation in the local, associated with the regional shoreline meteorological system, given favorable conditions for air pollution dispersion. The rainy period (winter) showed higher concentration levels, probably due to the worsening of the atmospheric conditions for dispersion. Those results represent a valuable register of the $PM_{2.5}$ in the region of Recife, as well as its dynamics associated with local climate, and should be very important for the next analysis, which will correlate health data, $PM_{2.5}$ levels, and sources responsibility, in the context of

INAIRA, the comprehensive project where six Brazilian Capitals are being studied.

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- 530

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