Influence of traffic on the elemental composition of PM_{10} and $PM_{2.5}$ in Oporto region

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Abstract

The aim of this work was to study the influence of traffic emissions on the physical and chemical characteristics of PM_{10} and $PM_{2.5}$, namely considering: concentration, size distribution and elemental composition. Four monitoring sites in the north of Portugal were selected: two sites directly influenced by traffic emissions and two rural background sites. PM_{10} and $PM_{2.5}$ samples were collected using low-volume samplers; the element analyses were performed by particle induced X-ray emission (PIXE). At the sites influenced by traffic emissions PM_{10} and $PM_{2.5}$ concentrations were 7-9 and 6-7 times higher than at the background sites. The presence of 17 elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb) was determined in both PM fractions; particle metal contents were 3-44 and 3-27 times higher for PM_{10} and $PM_{2.5}$, respectively, than at the backgrounds sites. The results also showed that in coastal areas sea salt sprays are important sources of particles, influencing PM concentration and distributions (PM_{10} increased by 46%, $PM_{2.5}/PM_{10}$ decreased by 26%), as well as PM compositions (Cl in PM_{10} was 11 times higher).
Keywords: air pollution, particulate matter, traffic emissions, PM_{10}, $PM_{2.5}$, PIXE, metallic composition, Portugal.

1 Introduction

Many European countries are nowadays concerned with the numerous negative effects of traffic. During the past 3 decades the motor vehicle traffic has been massively increasing: between 1970 and 1995 the use of cars in Europe Union doubled. The consequences of traffic have been well recognized: injuries, traffic

WIT Transactions on Ecology and the Environment, Vol 101, © 2007 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/AIR070061

noise, effects on metal health and wellbeing, and more importantly air pollution. Special efforts have been made during last two decades, aiming the reduction of adverse impacts of air pollution, despite that, air pollution in Europe is still a matter of concern, mainly related with impacts on the human health and on the environment. The levels and composition of traffic related pollutants in air depend on several factors such as the number of vehicles, types of used fuels, type and conditions of engines, type of environment and meteorological conditions; however, ozone (O_3), nitrogen oxides (NO_x), carbon monoxide (CO) are considered as the most serious traffic-related air pollutants, among them particulate matter (PM) being one of the most important.

In Europe, exhaust from motor vehicles is considered to contribute more than 50% for emission of PM_{10} (particles with aerodynamic diameter smaller than 10 μm) (Kunzli *et al* [1]). Previous research has mostly focused on vehicle exhaust particulate emissions, because it was generally assumed that fuel combustion was the primary mechanism by which the particles were formed (Sagebiel *et al* [2], Kleeman *et al* [3]). Nevertheless, tire, brake and clutch emissions, and resuspended dust also contribute to atmospheric particulate matter Mulawa *et al* [4].

PM has been intensively studied within many epidemiological studies in Europe and North America Dockery and Pope [5], Brunekreef and Holgate [6], Hoek *et al* [7], Alvim-Ferraz *et al* [8]. Those studies showed the association between the increase of ambient concentrations of PM_{10} (that can penetrate the respiratory tract) and especially $PM_{2.5}$ (particles with aerodynamic diameter smaller than 2.5 μm that can penetrate in the deeper parts of the lungs) and the increase of morbidity and mortality rates, caused by pulmonary and cardiovascular diseases; the smaller the particles, the more evident the health effects Kaiser [9].

Despite the enormous number of epidemiological studies, there is a remaining uncertainty, if it is the physical (namely size and shape) or the chemical PM characteristics that have the most important role on the adverse health effects. A typical sample of PM consists of several chemical substances among them crustal compounds, minerals and trace metallic elements (Harrison *et al* [10], Sondreal *et al* [11], Tripathi *et al* [12], Sharma *et al* [13]). Some of the trace metallic elements present in PM (As, Cd, Co, Cu, Hg, Mn, Ni, and Pb) are human or animal carcinogens (Manalis *et al* [14]), therefore EU has stressed the importance of this subject setting the Directive 2004/107/EC that defines target values and assessment thresholds of arsenic, cadmium, mercury, nickel and PAH (benzo(a)pyrene) in PM_{10}, requiring the respective long-term assessment. Nevertheless, the knowledge about the impact of PM metallic composition on health is still scarce, which justifies an increasing effort concerning the characterization of the metallic composition of smaller fractions of PM.

Many of the epidemiological studies related to PM consider only PM_{10}. Nevertheless, as most of the PM traffic emissions are in the fine fraction, more information on $PM_{2.5}$ should be provided namely concerning the levels and elemental composition, as the actual knowledge is still scarce on that. Thus, considering the relevance of that knowledge for a further evaluation of the

influence of traffic emission on public health, the work developed included the detailed characterization of PM_{10} and $PM_{2.5}$, sampled at sites directly influenced by traffic, as well as at reference sites. Bulk elemental composition of PM was determined by particle induced X-ray emission (PIXE). The specific objectives were to study the influence of traffic emission on PM_{10} and $PM_{2.5}$ characteristics, considering: (1) concentration and size distribution; and (2) bulk elemental composition.

2 Methods

Monitoring of PM_{10} and $PM_{2.5}$ was performed in the north of Portugal during winter and spring of 2005 at four sites: two directly influenced by traffic (Tr_1 and Tr_2) and two not directly influenced by anthropogenic emission (background Bc_1 and Bc_2). Sampling was performed for 21 consecutive days at sites Tr_1 and Tr_2, and for 10 and 22 consecutive days at sites Bc_1 and Bc_2, respectively.

Both the traffic sites were situated at a zone of Oporto (Paranhos district), where several public institutions, high and secondary schools, and universities are located. The area is near one of the most important access points to the highway and the traffic emissions are the main source of atmospheric pollutants (Salcedo *et al* [15], Pereira *et al* [16]). Site Tr_1 was situated about 30 m west from the highway while site Tr_2 was located at the car park entrance of one of the universities, at about 50 m east from one of the main streets.

Site Bc_1 was situated in the natural park of Alvão, located in the northern interior lands of Portugal, approximately 115 km east from Oporto. Site Bc_2 was situated approximately 13 km far from seacoast in a remote area, about 112 km north from Oporto city. Based on given classifications (Larssen *et al* [17]), both Bc_1 and Bc_2 were considered as rural (regional) background sites. The locations of all sites are shown at Figure 1.

The sampling equipment worked every day from 8.00 a.m. to 8.00 p.m. to perform monitoring periods of 12 hours. Such a period was chosen in order not to over-load filters for consequent chemical analysis. The collection of the different PM fractions was done using TCR TECORA Bravo H2 constant flow samplers, combined with PM_{10} and $PM_{2.5}$ EN LVS sampling heads in compliance with the norm EN12341. A sampling air flow rate of 38.3 L min^{-1} was applied. The particles were collected on polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring (2 μm porosity, Pall Life Science Teflo™).

PM masses were determined gravimetrically by subtracting the initial average mass of the blank filter from the final average mass of the sampled filter; the difference was then divided by the total volume of air passed through filter (at 25ºC and 101.3 kPa). The steps of pre- and post-sampling gravimetric mass determinations were the following: 24 h to equilibrate filters before weighing at room temperature (Mettler Toledo AG245 analytical balance weighing with accuracy of 50 μg) followed by weighing during the following 24-48 h. If the measurements for one sample differed more than 50 μg, they were discarded and the filters were repeatedly weighed until three reproducible values were

obtained. For the data treatment, the Student's t-test was applied to determine the statistical significance ($P<0.05$, two tailed) of the differences between the averages determined for all the sites. For elemental analysis the filters were cut in half. One half was analysed by particle induced X-ray emission (PIXE) while the other part was kept for possible replicates and other analysis. The PIXE analysis used a beam of 2.150 MV without a filter.

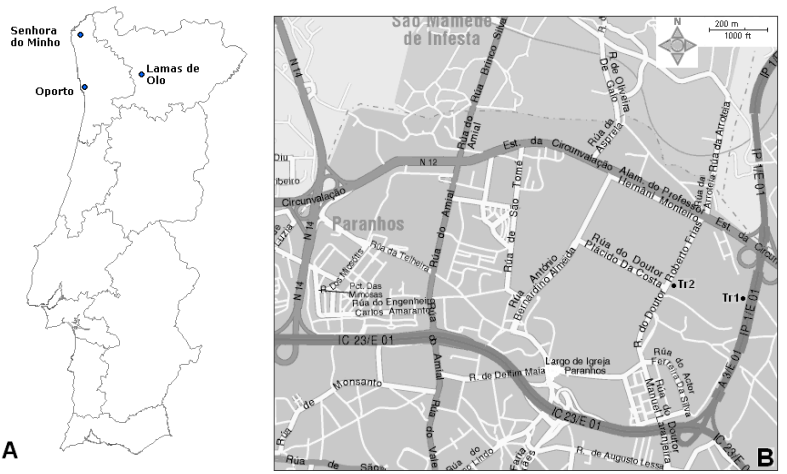

Figure 1: Monitoring sites: A) in Portugal B) in Paranhos district.

3 Results and discussion

3.1 PM_{10} and $PM_{2.5}$ concentrations

The means as well as other statistical parameters of PM_{10} and $PM_{2.5}$ measured at the two sites influenced by traffic emissions and at the two background sites are shown in Figure 2. The statistical analysis of these results indicated that: i) PM_{10} and $PM_{2.5}$ concentrations were significantly lower at the background sites than at the traffic ones; ii) the differences observed between PM_{10} means (as well as between $PM_{2.5}$ means) at Tr_1 and Tr_2 were not statically significant; iii) PM_{10} and $PM_{2.5}$ means were not significantly different at sites Tr_1, Bc_1 and Bc_2, demonstrating that most of PM_{10} fraction was composed by $PM_{2.5}$; and iv) PM_{10} means at Bc_1 and Bc_2 were significantly different, while no difference was observed for $PM_{2.5}$. In addition, it was found that at both Tr_1 and Tr_2 PM_{10} concentrations were well correlated with $PM_{2.5}$ as the correlation coefficient square (R^2) is 0.92 (Figure 3), indicating that PM_{10} and $PM_{2.5}$ at these sites were influenced by similar sources. In general, the results showed that traffic emissions increased about 7-9 times PM_{10} concentrations and about 6-7 times $PM_{2.5}$ concentrations.

To study the association between both PM fractions, the $PM_{2.5}/PM_{10}$ ratios were analyzed with more detail. The $PM_{2.5}/PM_{10}$ ratios were calculated from

each measurement and the means of $PM_{2.5}/PM_{10}$ as well as other statistical parameters are shown in Table 1.

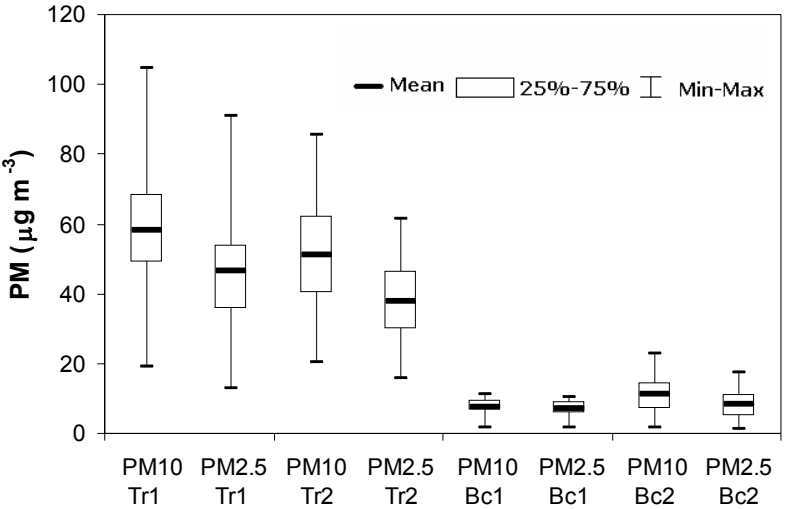

Figure 2: Atmospheric concentrations of PM_{10} and $PM_{2.5}$ measured at the four sites in Portugal: means, minima (Min) and maxima (Max) values, 25th and 75th percentiles.

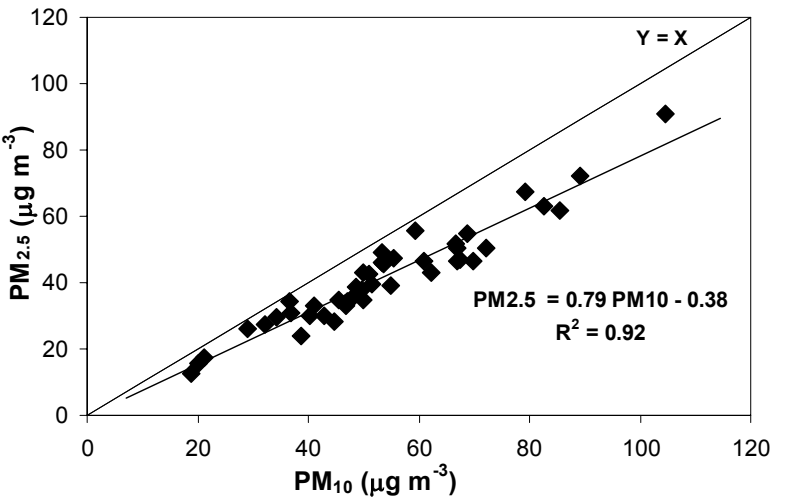

Figure 3: $PM_{2.5}$ and PM_{10} correlation for the traffic sites.

During the monitoring campaigns the differences observed between the means of the ratios at both traffic sites and Bc_2 were not statistically significant; however, $PM_{2.5}/PM_{10}$ ratios were slightly higher at sites Tr_1 and Tr_2. The mean

ratio obtained at site Bc_2 (0.72) was the lowest of all sites. As mentioned previously, site Bc_2 was located close to the seacoast. Sea salt sprays are mainly composed by coarse particles which justified the lower values observed for $PM_{2.5}/PM_{10}$. This conclusion was also supported by the comparison of particle levels (Figure 2). The means of PM_{10} were significantly lower at Bc_1 (distant from the seacoast) than at Bc_2 (close to the seacoast); nevertheless, $PM_{2.5}$ concentrations were not significantly different. Thus, the obtained result showed that sea salt spray plays an important role as particle source in coastal areas of Portugal and its contribution to PM_{10} particle distributions should be assessed. The highest mean ratio (0.91) was observed at site Bc_1. This value indicates that background PM_{10} was mostly composed of fine particles. At this moment, discussions among the scientific community suggest the implementation of $PM_{2.5}$ air quality standards, which could in the future replace present PM_{10} standards. As sites with similar characteristics in other European countries showed lower $PM_{2.5}/PM_{10}$ ratios (Van Dingenen *et al* [18]), the accomplishment of new $PM_{2.5}$ limits in Portugal might be more difficult than in other regions. As $PM_{2.5}$ have strong influence on lung diseases (Maynard and Howard [19]), information about high $PM_{2.5}/PM_{10}$ in Portugal is also relevant for the development of strategies to protect public health.

Table 1: Statistics for $PM_{2.5}/PM_{10}$ ratios at the four sites.

Site	$\frac{PM_{2.5}}{PM_{10}}$ mean	SD	Min	Max	25th percentile	Median	75th percentile
Tr_1	0.79	0.07	0.67	0.92	0.76	0.78	0.83
Tr_2	0.75	0.07	0.62	0.86	0.70	0.74	0.80
Bc_1	0.91	0.05	0.83	0.99	0.88	0.91	0.96
Bc_2	0.72	0.15	0.41	0.94	0.64	0.77	0.81

3.2 PM_{10} and $PM_{2.5}$ bulk elemental compositions

The emissions of particles related to traffic are consequence of fuel combustion, vehicular component wear, road degradation and roadway maintenance. The traffic-related PM include in their compositions metallic elements with anthropogenic origin such as V, Cr, Fe, Ni, Cu, Zn and Pb (Sansalone and Buchberger [20]), and also elements resulting from crust and road abrasion such as Mg, Al, Si, Ca, K and Ba Viana *et al* [21]. The following 20 elements were determined using the PIXE technique to characterize PM_{10} and $PM_{2.5}$ sampled at the two traffic and two background sites: magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), bromine (Br), arsenic (As) and barium (Ba); however, as the number of PM samples with As, Ba and Br was not significant, these elements were not included in further evaluations. The mean concentrations of elements in PM_{10} and $PM_{2.5}$ and the SD at the traffic and the

background sites are presented in Table 2. The results demonstrated that: i) at both traffic sites the levels of Mg, Al, Si, P, S, Cl, K and Ca in both fractions were significantly higher than at background sites; ii) the highest levels of Ti, Cr, Mn, Fe, Ni, Cu and Zn in PM_{10} were recorded at Tr_1 being 3-44 times higher than at background sites; iii) the highest levels of Cr, Mn, Fe, Ni, Cu and Zn in $PM_{2.5}$ were observed at Tr_1 being 3-27 times higher than at the background sites; iv) the highest levels of Pb in PM_{10} were observed at Tr_1, being 6-9 times higher than at Bc_1; v) the highest levels of Pb in $PM_{2.5}$ were recorded at Tr_1, being at traffic sites 3-4 times higher than at Bc_1; vi) the levels of V in PM_{10} at traffic sites were 4 times higher with respect to the background sites; and vii) the levels of V in $PM_{2.5}$ at sites Tr_1 and Tr_2 were, respectively, 5 and 10 times higher than at the background sites. As expected, the obtained results showed that at sites influenced by traffic particle metal contents were significantly higher than at the backgrounds sites. Thus, traffic emissions influenced the compositions of both PM_{10} and $PM_{2.5}$, increasing greatly their levels of metals.

The concentrations of all elements in $PM_{2.5}$ versus PM_{10} were evaluated. For the traffic sites, around 80-90% of S, Mn, Zn and Pb present in PM_{10} were detected in $PM_{2.5}$. This percentage was lower for P, K and Cr (60-80%) and even lower (below 50%) for Mg, Al, Si, Ca, Ti, Fe, and Cu. In general, at both traffic sites, the elements originated mostly from anthropogenic activities were predominantly present in the fine fraction (S, Mn, Zn, Pb, P, K and Cr) while the elements mostly originated from crust (Mg, Al, Si and Ca) mainly occurred in the coarse particles.

At both background sites, more than 90% of Ti and S present in PM_{10} were found in $PM_{2.5}$; this percentage was lower for Mn (63%) and even lower for P (below 50%); however, more than those no other similarities between both background sites were observed. At site Bc_1 more than 90% of Cr, Cu, Zn and Pb present in PM_{10} belonged to $PM_{2.5}$. This percentage decreased for Mg, Al, Si and Ca (60-80%) and dropped below 50% for V. At site Bc_2 more than 90% of Mg, Al, Si and Fe present in PM_{10} belonged to $PM_{2.5}$. This percentage was lower for V, Cu and Zn (60-80%) and even lower (below 50%) for P, K, Ca, Cr and Cl. At site Bc_2, chlorine was mainly present in coarse particles (42% in $PM_{2.5}$), which was on the contrary to Bc_1 where 70% of Cl present in PM_{10} was detected in fine fraction. As it was already referred, Bc_2 was situated close to the seacoast. As sea salt sprays are mostly composed by coarse particles, the presence of Cl mainly in PM_{10} at Bc_2 can be attributed to marine influence, confirming the previously referred conclusion obtained through the analysis of $PM_{2.5}/PM_{10}$ ratios at the two background sites. Concluding, sea salt sprays influence concentrations and compositions of atmospheric background particles as well as the distribution of Cl between PM_{10} and $PM_{2.5}$.

4 Conclusions

Traffic emissions increased about 7-9 times PM_{10} concentrations and about 6-7 times $PM_{2.5}$ concentrations; sites influenced by traffic showed to be influenced mainly by that source.

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Table 2: Mean concentrations of elements in PM_{10} and $PM_{2.5}$ at the four sites (ng m^{-3}).

	Tr_1				Tr_2				Bc_1				Bc_2			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Mg	111	54.3	45.2	40.7	127	83.6	43.5	29.0	24.3	13.3	22.3	9.59	30.4	21.6	17.3	7.95
Al	1350	941	493	405	1640	808	835	376	401	299	263	230	192	205	105	95.3
Si	2430	1600	886	657	2360	1170	1220	637	555	410	395	280	239	294	171	93.1
P	30.2	14.9	19.4	8.70	22.8	11.5	13.2	6.12	9.40	6.49	4.94	4.42	3.67	2.18	0.90	0.24
S	1270	416	1280	434	1010	490	866	357	790	331	847	307	563	566	648	517
Cl	631	405	432	417	957	969	253	230	49.6	19.4	29.1	6.58	567	512	73.4	95.8
K	834	461	632	374	625	246	432	211	166	97.5	147	65.8	70.2	48.3	40.4	36.3
Ca	889	555	275	195	623	336	296	139	89.6	79.7	51.0	41.3	74.9	63.7	28.5	25.4
Ti	50.8	27.4	19.7	12.6	43.5	19.1	25.9	15.1	13.1	9.53	9.88	5.50	8.60	7.41	5.64	5.51
V	14.7	11.0	5.18	3.10	15.5	8.95	9.76	8.42	3.79	3.18	1.27	0.39	1.13	0.46	0.56	0.21
Cr	8.69	3.81	4.55	2.59	6.08	3.41	3.05	2.23	7.64	9.04	1.49	0.39	2.79	0.53	0.72	0.59
Mn	13.4	5.83	11.4	10.2	7.97	3.95	6.63	3.86	3.93	1.92	2.59	2.14	4.38	1.02	1.58	1.34
Fe	1550	671	583	301	810	330	395	194	136	84.7	78.5	62.9	48.7	62.5	31.3	38.4
Ni	8.29	4.46	4.86	4.03	7.41	5.27	5.37	3.90	5.64	5.74	2.19	1.30	-	-	-	-
Cu	87.3	40.2	32.2	17.0	39.0	17.3	18.6	8.60	4.86	3.61	4.26	4.05	1.86	1.52	1.65	1.21
Zn	172	104	134	86.5	104	54.1	83.7	48.7	20.1	15.8	20.2	10.9	7.84	6.42	4.91	3.76
Pb	55.5	27.1	43.4	11.4	33.9	17.0	30.9	17.8	5.83	1.12	10.8	0.88	-	-	-	-

Results with 3 significant figures.

Background PM_{10} fraction was almost composed by fine particles; the fraction of fine particles was higher than usual, which means that to develop strategies to protect public health is fundamental.

At sites influenced by traffic emissions, particle metal contents were for PM_{10} 3-44 times higher and for $PM_{2.5}$ 3-27 times higher than at the backgrounds sites; traffic emissions increased greatly the levels of metals.

The sea salt spray plays an important role as particle source in coastal areas, influencing the concentrations and composition of PM, as well as the distribution of related elements between coarse and fine fractions; when influenced by sea salt PM_{10} increased by 46%, $PM_{2.5}/PM_{10}$ decreased by 26% and Cl in PM_{10} was 11 times higher.

Acknowledgements

The authors are grateful to Fundação Calouste Gulbenkian and to Fundação para Ciência e Tecnologia SFRH/BD/24228/2005 for the financial support for this work.

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