Artigo

AEROSOL PARTICLE SIZE DISTRIBUTIONS AT A TRAFFIC EXPOSED SITE AND AN URBAN BACKGROUND LOCATION IN OPORTO, PORTUGAL

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Aerosol size distributions from 6 to 700 nm were measured simultaneously at an urban background site and a roadside station in Oporto. The particle number concentration was higher at the traffic exposed site, where up to 90% of the size spectrum was dominated by the nucleation mode. Larger aerosol mode diameters were observed in the urban background site possibly due to the coagulation processes or uptake of gases during transport. Factor analysis has shown that road traffic and the neighbour stationary sources localised upwind affect the urban area thought intra-regional pollutant transport.

Keywords: particulate matter; number size distributions; traffic emissions.

INTRODUCTION

Several scientific studies have linked particulate matter (alone or in combination with other air pollutants) with a series of significant health problems, including premature death, respiratory related hospital admissions and emergency room visits, aggravated asthma, and acute respiratory symptoms, including worsening coughing and difficult or painful breathing, chronic bronchitis, and decreased lung function.[1-3] Diverse toxicological and epidemiological investigations have tried to associate health effects with particle features such as particle size and number concentration.[4-7] Ultrafine particles (diameter < 100 nm) have been shown to be more toxic and biologically active than the coarser sizes.[8,9] In addition to respiratory effects, ultrafine particles can yet be taken into the blood and lymph circulation of the human body and may, as a result, have a direct effect on the cardiovascular system.[10]

During the recent decade, differential mobility analyser (DMA) based aerosol number size measurements have been performed in various continental[11-20] and remote marine areas.[21-23] Vehicular emissions constitute one of the major emitters of ultrafine and fine particulate matter in urban environments, where air pollution plays an important role due to a high concentration of particle sources and a large population exposed to elevated particle concentrations.[14,15,20] To better characterise the urban particle sources and the fate of the particles in the atmosphere there is a need to perform field measurements. Since meteorological conditions and sources (e.g. composition of the vehicle fleet) can change appreciably from country to country, results reflect local characteristics and can not be generalised.[15] However, no such study involving sub-micrometer aerosols in Portuguese urban areas has been performed prior to the one presented here.

This study reports the results of a measuring campaign that was performed simultaneously at a roadside and at a background station in the urban area of Oporto, the second largest Portuguese city. Analysing comparatively the particle size distribution in both locations will provide an insight into particle transformation processes and into regulatory measures to reduce urban emissions.

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EXPERIMENTAL

Oporto has about 250000 residents and a population density of 6300 inhabitants per square kilometre. The city, part of a larger region of about 1.2 million inhabitants known as "Oporto Metropolitan Area" is located in the north of Portugal (41º 09'N, 8º 37'W) on the Douro river estuary on the coast of the Atlantic Ocean. Topographically this area is somewhat irregular, with a maximum altitude of about 400 m decreasing to the coast. The climate is North maritime, having warm and dry summers, mild and wet winters and spring and autumn as transition seasons. The annual average temperature is around 15 ºC, with less than 10 ºC between warmer and colder monthly averages. The annual air humidity is between 75 and 80%, and the total annual mean precipitation varies between 1000 and 1200 mm, about 40% of which in the winter season, and more than 100 days per year with precipitation equal to or higher than 1 mm. The most important stationary sources of atmospheric pollutants are an oil refinery, a petrochemical plant, a thermoelectric plant working with natural gas, a waste incineration unit, an international shipping port and an international airport (Figure 1S, Supplemental Material). Nevertheless, motor traffic is thought to be responsible for a significant amount of the pollutants emitted to the atmosphere.[24]

Two sampling sites were selected (Figure 1S, Supplemental Material), one at a roadside impacted directly by fresh car emissions ("Rotunda da Boavista" roadside site - RS) and the other in a residential area more distant from traffic emissions ("Rua do Melo" urban background site - UB). The sampling sites were chosen close to each other so that they were submitted to the same urban background atmosphere with differences in air composition only due to the fresher road emissions near the roadside sampling site. The roadside station is part of the city air pollution monitoring network. It is placed at about 3 m from the street, in the edge of a roundabout close to an intersection of highly traffic affected roads. The site was over the influence of about 60000 vehicles per day (ratio gasoline/diesel vehicles about 3 to 1) with a speed limit of 50 km h^{-1}. Besides light duty vehicles, the station was under the influence of heavy duty diesel passenger vehicles as there were some stopping's in the vicinities. Sampling took place on the roof of the station, at about 3 m height. The urban background site was sited at about 600 m to east from the roadside station and distant from traffic impacted roads. Sampling took place

at about 3 m height on the roof of a mobile monitoring station.

A 28 cm Hauke-type DMA[25] - built at Joint Research Centre, Ispra - using a re-circulating flow system[26] in connection with a TSI Model 3010 Condensation Particle Counter was used to measure particle numbers in 29 electrical mobility channels in the size range 6-700 nm. Corrections for 50% average channel efficiency, and for zero and multiple electron charging, were made.[27] No correction was made for the particle counter efficiency drop below 10-15 nm. It should be stressed that in differential mobility analysis, background noise and the lack of a calibration method cause difficulties of measuring freshly formed nucleation mode particles.[28] The monitoring program took place from June 30 to July 31, 2003. Besides the number size distribution of aerosol particles, the concentrations of NO and NO_2, CO, SO_2, O_3 and PM_{10} were simultaneously measured by using gas analysers from *Environnement S.A*. and *Thermo Scientific*. Some typical meteorological parameters such as temperature, pressure, wind speed, wind direction, humidity and solar radiation were also monitored. To fit the aerosol particle size distributions with the multi log-normal distribution function, the commercial algorithm DistFit™ (Chimera Technologies, USA) was used.

This program was part of a more extended research study that included the measurement of traffic counts, meteorological parameters, gaseous pollutants, aerosol mass and inorganic and organic aerosol composition, integrated into the EC funded project SAPPHIRE. Some of the SAPPHIRE results in Oporto have already been published.[29]

RESULTS AND DISCUSSION

The diurnal patterns for traffic are much smoother than their air quality counterparts (Figure 2S, Supplemental Material). This is almost certainly caused by the additional meteorological component of variation that affects the air quality measurements. In general, concentrations of traffic pollutants were higher during weekdays (Table 1), peaking during the rush hours in the morning (7:00-9:00) and late afternoon (20:00-22:00). It should be enhanced that the particle number concentrations presented a broader maximum, extending until noon, than the peaks of NO_x and CO. This may suggest that a fraction of PM can be produced through secondary reactions in the atmosphere.[30] At the roadside station, the Saturday profiles of hourly NO_x and CO concentrations presented a broad late morning into late afternoon shape, which overlap the weekday's patterns. This is a preferred day for shopping or short trips, representing a possible increase of individual transport. Since the background urban site registered a clear weekend reduction in concentrations (Table 1 and Figure 2S), the effect of NO_x and CO emissions thought intra-regional pollutant transport from neighbour stationary sources localised upwind, operating throughout the week, should be minor. The ratio between traffic counts and wind speed follows a similar daily profile when compared with that observed for NO_x concentrations. This correlation is based on the supposition that dilution and dispersion of local emissions are proportional to the wind speed. Given that it was found a better correlation between traffic counts/wind speed and NO_x than those between traffic counts/wind speed and CO, it seems that nitrogen oxides are mainly of local urban traffic origin, while carbon monoxide may be also related to biomass burning.[31]

Table 1. CO, NO_x, SO_2 and Particle Number average concentrations (Roadside / Urban Background values)

Day type	Particle concentrations (cm^{-3})	NO_x (ppb)	CO (ppm)	SO_2 (ppb)
Weekdays	31897 / 22219	45.8 / 19.4	0.37 / 0.25	9.2 / 6.2
Saturdays	31776 / 9866	48.5 / 2.48	0.48 / 0.16	5.4 / 0.88
Sundays	20630 / 16639	18.4 / 2.53	0.26 / 0.13	4.58 / 2.98

Two episodic patterns, in which particle number concentrations experienced an abrupt increase in the late morning and early afternoon, have been registered (Figure 3S, Supplemental Material). Since these boosts coincide with spikes of SO_2 and NW winds, the observed profiles most likely reflect the influence of the petrochemical complex located about 10 km northwest of the city centre. The increase in particle number concentration is chiefly observed for the smallest sizes. Sulphur dioxide and hydrocarbons emitted by the petrochemical refinery are probably precursors of these ultrafine particles.[30] It has been assumed that the principal gas-phase species involved in atmospheric nucleation is H_2SO_4, and that, if particle formation occurs, it does so via binary nucleation of H_2SO_4-H_2O. Also, it has been suggested that NH_3, an ubiquitous atmospheric component, augments nucleation rates, and thus ternary stable clusters (H_2SO_4-H_2O-NH_3) are formed.[30] New particle formation through nucleation may also take place after oxidation of volatile hydrocarbons. When nucleation does occur, the new particles grow by condensation and self-coagulation. Under polluted, urban type conditions, this growth can occur within few hours.[30]

The highest levels of ultrafine particle number concentrations were generally observed nearby the busy roundabout of Boavista in the city centre. Total number concentration (N) at this traffic exposed site varied approximately between 3600 and 107000 cm^{-3}, averaging 30500 cm^{-3}. The urban background station registered values from about 2000 to 105000 cm^{-3} and an average of 17500 cm^{-3}. These levels are comparable with those reported for the Helsinki area[32] and very far from the observed concentrations (200-2000 cm^{-3}) in continental Antarctica.[12] However, in a bigger metropolitan area like New Delhi, the total concentration can reach values of 280000 cm^{-3}.[33] It was observed a decreasing number concentration of particles with increasing distance from source, i.e. from the traffic exposed site to the urban background station. The decrease in number fraction results from mixing processes occurring during the aerosol transport. Because of intensive solar radiation, which causes a stronger destabilisation of air and thus a stronger convection and resulting mixing, this process is more intensive in summer days than in winter.[19]

All the particle number distributions can usually be fitted using two to four lognormal modes:[14] an accumulation mode (particle mean diameter > 90 nm), an Aitken mode (20-100 nm) and up to two nucleation modes (< 20 nm). The modal structure of the particle number size distributions depends on the different ambient conditions, source emission strengths and mixing between the background and local emissions of aerosol particles. The particle number size distribution that is directly influenced by traffic emissions was characterised by small geometric diameters. Here, 60 to 90% of the modal structures were dominated by the nucleation mode. During the 22:00-8:00 period, at the roadside station, the nucleation mode consisted of two submodes. The first one (< 10 nm) represents the fresh nucleation submode 1, which is produced by direct traffic emissions and gas to particle conversion. The aged nucleation submode 2 (10-20 nm) corresponds to particles that are formed in the atmosphere but are not of very recent origin.[12] During traffic rush hours in the morning and in the afternoon, the maximum in the nucleation mode was found for particles < 5 nm, whereas the aged submode was inexistent or relatively irrelevant (Figure 4S, Supplemental Material). On the other hand, the urban background size distributions were characterised by a nucleation mode dominated by geometric mean diameters in the range 15-20 (submode 2) during the 18:00-10:00 period, whilst the daytime presented submodes 1 and 2. However, in this receptor site, the geometric mean diameters of nucleation particles were a bit shifted to larges sizes.

Volume spectra were derived from the number size distributions assuming spherical particles (Figure 1). In spite of contributing for the most part to the number concentration, particularly during the rush hours at the traffic exposed site, the volume concentration of the smallest particle fraction (nucleation mode) was negligible. Particle volume is a proxy measure of particle mass and, contrasting with particle number, it is not influenced by coagulation and is less influenced by nucleation.[34] Moreover, particles added by traffic are much smaller than residential background particles, thus, they have a higher influence on particle number than volume. The increase in particle volume or mass, during the morning traffic peak, was consistent with suppositions of higher concentrations under congested conditions. Less variation was observed in particle volume compared to particle number size distributions.

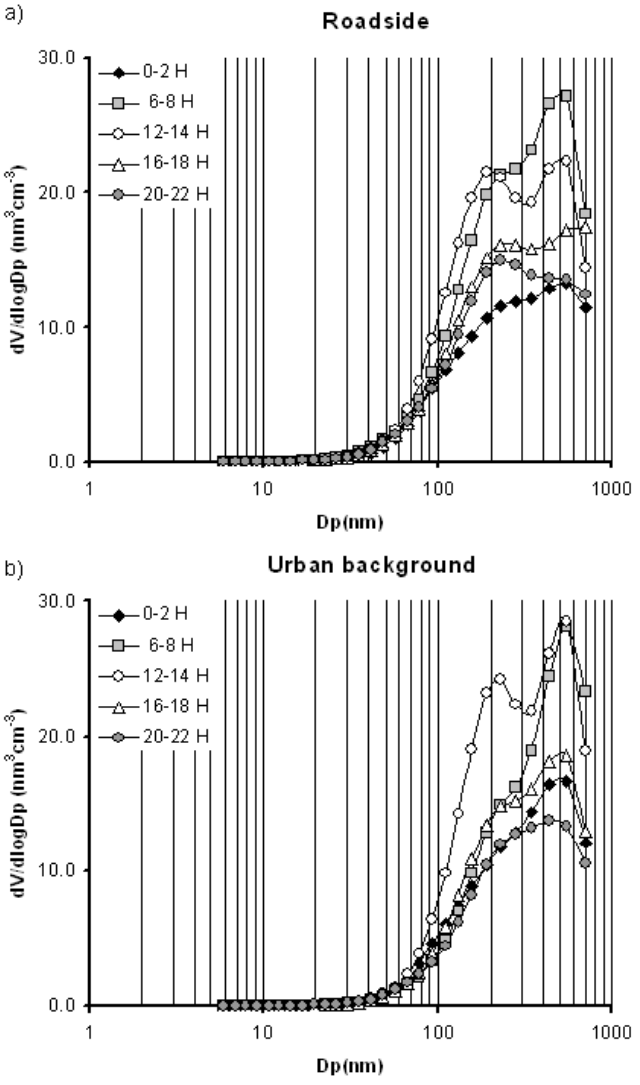

Figure 1. *Average particle volume distributions at the roadside and urban background stations during weekday 2 h periods*

The Aitken mode can be explained by coagulation and condensational growth of nucleation mode particles, whereas the accumulation mode is a more aged aerosol, advected with the regional scale circulation and formed by cloud processing and condensation.[30] Aitken mode particles are of great interest as they are intermediates between recently formed nucleation mode particles and particles able to act as cloud condensation nuclei.[12] The growth of the recently formed ultrafine particles results in a shift of the maximum diameter of the number size distribution. Therefore, during air mass transport from a traffic exposed site to the urban background, several processes may influence the number size distributions, such as coagulation, condensational growth, plume dilution and vertical mixing.[14] Particle scavenging may occur when large numbers of fine and coarse particles provide surface area onto which ultrafine particles diffuse and readily aggregate. Reductions in the emissions of these larger particles could reduce the available surface area and therefore increase the atmospheric residence time of ultrafine particles.[35] Second, there has been an influx of vehicles employing modern engine technology in Portugal. It has been hypothesised that improved efficiencies associated with modern combustion engines result in more complete combustion and larger proportions of particles < 30 nm. Increases in the number of diesel vehicles in Oporto could also contribute to increased ultrafine particle counts. The mean diameter of diesel engine emissions can be as small as 20 nm. The particulate soot emissions of heavy-duty engines are modal with geometric mean diameters between 60 and 80 nm. In laboratory tests, Hussein *et al* (and references therein)[14] observed that gasoline vehicle exhausts have mean diameters in the range 40-80 nm.

A striking feature of the data is the continued presence of a substantial concentration of emission mode particles, which suggests a persistent source of these aerosols that then grew by condensation and coagulation to produce the Aitken mode. At the roadside station, the daytime size distributions presented a minor mode at 30-50 nm, while during the nocturnal period the modal structure changed to 50-70 nm. The increase in aerosol geometric mean diameters observed during the night is probably driven by the growth of hygroscopic constituents of ultrafine PM such as NO_3^- and SO_4^{2-}.[36] At the background site, the Aitken and accumulation modes are merged into a broad mode, presenting geometric mean diameters generally > 70 nm. The shift in size distribution at the background site could be due to advection of vapour species and consequent formation of secondary organic aerosols after in situ photochemistry in a short time scale and transport of aged aerosols originally emitted at traffic exposed areas.[36] Thus, particle removal processes (e.g. deposition and coagulation), which are more efficient for particle sizes < 20 nm, and condensational growth are possible mechanisms for the reduction in particle number and for the shift to the larger diameters. Sometimes, newly formed particles were detected after sunrise, when gas phase photochemical reactions are activated by radiation, converting gaseous precursors into less volatile compounds, and vertical turbulent mixing is facilitated. Following their formation, the ultrafine particles grow into the Aitken mode particles by condensation of low-volatility vapours, which in turn keep on growing. The accumulation mode particles are believed to have formed via in-cloud processing of Aitken mode particles.[30]

Multivariate data analysis methods, like PCA (Principal Component Analysis), are powerful tools to handle large amounts of information, for the development of source-receptor relationships. The main application of PCA in data processing is to reduce the number of original variables to a simple set such that the maximum amount of the variance contained in the original variables is retained by a small number of principal components. Through an iterative procedure PCA is capable of deriving a number of orthogonal axes that correspond exactly to the number of obtained principal components. In a further refinement, the axes can be subject to orthogonal rotations in order to clarify their physical meaning. The PCA technique has been widely used in deducing source composition from air quality data and is well documented in the related literature.[37-39]

PCA with varimax normalised rotation (SPSS, v. 16.0) was applied separately to the roadside and urban background data sets of the half-hour average concentrations, for the 29 classes of dN/dlogDp obtained on weekdays, in order to maximise (or minimise)

the values of the loading factors of each variable analysed in relation to each rotated principal component. Four components were extracted, which encompass approximately 96% of the variability of the 29 parameters, at both sites. The explained fractions of variance (factor loadings) of dN/dlogDp are shown in Figure 2. In addition, PCA was performed separately, at the roadside and background locations, on the 29 classes of dN/dlogDp, together with 13 additional parameters (individual runs for each parameter) including concentrations of integrated particle number (N), surface area, volume, gaseous pollutants, meteorological variables and traffic density. The explained variance for the four-dimensional subspace associated with the 13 additional variables is given in Table 2.

The contribution of each source group to the particle size distributions at RS and UB was quantitatively assessed by means of multilinear regression analysis (MLRA). MLRA was applied to the experimental data, using as dependent variable the aerosol number concentration N and as independent variables the principal component factor scores. For uniformity reasons in PC definitions, PCA was performed again on a unique matrix involving measurements at RS and UB. As the factor scores obtained from the PCA are normalised, with mean zero and standard deviation equal to unity, the true zero for each factor score was calculated by introducing an artificial sample with concentrations equal to zero for all variables. The factor scores obtained for this artificial sample was subtracted from the factor scores of each one of the other samples. Results from MLRA, in the form of absolute factor contributions, are given in Figure 3, as average values for each half hour, along the day, during weekdays, at RS and UB sites, using only parallel measurements.

The first factor shows high loadings on nucleation mode particle, does not correlate with other gas-phase measurements and reveals a strong correlation with ground level solar radiation (UV – Table 2). The absolute scores peak during the day, a further indication that the production of nucleation mode particles is photochemically driven. The absolute PC1 values increase immediately in early morning at the roadside station and are maintained at relative constant high levels until evening at this site. On the other hand, PC1 absolute score has a strong peak at the beginning of the afternoon, decreasing to the evening and night, at the urban background site. The first factor also correlates with the wind speed, since this meteorological parameter favours the rapid transport of emissions not allowing enough time for particles to grow in size. It is associated with continental air masses (cos WindDir), which contain higher

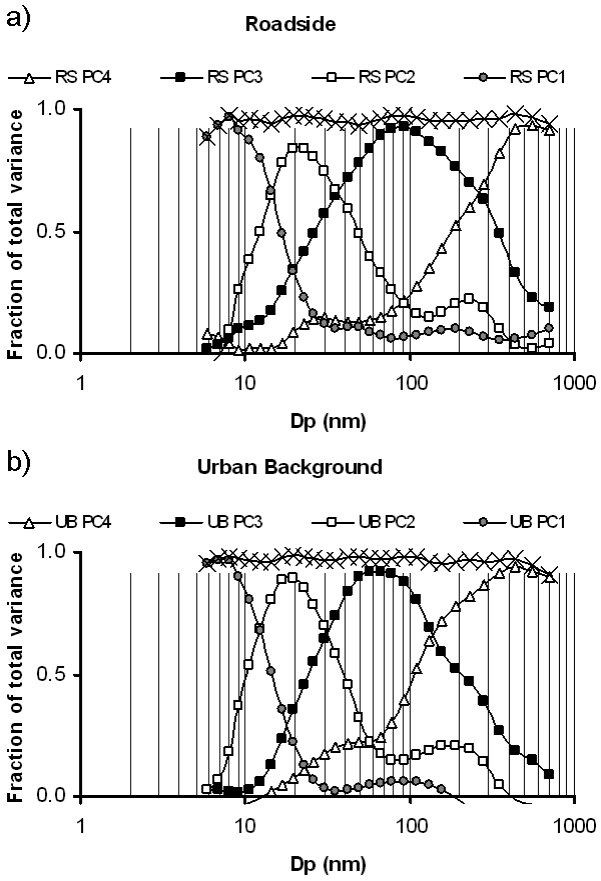

Figure 2. *Squared eingenvector loadings (explained fraction of variance) of the particle size spectrum variables (dN/dlogDp)*

Table 2. Component loadings of PCA and communalities (sum of the squared loadings) calculated with particle size characteristics, gaseous pollutants, meteorological parameters and traffic density

	RS					UB				
	PC1	PC2	PC3	PC4	Communality	PC1	PC2	PC3	PC4	Communality
Number concentration	0.65	0.53	0.51	0.19	1.00	0.60	0.54	0.54	0.23	1.00
Surface area	0.09	0.25	0.74	0.61	1.00	0.01	0.19	0.56	0.80	1.00
Volume	0.07	0.16	0.56	0.81	1.00	-0.05	0.11	0.37	0.92	1.00
CO	0.15	0.62	0.13	0.49	0.81	-0.18	0.05	0.54	0.53	0.79
NO_x	0.20	0.65	0.21	0.43	0.83	0.03	0.13	0.75	0.42	0.87
SO_2	0.20	0.13	0.71	-0.15	0.77	0.31	0.09	0.55	0.37	0.74
RH	-0.31	0.19	-0.36	0.49	0.71	-0.46	-0.32	-0.39	0.04	0.69
Temperature	0.28	-0.17	0.51	-0.27	0.67	0.32	0.34	0.40	0.02	0.62
UV	0.56	-0.30	0.24	-0.09	0.69	0.59	0.09	-0.04	0.20	0.63
WindSpeed	0.40	-0.41	-0.03	-0.40	0.70	0.51	0.01	-0.08	-0.18	0.55
sin WindDir	-0.39	0.47	0.00	0.06	0.61	-0.43	0.10	0.17	-0.02	0.47
cos WindDir	0.26	-0.41	-0.03	-0.50	0.70	0.50	0.02	0.06	-0.18	0.53
Traffic counts	0.36	-0.06	0.28	-0.13	0.48	-0.25	0.03	-0.16	-0.23	0.38

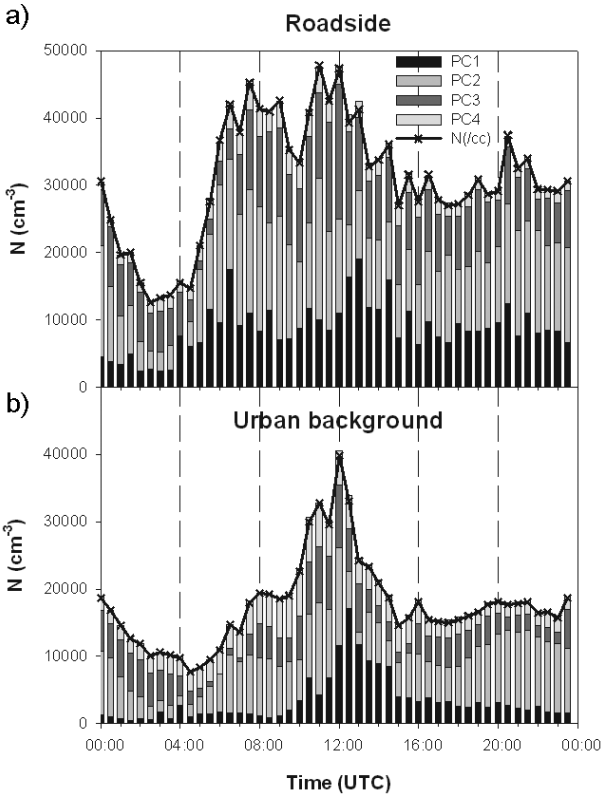

Figure 3. *Half-hour average daily distributions of PC1-PC4 source contributions to the total number of aerosol concentrations, N, at the roadside and urban background sites*

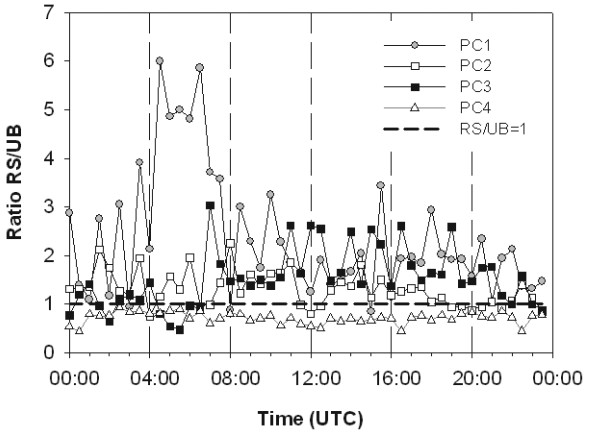

Figure 4. *Median values of RS/UB ratios of half-hour PC1-PC4 source contributions, normalised through division by the total aerosol volume concentrations, as daily profiles, during weekdays*

levels of precursors compared to clean air from the Atlantic, and is anticorrelated with northern winds (sin WindDir), given that the city centre is southly oriented.

The data sets present a second factor that has higher positive loadings on Aitken than on accumulation mode particles. For the measurements taken at the roadside station, this factor also loads on CO and NO_x and likely corresponds to the general direct emissions from traffic combustion.

The third factor is connected to Aitken/accumulation mode particles, presenting simultaneously high loadings of SO_2. This factor probably represents intra-regional pollutant transport of secondary particulate sulphur and also indicates growth by coagulation to larger spectra sizes.

The fourth factor represents a more aged aerosol, connected to the roadside traffic that is advected with the regional scale circulation. As the air masses are advected away from the traffic exposed site, the small size modes disappear likely due to a combination of the effect of coagulation, condensation (which would result in particle growth) and dry deposition.

The ratio RS/UB for each absolute PC score (normalised by dividing by the aerosol volume concentration to compensate for dilution of air when it is transported from roadside to urban background) permits a further insight into the origins of the aerosol size fractions. Results of the median half-hour values of RS/UB normalised absolute factor scores, taken in parallel during weekdays, are present in Figure 4. From the figure it is possible to conclude that, for most of the PC fractions, the RS/UB ratio does not appreciably changes, in average, along the day. This is an indication of similar sources of these PC at both sites. The RS/UB ratios are higher than unity for PC1-PC3, and lower for PC4, probably as a result of coagulation/condensation processes, that transfer mass from smaller to larger sizes during air transport away from fresh roadside emissions. The RS/UB ratios for PC1 peak to values much higher than unity at the early morning hours when traffic exhibits higher intensity and the atmospheric dispersion is weak. Concurrently, it is noticed a relative decrease of the RS/UB ratio of PC3 particles as a possible result of mass transfer between particle size classes by coagulation at the polluted roadside atmosphere. The ratio increase of PC1 during morning rush hours shows that the nucleation mode, at least at the RS, is traffic originated from fresh exhaust emissions. These, add to the photochemical formation processes revealing as a second peak at early afternoon that is more evident at UB.

CONCLUSIONS

The highest levels of ultrafine particle number concentrations were generally observed nearby the busy roundabout of Boavista in the city centre. The particle number size distribution that is directly influenced by traffic emissions was characterised by small geometric diameters, representing a fresh nucleation submode 1 (<10 nm), produced by direct traffic emissions and gas to particle conversion and an aged nucleation submode 2 (10-20 nm). Globally, the nucleation mode constituted 60 to 90% of the particle number concentrations over the size spectrum. The growth of the recently formed ultrafine particles results in a shift of the maximum diameter of the number size distribution to the Aitken nano-size range (< 50 nm). Coagulation and condensational growth during transport from the traffic exposed to the urban background site generates an Aitken and accumulation merged modes, presenting geometric mean diameters generally > 70 nm.

The distributions attributable to the diesel particles present smaller sizes than those generated by petrol vehicles. Besides the predominant contribution of traffic, the particle size number distributions are also affected by secondary formation processes, including sulphur aerosols generated from precursors emitted by the upwind petrochemical refinery.

Taking into account the allegedly harmful health effects of ultrafine particles and that scattering and absorption of light depend on the aerosol size, the results of the here reported measuring campaign could represent a basis for both modelling and epidemiological studies. In conjunction with additional monitoring programs and more valuable data, this study could also constitute the starting point to sustain traffic management policies and the implementation of potential emission reduction measures.

SUPPLEMENTAL MATERIAL

Additional information concerning the sampling locations, diurnal profiles of pollutants, patterns of pollution episodes and particle number size distributions on weekdays is available free of charge at http://quimicanova.sbq.org.br, as a PDF file.

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