AEROSOLS SESSIONS

CONCENTRATIONS OF PM10, PM2.5 AND PM1 IN URBAN AND RURAL SWITZERLAND - ANNUAL AND SEASONAL TRENDS AND SPATIAL VARIABILITY

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CHEMICAL CHARACTERISATION OF PM_{10} AND $PM_{2.5}$ MACROCOMPONENTS IN ITALY

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ELEMENT SOLUBILITY AND SIZE DISTRIBUTION OF AIRBORNE PARTICULATE MATTER IN THE LAZIO REGION (ITALY)

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RAPID EVOLUTION OF SIZE DISTRIBUTION AND CHEMICAL COMPOSITION OF INDIVIDUAL URBAN PARTICLES UNDER VARIABLE LOCAL METEOROLOGICAL CONDITIONS

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THE MEASURED SIZE FRACTIONATED AEROSOL NUMBER CONCENTRATIONS NEAR A MAJOR ROAD IN HELSINKI

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THE INFLUENCE OF TRAFFIC AND BUS DENSITY ON ULTRAFINE PARTICLE CONCENTRATIONS ON BUSES IN MANCHESTER, UK: A MEASUREMENT STUDY.

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COMPARING URBAN PARTICLE EMISSION FLUXES MEASURED ON THE BT TOWER (LONDON) WITH MEASUREMENTS FROM MANCHESTER AND EDINBURGH

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PM10, PM2.5-BOUND PAHS AND HEAVY METALS IN AN INDUSTRIAL AREA IN NORTHERN GREECE

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POLAR ORGANIC COMPOUNDS IN THE URBAN ATMOSPHERE OF TWO LARGE CITIES FROM THE NORTH AND SOUTH OF EUROPE

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DISPERSION OF FINE AND ULTRAFINE PARTICLES NEAR AN URBAN MOTORWAY: COMBINING MODELLING AND EXPERIMENTS

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ULTRA-FINE PARTICLES FROM TYRE AND PAVEMENT INTERACTION

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PARTICULATE AIR POLLUTION IN TRANSPORT MICROENVIRONMENTS

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IMPACT OF RESIDENTIAL WOOD COMBUSTION ON CARBONACEOUS AEROSOLS

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IMPACT OF A VEGETATION-COVERED URBAN BROWNFIELD ON AMBIENT PARTICLE CONCENTRATION

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PM_{10}, $PM_{2.5}$ AND BLACK CARBON MEASUREMENTS IN RIGA

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CONCENTRATIONS OF PM10, PM2.5 AND PM1 IN URBAN AND RURAL SWITZERLAND - ANNUAL AND SEASONAL TRENDS AND SPATIAL VARIABILITY

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ABSTRACT

Long-term parallel measurements of PM10, PM2.5 and PM1 have been performed at several sites with different exposition characteristics within the Swiss National Monitoring Network (NABEL).

At all sites the concentrations of the different size fractions were highly correlated on the level of daily values. Unless strong and variable local sources of coarse particles are present, parallel measurements of PM1, PM2.5 and PM10 seem to provide only limited additional information. Therefore, parallel measurements can be restricted to a few carefully selected sites in a monitoring network.

The comparison of daily PM values from different sites often also show quite high correlation. The data analysis indicates primarily meteorological reasons. Even distant sites show good correlations if they are situated in an area with similar meteorological conditions. However, the correlations drop drastically if this is not the case i.e. if the sites are divided by high topographical obstacles (Alps) or by an inversion layer.

1. INTRODUCTION

Measurements of PM10, which is considered to represent the thoracic fraction of the ambient particles (ISO 1995), have been performed within the Swiss National Monitoring Network (NABEL) already since 1997. Due to the increasing public interest for the finer alveolar fraction (PM2.5), the measurement programme of the network has been extended to PM2.5 measurements at seven sites in 1998. A preliminary comparison of these parallel measurements has been published earlier (Gehrig and Buchmann 2003). From 2003 also PM1 measurements were added to the measurement programme. This fraction provides, better than PM2.5, information on the particle sources, as PM1 represents in reasonable approximation combustion particles and secondary aerosol, while PM10-1 can be attributed to mechanically produced and geogenic particles. Long-term data sets of parallel measurements of the different PM fractions are still scarce if not lacking for Europe. Therefore, the Swiss data set forms a unique data basis for investigating the temporal and spatial behaviour of PM1 and PM2.5 compared to PM10. It includes meanwhile eight years of parallel PM2.5 and PM10 data and three years of parallel PM1 and PM10 data at various sites representing different important situations with respect to human PM exposure. This paper gives an overview of the measured concentrations and compares the temporal and spatial behaviour of the different size fractions.

2 MEASUREMENT PROGRAMME AND METHODS

All particle samplings were conducted with high-volume-samplers Digitel DA 80 (VDI 1996). The sampling inlet is operated at a flow of 30 m^3/h and meets the requirements of EN 12341 for reference equivalency (UMEG 1999). For PM2.5 and PM1 the same kind of instrument was used, but with correspondingly adapted sampling heads. Glass fibre filters of the type Ederol 227/1/60 were used for particle collection. The measurement uncertainty for the PM10 measurements has been quantified from collocated parallel measurements to be 10% (95% confidence interval for single daily values) in the concentration range 10–30 $\mu g/m^3$. The detection limit was determined from the standard deviation of field blanks to be 1 $\mu g/m^3$. Because the only difference between the applied method for PM10 and PM2.5 or PM1 is the number and diameter of the nozzles in the sampling heads, the same measurement uncertainty can be assumed for the PM2.5 and PM1 measurements.

3 RESULTS AND DISCUSSION

3.1 COMPARISON OF PM10, PM2.5 AND PM1 CONCENTRATIONS

Figure 1 gives an overview over the annual means of the concentrations of PM10, PM2.5 and PM1. From Table 1 it can be seen that the variability of the long-term mean PM2.5/PM10 ratios as well as the PM1/PM10 ratios is very low. The only exception is the street canyon site Bern, where the local traffic forms a considerable source of coarse dust, which results in clearly lower ratios.

Table 2 shows, that there is a high correlation of PM10 with PM2.5 at all sites. With the exceptions of the still high correlations at Bern (r=0.92) and Chaumont (r=0.91), all correlations were 0.95 or higher. The lower correlation at Bern reveals that the traffic induced coarse particles from abrasion and resuspension contained in PM10 follow different temporal emission patterns than PM2.5 and PM1, which are dominated by exhaust pipe emissions. This is plausible because mechanically produced particles, and in particular resuspension, depend not only on the vehicle frequency but also on the condition of the road surface (e.g. clean/dirty, wet/ dry). At the site of Chaumont, the lower correlation can be explained with the generally lower concentrations and the correspondingly higher relative measurement uncertainties.

The correlation coefficients between PM1 and PM10 are similarly high. For the reasons already explained above, also here with somewhat lower values at Bern and Chaumont.

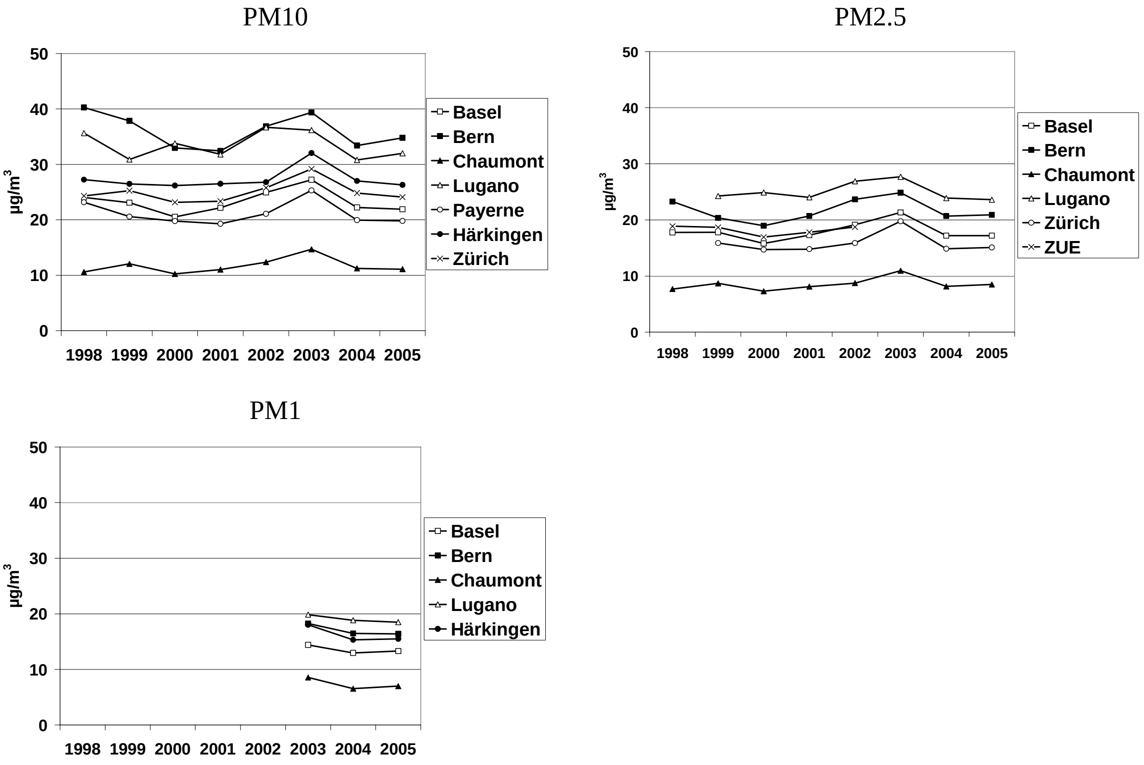

Fig. 1: Annual mean concentrations of PM10, PM2.5 and PM1 .

Tab. 1: Mean PM2.5/PM10 and PM1/PM10 ratios of the daily values

	PM2.5/PM10	PM1/PM10
Basel (Suburban)	0.76	0.60
Lugano (Urban background)	0.74	0.59
Zürich (Urban background)	0.75	
Payerne (Rural, 490 m a.s.l.)	0.75	
Chaumont (Rural, 1140 m a.s.l.)	0.75	0.63
Härkingen (Motorway)		0.59
Bern (Kerbside, street canyon)	0.61	0.49

Tab. 2: Pearson correlation coefficient (r) for PM10 vs PM2.5 and PM10 vs PM1 (daily values).

	PM2.5	PM1
Basel (Suburban)	0.95	0.92
Lugano (Urban background)	0.95	0.92
Zürich (Urban background)	0.97	
Payerne (Rural, 490 m a.s.l.)	0.97	
Chaumont (Rural, 1140 m a.s.l.)	0.91	0.89
Härkingen (Motorway)		0.92
Bern (Kerbside, street canyon)	0.92	0.88

3.2 SPATIAL VARIABILITY OF PM10, PM2.5 AND PM1 CONCENTRATIONS

Interesting information about the spatial variability of PM concentrations can be obtained from an analysis of the correlations of the PM concentration data between the different sites of the NABEL network. Table 3 shows the Pearson correlation coefficients r for the comparison of the daily values of different sites. It can be seen that the correlation coefficients for all mass fractions (PM10, PM2.5 and PM1) between the sites situated north of the Alps at moderate altitude (Basel, Bern, Payerne and Härkingen) are quite high, i.e. in the range of 0.84-0.92. This indicates that the variability of the daily concentrations is not primarily influenced by local events and sources, but are rather determined by meteorological conditions.

Chaumont, which is often (and in particular during wintertime) situated above the inversion layer shows much lower correlations. That indeed inversions are the reason for this can be shown by a separate evaluation of the correlation coefficients of this site with the nearby rural site of Payerne (distance 25km, difference in altitude 650m) for winter (0.56) and summer (0.91).

Lugano, the only site situated south of the Alps has (not surprisingly) low correlation with the other sites. This shows clearly that the high mountains of the Alps form an efficient obstacle for the distribution and homogenisation of fine particles.

Tab. 3: Pearson correlation coefficients (r) of the daily values of PM10, PM2.5 and PM1 measured simultaneously at different sites (2003-2005).

PM10

	Basel	Bern	Chaumont	Lugano	Payerne
Basel	1.00				
Bern	0.84	1.00			
Chaumont	0.60	0.45	1.00		
Lugano	0.48	0.49	0.31	1.00	
Payerne	0.89	0.88	0.60	0.51	1.00
Härkingen	0.88	0.89	0.47	0.50	0.89

PM2.5

	Basel	Bern	Chaumont	Lugano
Basel	1.00			
Bern	0.89	1.00		
Chaumont	0.55	0.52	1.00	
Lugano	0.51	0.52	0.27	1.00
Payerne	0.90	0.92	0.58	0.52

PM1

	Basel	Bern	Chaumont	Lugano
Basel	1.00			
Bern	0.85	1.00		
Chaumont	0.55	0.46	1.00	
Lugano	0.52	0.55	0.22	1.00
Härkingen	0.89	0.90	0.48	0.53

4 CONCLUSIONS

From the presented analysis of long-term parallel measurements of PM1, PM2.5 and PM10 concentrations in Switzerland the following conclusions can be drawn:

- At all sites the concentrations of the different size fractions were highly correlated on the level of daily values. Unless strong and variable local sources of coarse particles are present, parallel measurements of PM1, PM2.5 and PM10 provide only limited additional information. In order to make efficient use of the financial and personal resources, such parallel measurements can be restricted to a few carefully selected sites in a monitoring network.
- Also the comparison of daily PM values from different sites often show quite high correlation. The analysis of the Swiss data indicates that this has primarily meteorological reasons. Even distant sites show good correlations if they are situated in an area with similar meteorological conditions. However, the correlations drop drastically if this is not the case i.e. if the sites are divided by high topographical obstacles (Alps) or by an inversion layer. Particle transport modelling shows clearly the relevance of long-range transport of fine particles though robust quantification still seems to be difficult (EMEP 2004). Therefore, high correlations of PM at even distant sites could be expected due to a relatively homogenous distribution of long-range transported PM over large areas. However, the high daily variability of the PM concentrations can not be explained with long-range transport because on a regional scale the daily variability of the PM emissions is quite small. In fact, no matter whether the particles are locally emitted or long-range transported, it is mainly the meteorology (wind speeds, turbulence, vertical mixing, inversions etc.) which causes more or less effective dilution of the emitted pollutants and thus the daily fluctuation of the concentrations.

5 ACKNOWLEDGEMENTS

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6 REFERENCES

EMEP (2004). Transboundary particulate matter in Europe; Status Report 4/2004 (http://www.nilu.no/projects/ccc/reports.html).

Gehrig, R. and Buchmann, B. (2003). Characterising seasonal variations and spatial distribution of ambient PM10 and PM2.5 concentrations based on long-term Swiss monitoring data. Atmos. Environ. 37(19): 2571-2580.

ISO (1995). Air quality - Particle size fraction definitions for health related sampling. ISO 7708.

UMEG (1999). Prüfung des DIGITEL Staubsammlers DHA80 mit PM10-Einlass nach prEN 12341, UMEG Karlsruhe**:** 87.

VDI (1996). Messen von Partikeln - Messen der Massenkonzen-tration (Immission) - Filterverfahren - Filterwechsler Digitel DHA-80. VDI 2463, Blatt 11.

CHEMICAL CHARACTERISATION OF PM_{10} AND $PM_{2.5}$ MACROCOMPONENTS IN ITALY

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ABSTRACT

A method for determining the chemical composition of PM was applied to several field studies carried out in Central Italy. The method is able to take into account the compounds typically constituting more than 1% of the PM mass and is generally able to reconstruct more than 90% of the collected mass.

The results allowed us to highlight the quantitative relevance of secondary compounds: these constitute three quarter of regional background PM_{10} (20-25 ug/m^3 over about 30 ug/m^3) and 40-50% of urban PM_{10}; in urban locations primary pollution accounts for another 30% of PM_{10}.

The study of the mixing properties of the lower boundary layer showed that atmospheric dilution plays a major role in determining pollution events. Finally, for Central and Southern Italy, the frequency of natural events (sea-salt aerosol and, mainly, desert dust intrusion) and their influence on the exceedances of EU limit values for PM were pointed out.

1. INTRODUCTION

A comprehensive interpretation of pollution phenomena due to atmospheric particles requires the integration of many different approaches, ranging from the analysis of the meteorological situation (and especially the dilution properties of the lower boundary layer) and reconstruction of the back-trajectories of the air masses, to the determination of the number of particles in the different size fractions, analysis of the shape and composition of the single particles and apportionment of the main sources. One of the most important approaches, however, is the chemical determination of the main components (typically more than 1% of the total mass) of the atmospheric particulate matter. Mass closure studies for atmospheric particles are reported in: Perrino et al., 2006, Querol et al, 2004, Putaud et al., 2004, Harrison et al, 2003, Marcazzan et al., 2001.

We report here the results obtained in the reconstruction of the chemical composition of particulate matter during some field studies carried out in Central Italy. The joined use of this method and of the other approaches described above allowed us to obtain reliable results in the interpretation of particulate pollution phenomena in this geographic area.

2. METHODOLOGY

The sampling procedure involves the collection of PM_{10} and $PM_{2.5}$ fractions on both a Teflon and a quartz filter membranes and the determination of their mass concentration, on Teflon filters, by the gravimetric procedure or by the beta attenuation method. After the sampling, quartz filters are analysed for their elemental carbon and organic carbon content (EC/OC) by means of a thermo-optical analyser (*OCEC Carbon Aerosol Analyser*, Sunset Laboratory, OR-U.S.A.). Teflon filters are analysed for their metal content (Al, Si, Fe, Na, K, Mg, Ca, S) by energy-dispersion X-ray fluorescence (ED-XRF, *X-Lab 2000*, SPECTRO), then extracted in a water solution and analysed for their anionic (Cl^-, NO_3^-, $SO_4^=$) and cationic (Na^+, NH^{4+}, K^+, Mg^{++}, Ca^{++}) content by ion chromatography (IC, *DX100*, DIONEX). By following this procedure, the main component of the collected particulate material can be identified and quantified and a general picture of the aerosol composition can be obtained. The scheme of the procedure is reported in Figure 1; a more detailed description is reported in Perrino et al. (2006).

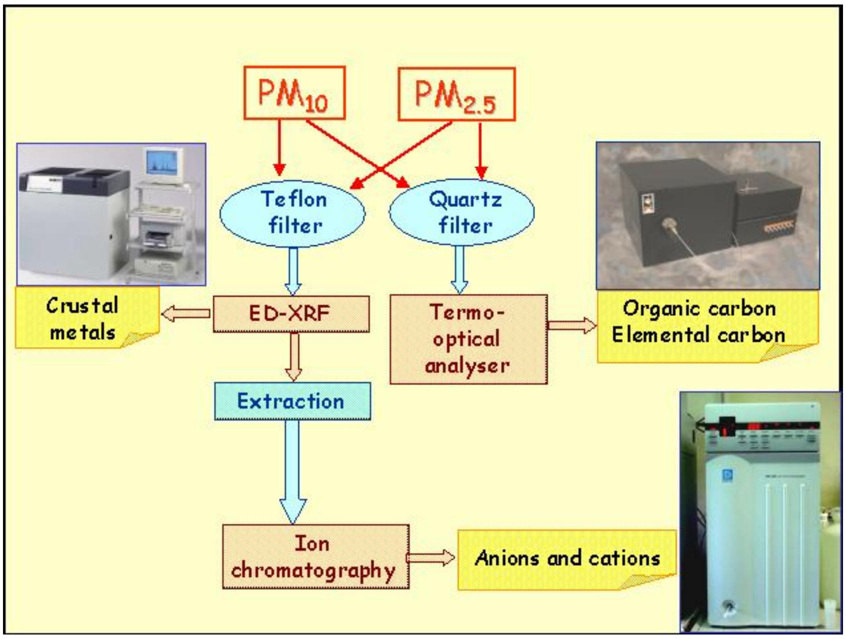

Figure 1: Scheme of the sampling and analysis procedure for the reconstruction of PM chemical composition.

The mixing properties of the

lower atmosphere were studied by means of a natural radioactivity monitor, operating on a 1-h basis (*PBL Mixing Monitor*, FAI Instruments, Fontenuova, RM-I). Natural radioactivity can be considered as a good tracer of the dilution properties of the lower boundary layer and its measurement constitutes a reliable tool for uncoupling the variations in pollutant concentration which are due to changes in the emission rate from those due to the increase of the air volume available for dilution (Kataoka et al. (2001), Perrino et al. (2001), Sesana et al. (2003)). The size distribution of atmospheric particles in the range 0.3 – 10 μm was continuously determined by means of a laser optical particle counter.

Samplings were carried out in Rome and in Montelibretti, a semi-rural area about 30 km from the centre of Rome.

3. RESULTS AND DISCUSSION

The main chemical components of PM (ions, metals and EC/OC) have been grouped into four classes: crustal matter (calculated as the sum of Al, Si, Fe, K, Ca, Mg and Na oxides - Chan et al., 1997), sea-salt aerosol (calculated from Na^+ and Cl^-), primary anthropogenic pollutants (calculated as EC plus an equivalent amount of OC – Viidanoja et al., 2002) and secondary compounds. These have been calculated as the sum of nitrate, sulphate, ammonium and the remaining amount of OC multiplied by a factor that takes into account the non-carbon content of organic molecules; this factor ranges from 1.6 in traffic locations to 2.1 in background sites (Turpin and Lim, 2001). The time pattern of the mass concentration of the four groups of components at a traffic station in Rome during 2005 is reported in Figure 2.

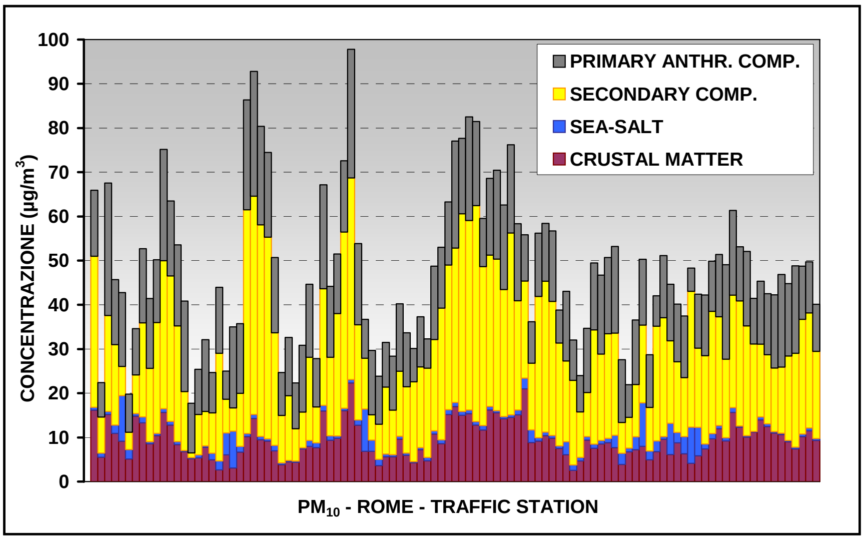

Figure 2: Reconstruction of the chemical composition of PM_{10} at a traffic station in Rome

The data show that PM_{10} concentrations higher than the EU yearly limit value of 40 μg/m^3 and of the daily limit value of 50 μg/m^3 are very often detected and that most of the PM mass is always constituted by secondary compounds.

Comparing the yearly average composition of PM_{10} at the traffic station with the values recorded at the urban background station of Rome, at the semi-rural station of Montelibretti and at the regional background station, we obtain the data reported in Figure 3, where organic and inorganic secondary components are separately shown. It is apparent that the concentration of secondary compounds is homogeneous over the whole region, while the concentration of primary anthropogenic components steadily decreases when moving from the traffic station towards the urban background, the semi-rural and the regional background station. Crustal components are slightly lower at the regional background station with respect to the other sites, probably because of the lower impact of traffic-generated re-suspension of

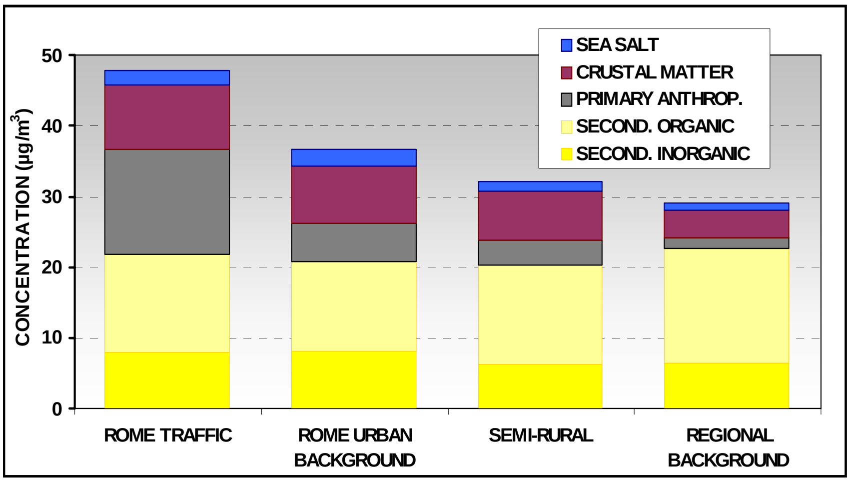

Figure 3: Chemical composition of PM_{10} at different sites in Central Italy.

particles. Sea-salt concentration also decreases when moving from Rome, which is about 20 km from the coast, to Montelibretti and to the regional background station, sited inland.

The quantitative relevance of secondary particles and their homogeneous distribution over the territory of Central Italy have severe implications in terms of possibilities of PM decrease as a consequence of temporary reductions of traffic emissions. These actions, in fact, may have a direct impact only on the concentration of primary anthropogenic compounds, which constitute only about 30% of PM_{10} at the traffic stations and about 15% of PM_{10} at the urban background station.

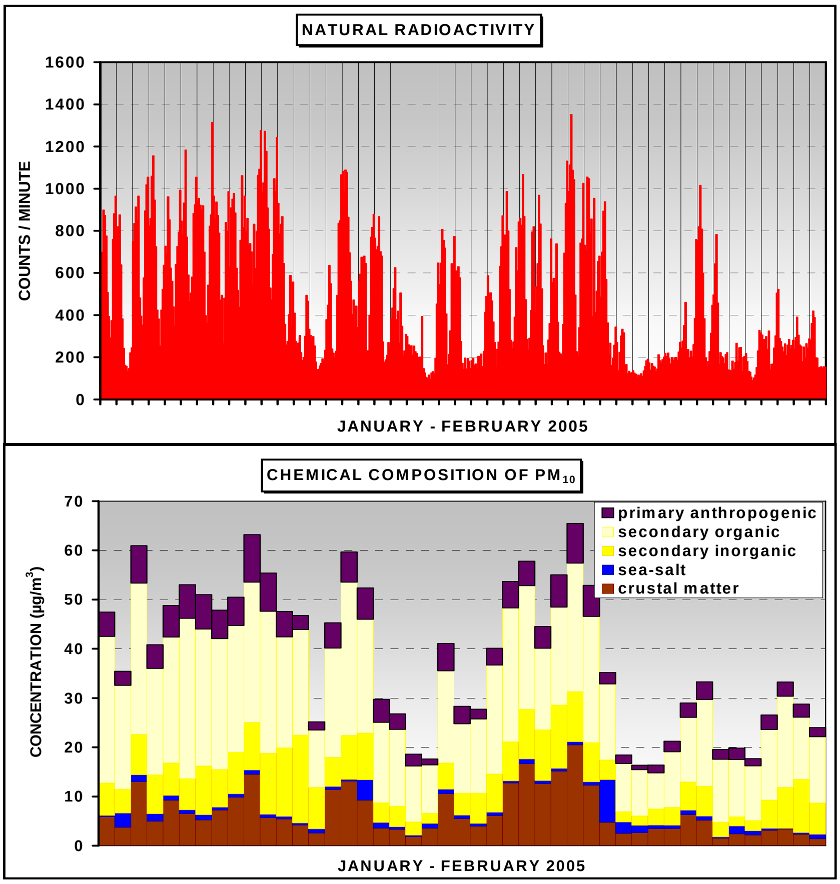

Figure 4: Increase in PM_{10} as a consequence of atmospheric stability, traced by natural radioactivity.

The strong link between the mass concentration of atmospheric particulate matter and the dilution properties of the lower boundary layer is shown in Figure 3, where the temporal pattern of natural radioactivity is compared with the time variations of PM_{10} concentration in Montelibretti.

Since the variations in the emanation rate of Radon from the soil can be considered negligible in a time scale of some days and a space scale of some kilometres, Radon concentration in the air only depends on the dilution factor and Radon progeny can be considered as a good natural tracer of the mixing properties of the lower boundary layer. Increases in the value of natural radioactivity indicate atmospheric stabilization, while decreasing values indicate a rise in the height of the boundary layer and constantly low values of natural radioactivity indicate advection. The study of natural radioactivity pattern permits the quick and easy identification of the periods when particulate matter concentration is expected to increase because of the accumulation of anthropogenic pollutants and secondary compounds (atmospheric stability periods) as well as of the periods when low pollution levels are expected (advection and daily convective mixing). The data reported in Figure 3 show that PM concentration increases when night-time and especially daytime values of natural radioactivity are high; during periods of low natural radioactivity, instead, PM concentration is low.

In case of advection, PM values are generally low, with the exception of African dust outbreaks. During these events, Central and Southern Italy may undergo a relevant increase in PM concentration due to the intrusion of desert dust particles. These events can be well identified by calculating the back-trajectories of the air masses (Hysplit model, run by NOAA) and by applying specific models as the DREAM model. In addition, the intrusion of desert dust can be locally identified by determining the ratio between the number of particles in the coarse and in the fine fractions.

Figure 5 shows, for the dust event of June 2006 and for the site of Montelibretti, the back-trajectories, the ratio between the number of particles in the size range > 1.5 µm and in the size range between 0.5 and 1 µm, the chemical composition of PM_{10} and the vertical profile of the dust load calculated by the DREAM model. The data show that the last ten days of June 2006 were characterised by a relevant intrusion of African dust, with two peaks during 20th-23rd and during 28th-30th. The events are clearly indicated by the increase in the ratio between coarse and fine particles; these data also indicate that the first peak, more than the second one, was characterised by a predominance of the coarse fraction. The analysis of the chemical composition of PM_{10} during the episode shows, as expected, a very significant increase in the crustal components: this component alone accounts for more than 40 µg/m^3 of PM_{10}.

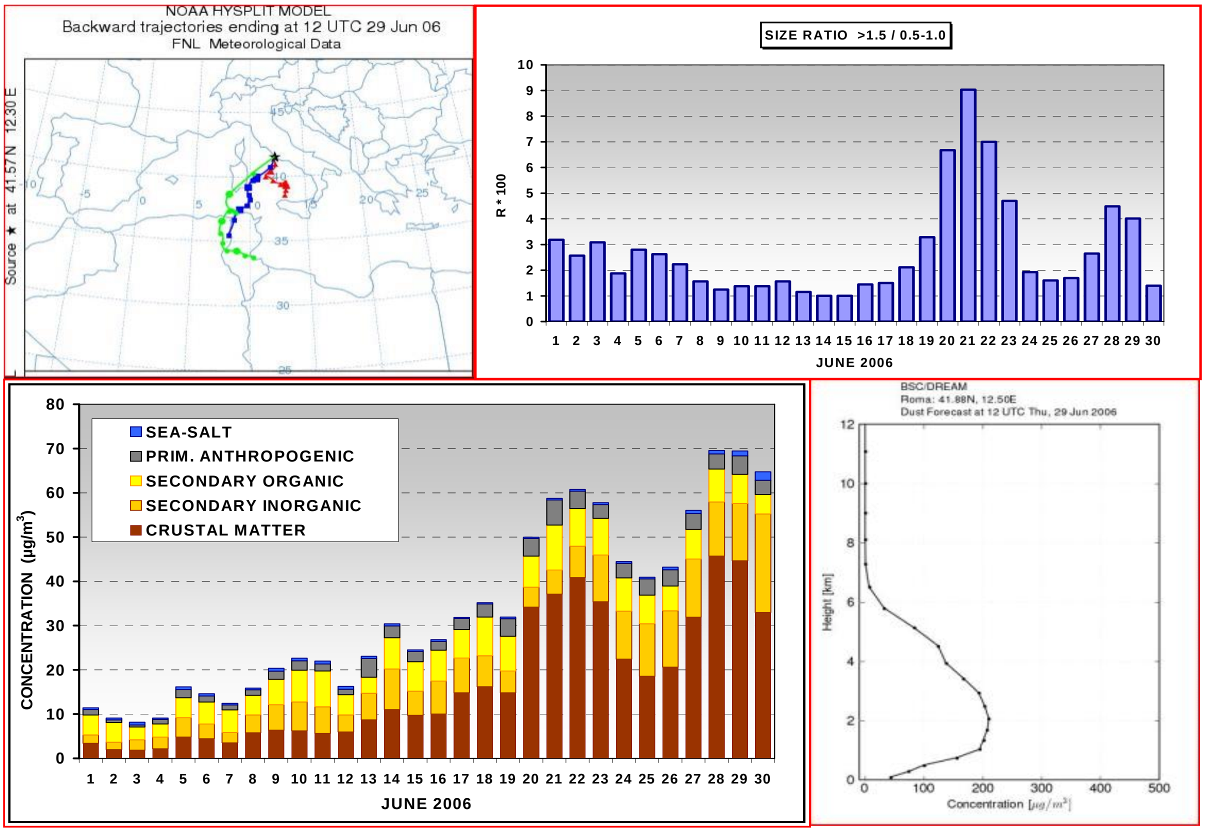

Figure 5: Impact of a Saharan dust outbreak over Central Italy. From upper left figure: back-trajectories of the air masses as calculated by the HYSPLIT model run by NOAA on June 29 (http://www.arl.noaa.gov/ ready/hysplit4.html); ratio of the number of particles in the size range > 1.5 µm and between 0.5 and 1 µm; chemical composition of PM_{10}; vertical profile of dust over Rome calculated by the DREAM model on June 29 (http://www.bsc.es/projects/earthscience/DREAM/).

4. AKNOWLEDGEMENTS

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5. REFERENCES

Chan, Y.C., Simpson, R.W., McTainsh, G.H. and Vowles, P.D.: 1997, “Characterisation of chemical species in PM2.5 and PM10 aerosols in Brisbane, Australia”, *Atmos. Environ.* **31**, 3773-3785.

Harrison, R.M., Alan, M.J., Royston, G.L.: 2003, “A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites”, *Atmos. Environ.* **37**, 4927-4933.

Kataoka. T., Yunoki, E., Shimizu, M., and Mori, T.: 2001, “A study of the atmospheric boundary layer using radon and air pollutants as tracer”, *Boundary-Layer Metereol*. **101**, 131-155

Marcazzan, G.M., Vaccaro, S., Valli, G., Vecchi, R.: 2001, “Characterisation of PM10 and PM2.5 particulate matter in the ambient air of Milan (Italy)”, *Atmos. Environ.* **35**, 4639-4650.

Perrino C., Pietrodangelo A. and Febo A. 2001. An atmospheric stability index based on radon progeny measurements for the evaluation of primary urban pollution. Atmos. Environ. 35, 5235-5244.

Perrino C., Canepari S., Cardarelli E., Catrambone M., Sargolini T. : 2006, “Inorganic constituents of urban air pollution in the Lazio Region (Central Italy)”, Env. Monit. Assess. in the press.

Putaud, J.P. et al.,: 2004, “A European aerosol phenomenology-2 : chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe”, *Atmos. Environ.* **38**, 2579-2595.

Querol, X., et al.: 2004, “Speciation and origin of PM10 and PM2.5 in selected European cities“, *Atmos. Environ.* **38**, 6547-6555.

Sesana, L., Caprioli, E., and Marcazzan, G.M.: 2003, “Long period study of outdoor radon concentration in Milan and correlation between its temporal variation and dipersion properties of the atmosphere”, *J. Environ. Rad.* **65**, 147-160.

Turpin, B.J. and Lim, H.: 2001, “Species contribution to PM2.5 mass concentration: revisiting common assumptions for estimating organic mass”, *Aerosol Sci. Technol*. **35**, 602-610.

Viidanoja, J., Sillanpaa, M., Laakia, J., Kerminen, VM, Hillamo, R., Aarnio, P., Koskentalo, T. : 2002 « Organic and black carbon in PM2.5 and PM10 : 1 year of data from an urban site in Helsinki, Finland. Atmos. Environ., 36, 3183-3193.

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ELEMENT SOLUBILITY AND SIZE DISTRIBUTION OF AIRBORNE PARTICULATE MATTER IN THE LAZIO REGION (ITALY)

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ABSTRACT

Within the "Polveri Fini" Project funded by Lazio Region, PM10 and PM2.5 24 h-samples were daily collected from October 2004 to July 2005 at six sites of different typologies. About 1000 samples of airborne particulate matter (PM) have been chemically fractionated (extract and mineralised residual) by different element solubility, achieving a meaningful elemental characterization of the single PM sample. The dimensional distribution of the two chemical fractions has been also investigated. Results show for most of the investigated elements significantly different size distributions of the two solubility fractions and, in particular, the extract can be mainly related to *fine* particles. On the other hand, element contributions in *coarse* particles from traffic-related sources are mainly found in the residual fraction. These behaviours are cleanly observed for some metals (As, Cd, Pb and V) of critical importance for the environment.

1. INTRODUCTION

Elemental chemical fractionation in PM has been applied over the recent years mainly with the aim of collecting information on bio- and environmental availability of metals and to the purposes of source characterization and apportionment studies. In this paper the use of chemical fractionation on PM samples collected during the "Polveri Fini" project has been aimed towards improving the understanding of the behaviour of elements solubility in the PM from traffic-related sources. Results are discussed about the solubility behaviour of 12 elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Ti and V) in two chemical fractions (extract and mineralised residual) with respect to their dimensional distribution between the PM2.5 and the PM(10-2.5) size fractions in the period of the "Polveri Fini" Project.

2. METHODOLOGY

PM10 and PM2.5 24 h-samples were daily collected from October 2004 to July 2005 at six sites of different typologies (traffic, urban background, regional background) in the Lazio region (Italy). About 1000 samples of airborne particulate matter (PM) have been chemically fractionated by a sequential leaching procedure previously optimised and validated by our laboratory [Astolfi, M. L. et al. 2006; Canepari, S. et al. 2006[1]; Canepari, S. et al. 2006[2]; Canepari, S.et al., 2006[3] , Perrino, C. et al., 2007]. Further experiments were carried on PM samples collected by a 13-stage impactor (Dekati).

3. RESULTS AND DISCUSSION

As commonly expected, the average total concentrations (sum of the extract and mineralised residual fractions) of almost all analysed elements increase with the vehicular traffic load at different sites. Indeed, peculiarly high total concentrations have been observed for Cu and Sb at Montezemolo (traffic) and Villa Ada (urban background) sites in Rome. At traffic sites of Latina and Viterbo concentrations lower than in Rome were found, as expected given the smaller size of these cities, while at Fontechiari site (regional background) the lowest concentrations were observed for all the elements. Nevertheless, also at Montelibretti (semi-rural, about 25 km NE of Rome), where the chemical labs of the C.N.R. Research Area are located, unexpected high concentrations of some elements, i.e. Ni and Cr, were found.

Aimed to a thorough investigation, results of the chemical fractionation by the leaching procedure applied have been combined with the information coming from the size fractionation of collected PM. This has been obtained by separating the element contribution determined in the PM2.5 from that calculated as PM(10-2.5) on a daily basis. However, results of this calculation refer only to sites where PM10 and PM2.5 samples were collected in parallel (Villa Ada, Latina, Montelibretti and Fontechiari).

As showed in figure 1 element concentration differences with site are less evident for PM2.5 than for PM(10-2.5) and change widely among the analysed elements.

Solubility percentages differ depending on the element and size, and are above 70% for As, Cd and V in the

PM2.5, whereas less than 30% for Cu, Ni, Cr and Sn in the same size fraction.

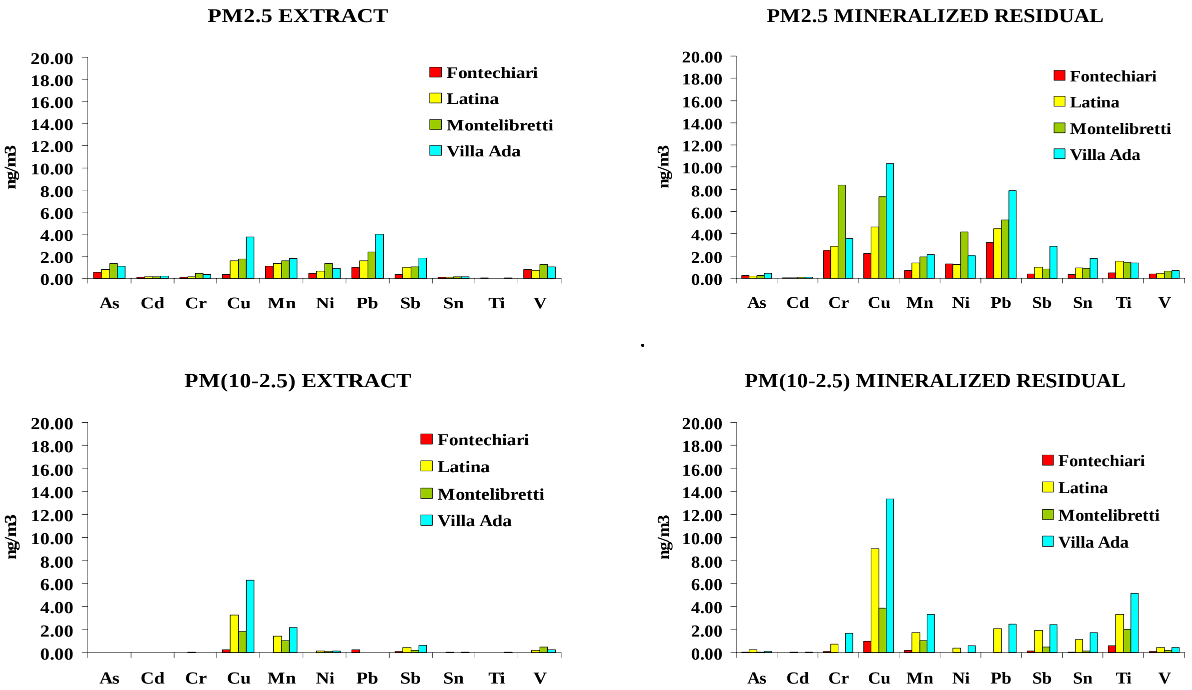

Figure 1. Median concentrations of investigated elements in the considered dimensional and chemical fractions

The combination of size and chemical fractionation permitted, moreover, to relate the unexpectedly high total concentrations of Ni, Cr and other metals found at Montelibretti site to a source which selectively contributes to the insoluble forms of these elements in the PM2.5 size fraction. Element concentrations in the PM(10-2.5) are evidently dependent, as expected, on the different site typologies and vehicular traffic burden. Indeed, almost all investigated elements show very low concentrations in the PM(10-2.5) at Fontechiari (regional background), while they achieve the maximum concentration, in the same size fraction, at Villa Ada. Moreover, with exception of Cu and Mn, concentrations in the extract of PM(10-2.5) are generally low and, therefore, the percentage solubility in the PM(10-2.5) extract is far lower than in the PM2.5 extract.

The PM size influence on the solubility behaviour of analysed elements was further investigated by applying the chemical fractionation procedure to a set of PM samples properly collected by a 13-stage Dekati impactor during a sampling period of 14-days (21 Oct. – 3 Nov. 2005). Analyses of these samples show, for most elements, considerably meaningful differences in the dimensional distribution of the two fractions at different solubility (figure 2). In some cases, like V, Cd, Pb and As, an almost quantitative separation has been observed between the soluble (prevailing in the smaller size stages) and insoluble (mainly in the larger size stages) fractions. For other elements differences of the solubility behaviour between size fractions within the *fine* mode and those in the *coarse* mode were less evident, but resulted nevertheless noticeable.

Taking into account these results, whose strength will be further tested on other site typologies, and given also the information in literature on source profiles, the chemical fractionation procedure used in this work seems to help the identification of contributions from different traffic-related sources without need of applying also a size fractionation. Indeed, the analysis of the extract and residual chemical fractions leached on PM10 samples provides almost independent information on the *fine* and *coarse* element contributions, at least for those elements (mainly As, Cd, Pb and V) for which meaningful differences in the dimensional distribution of the two solubility fractions are found. In general, however, most elements show lower solubility in the *coarse* fraction, while some other, like Cu and Mn, seem to be less useful to this aim, since both extract and residual fractions can be mainly related to the *coarse* mode.

These results lead to some due considerations on how the extract and residual element concentrations behave differently with respect to site typologies.

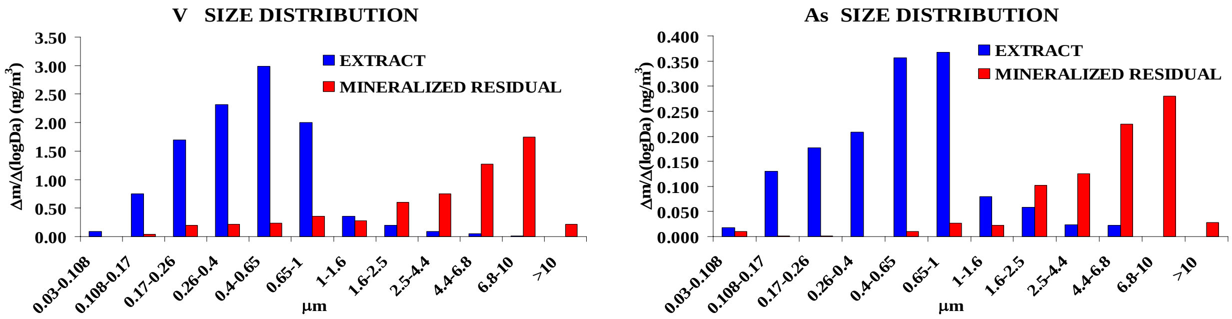

Figure 2. dimensional distribution of extract and mineralized residual fractions of V and As

The element concentration differences between Montezemolo (traffic) and Villa Ada (urban background), observed both for the PM10-extract and PM10-residual fractions, indicated that concentration increases due to traffic load relate almost solely, with the exception of As, to the mineralised residual fraction. Similarly, differences between Montezemolo (traffic) and Fontechiari (regional background) showed comparable concentration profiles, confirming again that concentration increases due to the distance from vehicular traffic over the regional background are mainly found in the residual fraction. From these observations and on the basis of results given by the analyses on samples from the 13-stages impactor (figure 2) we can assume that the elemental residual fraction is mainly linked to the *coarse* mode. Therefore the concentration increases observed at traffic sites seem to be mainly associated with *coarse* particles, likely from abrasion of vehicles machinery and road dust re-suspension.

The hypotheses above can be verified by combining the analysis of the atmospheric dispersion conditions in the PBL with results on the dimensional distribution PM2.5 – PM(10-2.5) and with results on the element solubility fractionation. Diverse size fractions are expected, indeed, to behave differently with respect to non-advective atmospheric dispersion and, on the basis of results given by the chemical fractionation applied, this could also be seen in the solubility behaviour of elements in the size fractions PM2.5 and PM(10-2.5).

Therefore, the temporal trends of element concentrations in the extract and residual fractions have been investigated with respect to the natural radioactivity [Canepari, S. et al. 2006[3], Perrino, C. et al. 2001;] for a selected short period of the "Polveri Fini" campaign (22 Jan. -18 Feb. 2005). The trends of natural radioactivity indicate that some days of advection (24-31 Jan., 2, 5, 15-16 Feb.) alternated with longer stability periods, during which pollutants are expected to concentrate in ambient air due to poor atmospheric dilution.

In figure 3 the extract and residual fractions of V in the PM2.5 and PM10 of Villa Ada and in the PM10 of Montezemolo are reported. The difference between the element trends in the PM2.5 and in the PM10 represents with acceptable approximation the element content in the *coarse* fraction, while the distance PM10 Montezemolo– PM10 Villa Ada represents the element concentration increase with decreasing distance of the site from traffic-related sources.

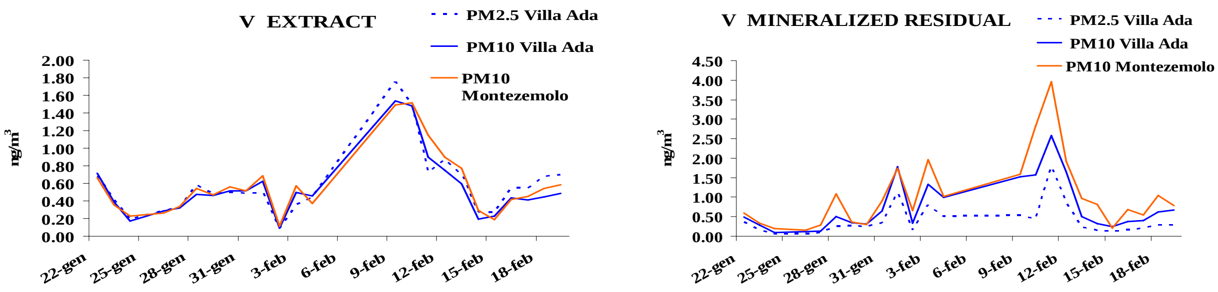

Figure xx. Temporal trends of extract and mineralized residual fraction of vanadium

All trends almost overlap for V in the extract, in agreement with results found from the trials with the multi-stage impactor and also taking into account that *fine* particles typically are more evenly spread by atmospheric dispersion. The same behaviour has been observed also for the extract fractions of Cd, Pb and As. On the other side, noticeable differences are observed between the Villa Ada PM2.5 and PM10 trends and between the Villa Ada PM10 and Montezemolo PM10 trends of V in the residual. This behaviour is found for the residual fraction of all investigated elements and also for the extract of those elements, like Mn, whose dimensional distribution indicates a prevalent *coarse* mode.

Moreover, almost all elements showed clean differences of temporal trend between the extract and residual fractions, and this is as far evident as more their solubility fractions show differences in the dimensional distribution. These results confirm that sources of different categories affected the collected PM samples and their relative contributions are traceable by chemical fractionation.

Table 1 . Correlation matrix of residual elements in the Montezemolo PM10

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sn	Ti	V
As	1,0											
Cd	0,8	1,0										
Co	0,8	0,9	1,0									
Cr	0,6	0,9	0,7	1,0								
Cu	0,7	0,8	0,6	0,8	1,0							
Mn	0,7	0,9	1,0	0,8	0.8	1,0						
Ni	0,7	0,8	0,7	0,9	0,8	0,7	1,0					
Pb	0,5	0,5	0,3	0,4	0,4	0,4	0,5	1,0				
Sb	0,7	0,8	0,6	0,9	0,9	0.8	0,8	0,4	1,0			
Sn	0,7	0,8	0,7	0,9	0,9	0,8	0,9	0,4	1,0	1,0		
Ti	0,6	0,7	0,9	0,4	0,3	0,9	0,4	0,2	0,3	0,4	1,0	
V	0,6	0,7	0,9	0,5	0,5	0,8	0,5	0,2	0,4	0,5	0,9	1,0

As a matter of fact, the temporal trend and dimensional distribution of the residual fraction were strictly comparable for many elements, as reported by the correlation matrix of residual elements in the PM10 collected at Montezemolo during the whole sampling period of the "Polveri Fini" project (table 1).

This suggests that contributions to the insoluble forms of many elements were influenced by a shared source, indicating thus the likely relevant role of traffic-related contributions like machinery abrasion and dust re-suspension at urban sites.

4. CONCLUSIONS

Results indicate that the application of the chemical fractionation allows to increase the selectivity of elements as tracers of emission sources. In particular a good selectivity has been found for the residual fractions of some elements with respect to non-combustive traffic-related sources. Moreover, the extract fractions of As, V, Cd and Pb in the PM10, whose critical environmental importance is well known, are linkable to the *fine* particles contribution only.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Astolfi, M. L., Canepari, S., Cardarelli, E., Ghighi, S. 2006. Chemical fractionation of elements in airborne particulate matter: First results on PM10 and PM2.5 samples in the Lazio Region (central Italy). Annali di Chimica, 96, 183-194.

Canepari, S., Cardarelli, E., Giuliano, A., Pietrodangelo, A. 2006[1]. Determination of metals, metalloids and non-volatile ions in airborne particulate matter by a new two-step sequential leaching procedure. Part A: Experimental design and optimisation. Talanta, 69, 581–587.

Canepari, S., Cardarelli, E., Pietrodangelo, A., Strincone, M. 2006[2]. Determination of metals, metalloids and non-volatile ions in airborne particulate matter by a new two-step sequential leaching procedure. Part B: Validation on real equivalent samples. Talanta, 69, 588-595.

Canepari, S., Cardarelli, E., Perrino, C., Catrambone, M., Pietrodangelo, A., Strincone, M. 2006[3]. Two-stage chemical fractionation method for the analysis of elements and non-volatile inorganic ions in PM10 samples: Application to ambient samples collected in Rome (Italy). Atmospheric Environment, 40, 7908–7923.

Perrino, C., Pietrodangelo, A., Febo, A. 2001. An atmospheric stability index based on radon progeny measurements for the evaluation of primary urban pollution. Atmospheric Environment, 35, 5235–5244.

Perrino, C., Canepari, S., Cardarelli, E., Catrambone, M., Sargolini, T. Inorganic constituents of urban air pollution in the Lazio region (Central Italy). Environmental Monitoring and Assessment, published on-line, DOI 10.1007/s10661-006-9269-7.

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RAPID EVOLUTION OF SIZE DISTRIBUTION AND CHEMICAL COMPOSITION OF INDIVIDUAL URBAN PARTICLES UNDER VARIABLE LOCAL METEOROLOGICAL CONDITIONS

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ABSTRACT

Sampling of aerosols generally takes several hours to collect enough particulate matter for subsequent chemical analysis. Unlike many bulk techniques, single-particle analysis by automated scanning electron microscopy combined with energy-dispersive X-ray spectrometry (SEM-EDX) requires light sample loadings with sampling times as short as a few minutes. Single-particle analysis of short-term aerosol samplings can provide information on the rapid evolution of size distribution and chemical composition of pollution aerosols. The aim of this work is to evaluate automated particle analysis performed by SEM-EDX. The first sampling campaign corresponded to a stable atmospheric situation. Low temporal variation in PM_{10} and $PM_{2.5}$ mass concentrations during samplings was observed. These conditions were suitable for estimating the lower particle number to observe to yield representative results. During a second sampling campaign under variable atmospheric conditions, the ability of automated SEM-EDX to observe short temporal variation in particle chemical composition was demonstrated.

1. INTRODUCTION

Traditionally, bulk analysis is done on totally-filtered air samples collected during several hours. However, only particles whose aerodynamic sizes fall into a limited range have a high probability for deposition and retention in the lower respiratory system. As a result, bulk analysis is more and more carried out on size-segregated particles collected by means of cascade impactors.

However, atmospheric aerosols typically consist of an external mixture of particles that are themselves composed of internally-mixed compounds. To this regard, single-particle analysis is considered a complementary technique to bulk analysis. Depending on the size fraction and on the total particle number concentration, sampling times as short as 1 min can be taken for appropriate particle loadings. Such short sampling times raise the question of representativeness compared to bulk analysis. On the other hand, long sampling times are not suitable to account for a rapid evolution of atmospheric particles near emissaries.

The main purpose of this study is to evaluate automated single particle analysis performed by SEM-EDX applied to atmospheric aerosols under rapidly evolving atmospheric conditions. In the present work we report results from two sampling campaigns that took place in an urban area that is strongly influenced by port and industrial activities. The study of the size-resolved elemental composition by automated SEM-EDX is used to reveal whether variations in physico-chemical properties of individual particles were due to addition of new types of particles or if the same types of particles were present but with different relative abundances.

2. METHODOLOGY

The sampling took place on the university campus of Dunkirk (Nord-Pas de Calais, France) in November 17th 2005 and February 1st 2007 (Figure 1). Dunkirk conurbation is densely industrialized in its Western part. It houses a major oil refining complex and the largest steel manufacturing plant in France.

Figure 1: Map of the sampling location in Dunkirk, France (51.02°N; 2.20°E). The sampling site (★) is located 100 meters West from the closest air quality monitoring station (●) and approximately 3 km East from the industrial area.

Aerosol samples were collected during 10 min each at the top of a 4-m high mast by means of a 3-stage cascade impactor (Dekati PM-10) with a flow rate of 30 L min^{-1}. Dekati PM-10 impactor is made up of 3 consecutive stages to segregate coarse and fine fractions. Stage 1 removes particles of equivalent aerodynamic diameter larger than 10 µm. Stage 2 collects particles below 10 µm and above 2.5 µm in diameter ($PM_{10-2.5}$ size fraction). Stage 3 collects particles below 2.5 µm and above 1 µm in diameter ($PM_{2.5-1}$ size fraction). Atmospheric particles impacted on boron substrates, specifically developed for the purpose of particle microanalysis (Choël et al., 2005). A weather station recorded automatically local meteorological conditions every half hour (Table 1).

Table 1: Local meteorological conditions

Date	Time	Temperature (°C)	Humidity (%)	Wind speed (m s^{-1})	Wind direction
17/11/2005	12:30	7.9	67	5.4	NNW
	13:00	8.1	61	5.4	NW
	13:30	7.9	62	4.9	NNW
01/02/2007	16:00	1.3	86	0.4	W
	17:00	1.1	87	0.4	WSW
	18:00	1.2	87	0.9	WSW
	19:00	1.3	86	0.9	WSW

Elemental analysis of individual atmospheric particles was performed using a LEO 438VP scanning electron microscope outfitted with an ultrathin window EDX detector. Automated particle analysis was performed using the commercially available Link ISIS Series 300 Microanalysis system (Oxford Instruments). Approximately 1000 particles per sample were analyzed to obtain data statistically representative of the collected aerosols. Electron images were acquired using a scintillator type backscattered electron detector with a magnification of 6000×. X-ray spectra were collected with an acquisition time of 20 s, at an accelerating voltage of 15 kV and a probe current of 200 pA. Each particle was morphologically characterized by its equivalent diameter calculated from the area of its two-dimensional projection considering it a sphere. Only particles with diameters greater than 0.3 µm were considered. Net X-ray intensities obtained by non-linear least-squares fitting of spectra were converted into atomic concentrations after applying a reverse Monte Carlo quantitative procedure (Ro et al., 2003).

3. RESULTS AND DISCUSSION

3.1 Mass concentrations

The closest air quality monitoring station in downtown Dunkirk located 100 meters away from our sampling site and operated by ATMO Nord-Pas de Calais recorded PM_{10} and $PM_{2.5}$ mass concentrations (Figure 2). Low temporal variation of PM_{10} and $PM_{2.5}$ mass concentrations during the preceding hours and during samplings was observed on November 17th 2005.

During the second sampling period, the PM10 station recorded a pollution event with a significant increase in PM_{10} and $PM_{2.5}$ mass concentrations. This corresponded to a plume of dusts originating from the chimneys of the nearby steel manufacturing plant. This plume was flying over the town centre at the time of sampling.

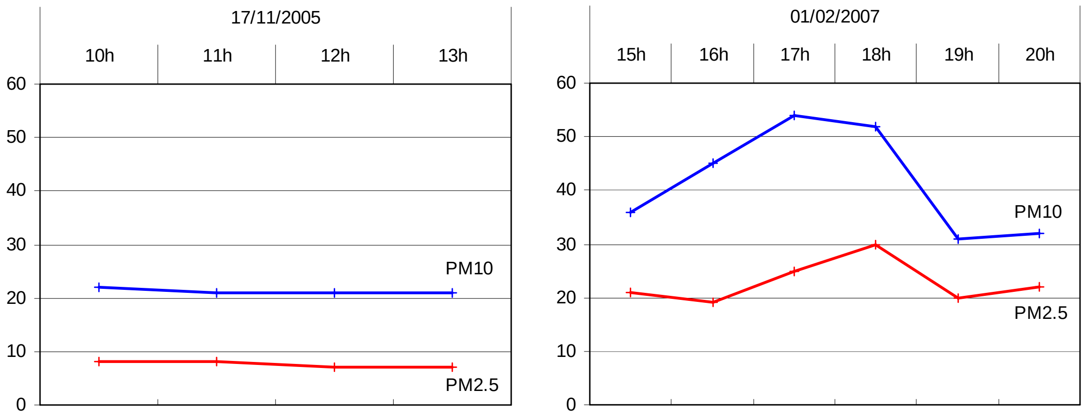

Figure 2: Hourly values of PM_{10} and $PM_{2.5}$ mass concentrations (in µg m^{-3}).

3.2 Particle number concentrations

Total particle number concentrations were measured by an optical particle counter (Malvern 3016). During the first sampling campaign, no significant temporal evolution of the particle size distribution was observed between the three successive samples (Figure 3). As a result, both mass and number concentrations were stable over the first sampling period. This corresponded to a stable situation suitable for evaluating single-particle analysis performed by automated SEM-EDX.

During the second sampling campaign, comparison of the four successive samples indicates a significant temporal evolution of the particle size distribution (Figure 3). The particle number concentration was ten times higher than the first day of sampling. The shape of the size distribution for the last 10-min sampling is clearly different from the first ones. Coarse particles were relatively more abundant at the end of sampling. A rapid evolution of the particulate load in terms of mass and number concentration was thus confidently witnessed. In the next part, single-particle analysis is used to provide information on the chemical composition of the sampled aerosols.

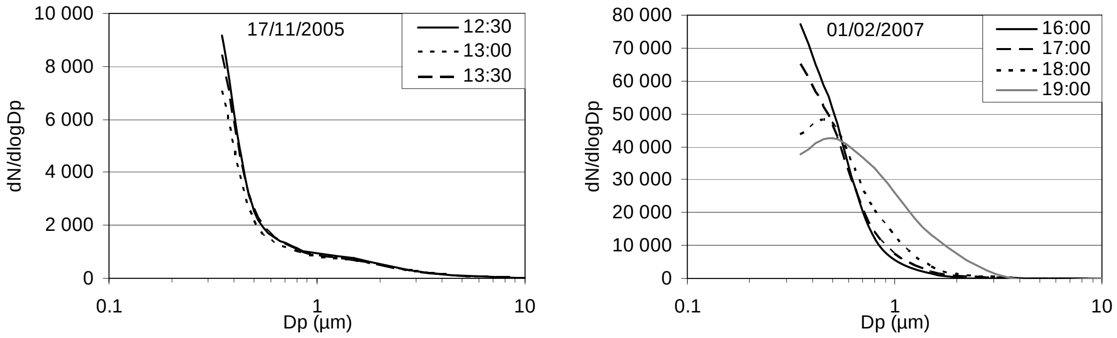

Figure 3: Size distributions (in particle number per cubic centimeter of air) for the two sampling periods.

3.3 SEM-EDX measurements

Good agreement was found between the dry size distribution of particles obtained from SEM-EDX data acquired by two operators on the same impaction area. Analysis by automated SEM-EDX of different impaction areas of the same size fraction ($PM_{2.5-1}$) resulted in similar size distributions of particles. These observations prove the validity and reliability of the parameter setting methodology used for automated particle detection and size measurements.

Particles were classified according to characteristic X-ray intensities of their constituting elements and calculated atomic concentrations. The number of particles necessary to analyze so as to yield representative results about the dry size distributions of $PM_{2.5-1}$ and $PM_{10-2.5}$ was determined by comparing dry size distributions obtained for subsets of SEM-EDX data against the full dataset. Physical properties of the $PM_{2.5-1}$ size fraction were well characterized by analyzing approximately 500 particles. Comparison of relative abundances of particle types according to the number of particles considered showed that chemical properties of the same size fraction converged to within 10% of their final values after analyzing about 1000 particles. These threshold values depend on the number of particles populating a particle type and on the heterogeneity of the sample studied.

The study of the size-resolved elemental composition by automated SEM-EDX allowed here to know whether variations in physico-chemical properties of individual particles were due to addition of new types of particles that could come from local emissaries, or if the same types of particles were present but with different relative abundances (Choël et al., 2006). As an example, Figure 4 represents relative abundances of particle types obtained for $PM_{2.5-1}$ size fraction collected during the first sampling period. Marine particles represented 87% of all particles. Direct observation at the particle scale allowed distinguishing between newly formed (58%), partly converted (10%) and completely converted seasalts to sodium nitrates and sulfates (19%). Mix particles comprised Marine/Continental (62%), Marine/Metallic (20%), Carbonaceous/Marine (15%), Carbonaceous/Metallic (2.5%) particles. Metal-bearing particles accounted for 3.2% of all particles. Submicrometer-sized particles represented 85% of metallic particles with an average diameter of 0.7 µm. 99% of metallic particles were composed of iron oxides due to nearby steelworks emissions.

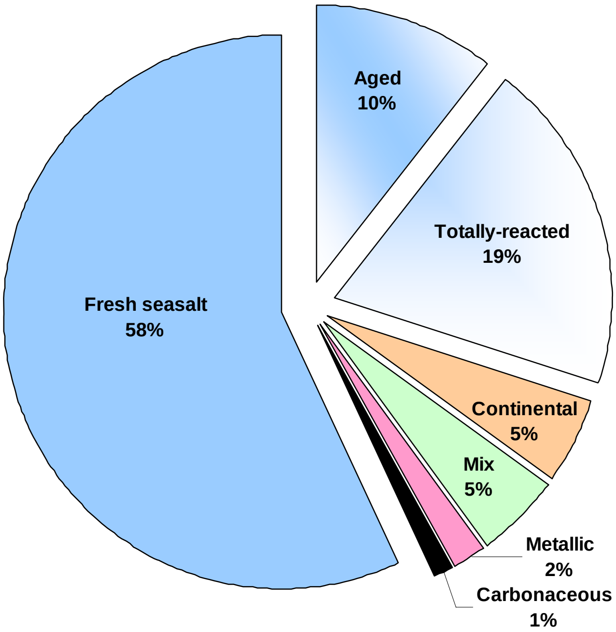

Figure 4: Relative abundances of particle types obtained for $PM_{2.5-1}$ size fraction collected during the first sampling period.

4. CONCLUSIONS

Analytical procedures for particle analysis should be guaranteed before undertaking intensive field samplings. The first part of the work was devoted to the validation of our sampling methodology and the automated single-particle analysis applied to urban aerosols collected under a stable atmospheric situation. The lower particle number necessary to observe so as to yield representative results was estimated at 500 and 1000 for physical and chemical properties respectively. In the second part of the work, a sampling campaign was carried out under variable local meteorological conditions. The ability of automated SEM-EDX to observe short temporal variation in particle chemical composition was investigated. Nearby steelworks was shown to have a considerable impact on the atmospheric particle load, notably with the ubiquitous presence of submicrometer iron oxides spherules. Single-particle analysis also gave information about chemical reactions occurring in the atmosphere. The technique, used in conjunction with an adequate particle carrier and an efficient data processing, allowed to distinguish particles in various stages of conversion as illustrated by the rapid conversion of fresh seasalts under the influence of gazeous anthropogenic emissions.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Choël, M., Deboudt, K., Flament, P., Lecornet, G., Perdrix, E. and Sobanska, S., 2006. Fast evolution of tropospheric Pb- and Zn-rich particles in the vicinity of a lead smelter. Atmospheric Environment, 40: 4439-4449.
Choël, M., Deboudt, K., Osán, J., Flament, P. and Van Grieken, R., 2005. Quantitative determination of low-Z elements in single atmospheric particles on boron substrates by automated scanning electron microscopy-energy-dispersive X-ray spectrometry. Analytical Chemistry, 77(17): 5686-5692.
Ro, C.-U., Osán, J., Szalóki, I., de Hoog, J., Worobiec, A. and Van Grieken, R., 2003. A Monte Carlo program for quantitative electron-induced X-ray analysis of individual particles. Analytical Chemistry, 75: 851-859.

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THE MEASURED SIZE FRACTIONATED AEROSOL NUMBER CONCENTRATIONS NEAR A MAJOR ROAD IN HELSINKI

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ABSTRACT

This study presents evaluation of the size fractionated aerosol number concentrations measured near a major road of Itäväylä in Helsinki, during autumn 2003 and winter 2004. The measurement system contained also electronic traffic counts, on-site meteorological measurements, and urban background concentration measurements. We evaluated the temporal variations and the dependencies on local meteorological conditions of the measured aerosol number concentrations and size distributions.

The daytime ultrafine particle (UFP) number concentrations at the roadside site were approximately an order of magnitude higher than those at the urban background site, due to vehicular emissions from the road. The modal structure of urban background aerosol particles in Helsinki can be fairly well characterized by 2–3 lognormal modes: an accumulation mode (GDM > 100 nm) representing regional background characteristics, and two UFP modes (GMD < 100 nm).

1. INTRODUCTION

Traffic is the most important source of air pollution in urban centers, and therefore, there is an urgent need for good-quality experimental data that has been specifically produced for model validation and evaluation purposes, especially regarding particulate matter. For model evaluation, air quality data have to be combined with simultaneous measurements of traffic flow and meteorological parameters, together with information about local topography and buildings. Evaluation of roadside dispersion models is seriously hindered by the scarcity of appropriate experimental datasets (e.g. Kukkonen et al. 2001).

The main objectives of this paper are to investigate and evaluate size-fractionated aerosol number concentrations that were measured within the SAPPHIRE ("Source Apportionment of Airborne Particulate Matter and Polycyclic Aromatic Hydrocarbons in Urban Regions of Europe", 2003 – 2006) project in Helsinki. SAPPHIRE measurement campaigns were conducted in several major European cities including Athens, Birmingham, Copenhagen and Oporto. The size-fractionated aerosol and meteorological measurements were performed simultaneously at a roadside site and a background site during August 23 – September 19, 2003 and January 14 – February 11, 2004. Traffic flows were also measured electronically. The results can be utilized especially for investigating particulate matter originating from urban vehicular traffic.

2. METHODOLOGY

The measurement campaigns were performed during August 23 – September 19, 2003 and January 14 – February 11, 2004 at two locations simultaneously. The roadside site (Herttoniemi) was located about 6 km east of Helsinki city centre, in a suburban surroundings at the distance of 65 m from a majos highway. The urban background site (Kumpula) was located in a campus area 5 km northeast from the city centre, with a distance of approximately 200m from a densely trafficked major highway. The locations are presented in the Figure 1.

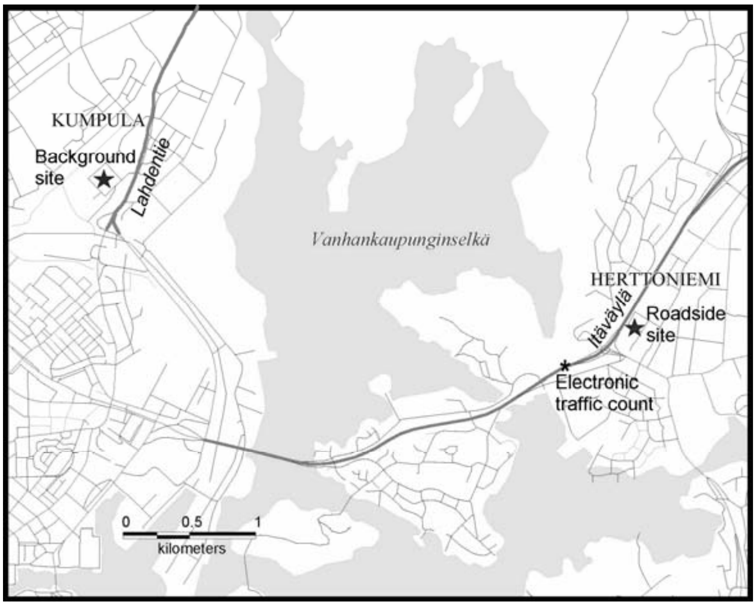

Figure 1. Measurement sites and traffic count locations (marked with stars). The map also shows the road and street network; the nearby major roads are indicated with dark lines. Grey area is a part of the Baltic Sea. The north is directed upward in this map. This map provided by Ground map material (C) National Land Survey of Finland, license number 158/MYY/06.

The aerosol particle measurements consisted of high-time resolution data on particle number size distributions (dry size between 8–320 nm at the urban background station and between 3–800 nm at the roadside site). The aerosol measurements at the background station were performed with a differential mobility particle sizer (DMPS) (e.g. Aalto et al. 2001), whereas at the roadside site they were measured with a twin scanning mobility particle sizer (SMPS) consisting of the first pairing of an ultrafine DMA (HAUKE-type, 10.9 cm in length) and an ultrafine CPC TSI 3025 for the particle size range of 3–50 nm and second pairing of a DMA (HAUKE –type 28 cm in length) with a CPC TSI 3010 for the size range of 10–800 nm.

The on-site meteorological measurements at the roadside station (Herttoniemi) included temperature and relative humidity at 5m height, and temperature, wind speed and direction at 8m height. We measured the meteorological parameters (1-minute time resolution) with MILOS500 (Vaisala) automatic weather station. Atmospheric stability parameters and the mixing height were evaluated using the meteorological pre-processing model developed at the Finnish Meteorological Institute, MPP-FMI (Karppinen et al., 2000), utilizing the meteorological database of the FMI, combining the data from the stations at Helsinki-Vantaa airport (north of Helsinki) and Isosaari (an island south of the centre of Helsinki). The mixing height of the atmospheric boundary layer was evaluated based on synoptic observations and the sounding observations made at Jokioinen (in a rural area in Southern Finland). The electronically counted traffic density data was available from the Helsinki City Planning Department.

3. RESULTS AND DISCUSSION

The daytime ultrafine particle (UFP) number concentrations at the roadside site were found to be approximately an order of magnitude higher than those at the urban background site, due to vehicular emissions from the road. The total particle number concentrations show a clear diurnal variation at both sites; this variation is closely correlated to the corresponding variation of the traffic density. The road contribution to the particle number size distribution was substantial in daytime and especially high during the traffic rush hours.

An example of the measured data is presented in graphic form in the Figure 2 a-e for the time period of August 25th -26th, 2003. This was a downwind situation at the Itäväylä site, and the weekdays were Tuesday and Wednesday.

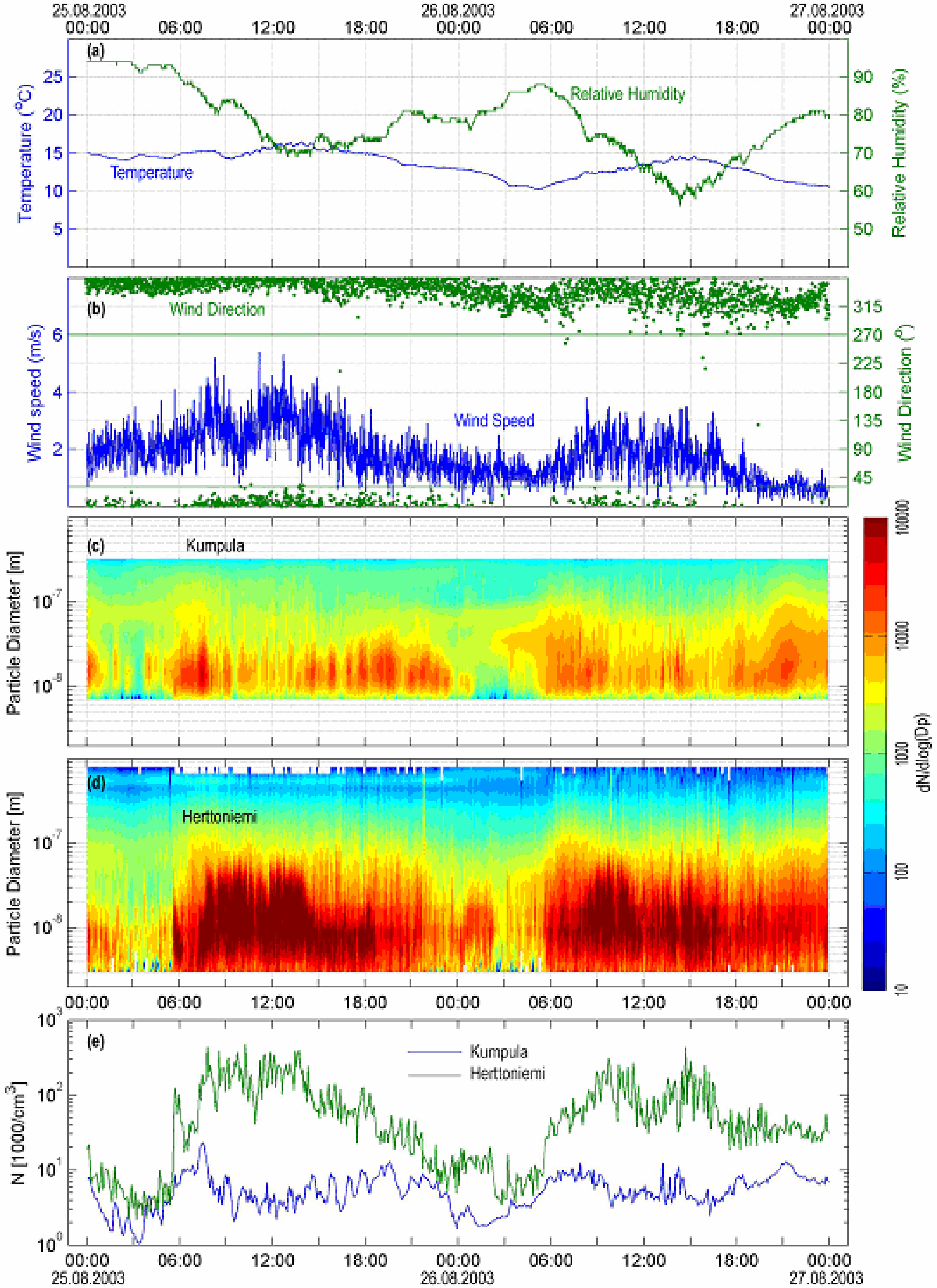

Figure 1. (a–b) relevant meteorological variables, (c–d) the particle number distribution spectra at the roadside site (Herttoniemi) and the urban background site (Kumpula), and (e) particle number concentrations between 8–320 nm at both sites. This case represents the direct influence of traffic emissions on the particle number size distributions at the roadside site in autumn. Hussein et al. (2007).

The road contribution to the particle number size distribution (defined as the difference between the concentrations at the roadside and the urban background site for the downwind cases) is substantial during the daytime, and especially high during the traffic rush hours. The UFP number concentrations at the roadside site were approximately an order of magnitude higher than those at the urban background site during daytime. However, in downwind conditions at night, the total particle number concentrations were only slightly higher at the roadside site in comparison to the background site.

The number of modes of urban aerosols is dependent on the local sources (e.g. Hussein et al. 2004 and 2005). Analysis of the modal structure of aerosol particles measured at the roadside and background sites revealed that the modal structure of urban background aerosol particles in Helsinki can be fairly well characterized by 2–3 lognormal modes: an accumulation mode (GDM > 100 nm) that represents regional background characteristics, and two UFP modes (GMD < 100 nm) that represent urban characteristics. An additional mode (GMD < 25 nm) with concentrations over 50000 cm^{-3} is required to describe the size distributions at the roadside site during downwind conditions. A similar modal structure for both sites was obtained during upwind conditions.

The measurement campaign did not include measurements of vehicular emissions on-site, which limits the use of the data for modeling purposes.

4. CONCLUSIONS

This study investigates the size fractionated aerosol number concentrations that were measured in Helsinki at a roadside site during autumn 2003 and winter 2004. In addition to measurement of aerosol size distributions and number concentrations, the measurement system contained also electronic traffic counts, on-site meteorological measurements, and urban background concentration measurements. The daytime ultrafine particle (UFP) number concentrations at the roadside site were found to be approximately an order of magnitude higher than those at the urban background site, due to vehicular emissions from the road. The modal structure of urban background aerosol particles in Helsinki could be fairly well characterized by 2–3 lognormal modes: an accumulation mode (GDM > 100 nm) representing regional background characteristics, and two UFP modes (GMD < 100 nm).

5. ACKNOWLEDGEMENTS

This study is a part of the EC-FP5 project SAPPHIRE (Source Apportionment of Airborne Particulate Matter and Polycyclic Aromatic Hydrocarbons in Urban Regions of Europe; project number: EVK4-2002-00089). This work was also a part of the KOPRA project and co-operation with the LIPIKA project (629/31/02), both funded by the National Technology Agency (TEKES) in Finland. We also acknowledge the funding from the Ministry of the Environment and the Ministry of Trade and Communications. We would like to thank Hannu Seppälä of the Traffic Planning Division at the Helsinki City Planning Department and Kari Mäkelä of the Technical Research Center (VTT) for the traffic density data.

6. REFERENCES

Aalto, P., Hämeri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J. M., Hoell, C., O´Dowd, C., Karlsson, H., Hansson, H.-C., Väkevä, M., Koponen, I. K., Buzorius, G., Kulmala, M. 2001. Physical characterization of aerosol particles during nucleation events, Tellus 53B, 344-358.

Hussein, T., Puustinen, A., Aalto, P.P., Mäkelä, J.M., Hämeri, K., Kulmala, M. 2004. Urban aerosol number size distributions, Atm. Chem. Phys. 4, 391–411.

Hussein, T., Hämeri, K., Aalto, P.P., Kulmala, M. 2005. Modal structure and spatial-temporal variations of urban and suburban aerosols in Helsinki area. Atmospheric Environment 39: 1655–1668.

Hussein, T., Kukkonen, J., Korhonen, H.,Pohjola, M., Pirjola, L., Wraith, D., Härkönen, J., Teinilä, K.., Koponen, I.K., Karppinen, A., Hillamo, R., Kulmala, M., 2007. Evaluation and modeling of the size fractionated aerosol number concentration measurements near a major road in Helsinki. Submitted to Atmospheric Chemistry and Physics, December 2006.

Karppinen, A., Joffre, S. M. and Kukkonen, J. 2000. The refinement of a meteorological preprocessor for the urban environment, International Journal of Environment and Pollution 14, pp. 565-572.

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THE INFLUENCE OF TRAFFIC AND BUS DENSITY ON ULTRAFINE PARTICLE CONCENTRATIONS ON BUSES IN MANCHESTER, UK: A MEASUREMENT STUDY.

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ABSTRACT

Little information exists regarding the exposure of bus commuters to UFP. Ad-hoc measurements of UFP number concentrations on buses in south Manchester were made in order to grasp the key variables which control those concentrations, and thus commuter exposure. Preliminary results support a relationship between UFP and NO_x concentrations, although the chosen route is also a significant modulator. Another key variable may be the amount of time spent travelling behind a gross polluter, for example, another bus. Results have been used to inform the design of a future bus commuting study.

INTRODUCTION

In recent years, concern surrounding the hazardous health effects of particulates (PM_{10}) has become widespread and is associated with such conditions as lung function decline in children, increased hospital emissions for cardiovascular disease, aggravation of asthma, and increased mortality and morbidity (Holgate, 1999). It is now widely suspected that the toxicity of ambient particulate matter is most strongly associated with the finer fractions. In particular, ultrafine particles (UFP) - particles with an aerodynamic diameter less than 0.1μm and primarily formed from combustion emissions – are receiving more attention. Studies have shown that when equal doses (in terms of mass) are given to animals, the UFP are more toxic than their larger equivalents (Pekkanen and Kumala, 2004). UFP are number dependant, not mass (Buzorius et al., 1999), and being so small they can be present in high numbers but account for very little of the actual measured mass. Their significance may therefore be underestimated during traditional particulate matter measurements. Although particle number concentrations may be a better metric for the assessment of public health burden than PM_{10}, the lack of available data concerning environmental exposure to particle number concentrations impedes our ability to test this hypothesis. UFP are less influenced by non-local emissions than PM_{10} and exhibit greater spatial gradients close to sources, which in urban areas is road traffic. Within the urban environment UFP account for more than 80% of particulate matter in terms of number (Hitchins et al., 2000) and in the UK, the main source of these UFP is road traffic (AQEP, 2005); consequently peak concentrations tend to occur near to roads. Journey-time exposures may contribute a disproportionately large fraction of total personal exposures to UFP (Gulliver and Briggs 2005); there is some evidence that it is these short-term peak exposures which are responsible for adverse health effects, with peak exposures of less than 1hour being the most damaging to health (Gullliver and Briggs, 2004; Kleinman et al., 2005), therefore even a short commute can be responsible for a person's daily peak exposure.

An initial scoping study into the number concentrations of particles to which commuters are exposed, and some of the influencing factors, has been conducted in advance of a more systematic campaign. Measurements of particle number concentrations have been made on a number of bus journeys between Manchester city centre and various locations in suburban south Manchester in various seasons and a range of ambient air quality conditions. The overall aim of the study is to assess the inter- and intra-variability of bus journeys on a number of routes, to ascertain whether the biggest differences occur between or within journeys of identical route, and to grasp the most important determinants of exposure. In the absence of particle number standards as well as a limited monitoring network (a single condensation particle counter is situated at Piccadilly Gardens in central Manchester), it is important to determine where and when exposure occurs. There are numerous studies on air pollution concentrations experienced during commuting, although the subject is far from exhausted. Pollutant concentrations have been measured on multiple modes of transport, and several studies have focused on buses (Gomez-Perales et al., 2007; Tainio et al., 2005; Gee and Raper., 1999). Indeed, buses in Manchester were the focus of this latter study, comparing on-board concentrations aboard buses on 2 routes with that of cyclists along the same route. However, with the exception of Kaur et al (2006), these studies tend to concentrate on PM_{10}, $PM_{2.5}$, black smoke or organic pollutants. Previous studies also focus on one or two fixed routes whereas this study encompasses a wider area, measuring along a variety of routes that are representative of bus commuters of south Manchester and which exhibit different fleet and traffic characteristics.

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METHODOLOGY

A pilot study was conducted on buses in and around Manchester between November 2005 and November 2006 in order to elucidate the key factors controlling onboard UFP concentrations and thus inform a more systematic subsequent study. Measurements were taken at various times throughout the day ranging from 8am and 7pm, encompassing both peak and off-peak times. Approximately 20,000 people regularly commute into central Manchester by bus, and bus trips constitute around one quarter of all regular journeys. The study was conducted within the innermost 5km of south Manchester and includes measurements on the busiest bus route in Europe (Oxford Rd) with buses as frequent as every 14 seconds.

Measurements were made using a portable condensation particle counter (TSI P-Trak Model 8525). The P-Trak records particulate number concentrations of diameter nominally between 0.02–1μm, which will be dominated by UFP, at a frequency of 1 Hz thus facilitating the high resolution and fast response requirement needed for short-term exposure assessment. The P-Trak is small enough to be easily transported on and off buses.

For the initial scoping study, a number of potential variables were investigated in order to determine their importance. These were broken down into several individual studies: 1) UFP and NO_x. The relationship between mean on-bus UFP concentrations and urban background ambient air quality represented by NO_x concentrations measured at a central rooftop monitoring site in Manchester (Manchester Town Hall) were compared. 2) Traffic density. UFP were measured on buses serving routes with different traffic characteristics. 3) Bus Chase. To observe whether driving directly behind a bus affects the exposure to UFP. This was realised by measuring the outside air whilst following various buses in a car with a video camera on a fairly quiet section of road. 4) Bus Direction. To investigate if buses carried polluted air from the city centre to the suburbs. UFP were measured on buses travelling on a single route both towards and away from the city centre.

RESULTS AND DISCUSSION

A comparison between measured on-bus UFP and urban background NO_x was deemed appropriate due as both are formed primarily through combustion emissions. Figure 1 demonstrates this relationship with results segregated by bus route (the results are also summarised in Table 1 which illustrates the ratio of UFP in different microenvironments to background NO_x, highlighting the contribution of the local environment to UFP exposure). As shown in Figure 1, a relationship between UFP and NO_x appears here but route is also a significant modulator. The steepest slope is seen on buses operating mainly on Princess Road. This is the busiest road in the study area with approximately 50,000 vehicles per weekday, including considerable light and heavy goods vehicles. The slightest slope belongs to routes 85 and 86 which operate on a pair of complex routes with traffic flows ranging from under 10,000 up to 20,000 per day. The intermediate slope belongs to measurements made on Oxford Road/Wilmslow Road, which is unique in its unusually high frequency and high fraction of buses, typically around 100 per hour, and representing 10% of all vehicles, respectively. In addition, a large proportion of the bus fleet serving Oxford Road are pre-Euro II (pre-1996) buses (approximately 30-50 % compared to a city average of 20%). These results lead us to tentatively conclude that the general level of traffic on a bus's route is a significant determinant of UFP exposure of bus passengers.

Table 1: Indicative order of magnitude of relationships between measured UFP concentrations and central background NO_x

Location	UFP (cm^{-3}) : NO_x ($\mu g\ m^{-3}$)
From home to boarding bus at suburban location (A and B above)	1:100
From alighting bus to city centre workplace (D above)	1:1000
On-bus, Routes 85/6	1:700
On-bus, Oxford Rd/Wilmslow Rd	1:2000
On-bus, Princess Rd	1:3500

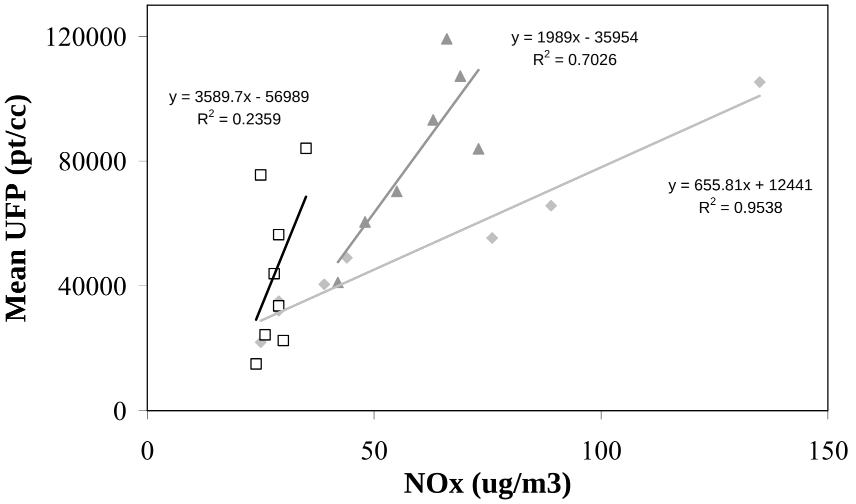

Figure 1: Mean on-bus UFP concentrations for each journey plotted against the NO_x concentration recorded at the Manchester Town Hall site for the corresponding hour. Black-out-line squares = Princess Rd, grey triangles = Oxford Rd, light grey diamonds = routes 85/86.

Many of the measurements indicated a link between high on-bus UFP concentrations and travelling behind a gross polluter such as another bus. The bus chase study indicated that emissions of UFP were much higher from older buses (pre-Euro II, pre-1996). However, once the bus encounter was over the outdoor UFP concentrations fell rapidly – within seconds (see Figure 2-4), whereas post-encounter on-bus concentrations tended to decay much more slowly (Figure 5).

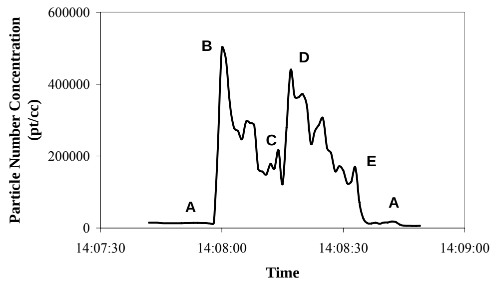

Figure 2

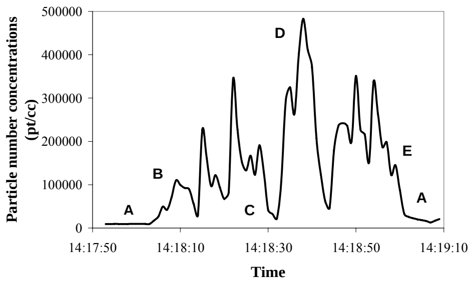

Figure 3

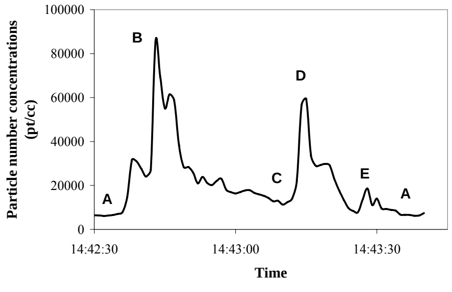

Figure 4

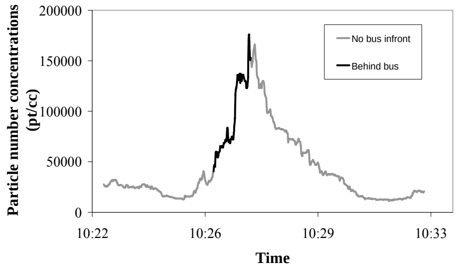

Figure 5

Figures 2-4: Outdoor UFP concentrations measured whilst following a Euro II, Euro I and Euro III bus, respectively. Notation A - on a side road waiting for a bus; B - pulling-out behind a bus; C - idling at a traffic light; D - accelerating on green; E - bus turns off; A - back to clear ahead. Figure 5: the on-bus effects from a 1 minute encounter with a pre-Euro II bus. Concentrations still detected 4 minutes after the polluting bus had been overtaken. The dark line represents the time spent travelling behind a bus.

Earlier surveys suggested that the direction a bus is travelling in (i.e. towards or away from the city centre) could be a significant variable and may influence UFP concentrations on a bus. This notion was supported by observations of a gradient in urban background concentrations between the city centre and suburbs, as well as the presence of higher traffic density and congestion nearer the city centre. Additionally, the inherent time lags associated with a restricted (on-bus) ventilation rate implies that a bus leaving the city centre could trap relatively polluted air inside and that indoor concentrations would decay more slowly than the concentrations outside the bus as it progressed into the suburbs. Repeated same-day measurements were made on a relatively unpolluted (low traffic) section of Manchester's number 85 service. Although a variety of concentrations were measured the results were inconclusive in terms of the influence of direction. We suspect that this issue is a complex one, being intimately linked to the fine details of ventilation and any local sources encountered during each journey.

CONCLUSION

Initial results indicate that the on-bus UFP concentrations may be estimated by reference to urban background NO_x concentrations measured at a fixed point though the local traffic density must also be accounted for. Such background measurements, however, do not capture the way that the bus moves through a variable concentration field. Conclusions were unable to be drawn on whether the direction of movement through this varying background was a significant factor. Work is ongoing to investigate how a GIS-based description of the spatial variation in background pollution can improve the knowledge of this variable.

Local emissions were found to be important in two ways: firstly, the general level of particle emission on the road along which the bus is travelling was found to be important as indicated by the higher UFP:NO_x ratio found on routes with busy traffic; secondly, intermittently high concentrations could be experienced on the bus when it followed gross polluters, particularly older buses. The effect of brief encounters with such buses was extended in time by the lag introduced by restricted ventilation especially older buses, therefore higher concentrations in general would be expected on routes with a higher frequency of buses. High frequency routes are inevitably the routes carrying the most passengers, and therefore the most important for exposure. For these reasons a key element of a subsequent study involved gathering data on the nature of these inter-bus encounters, with a focus on the very high frequency route of Oxford Road.

REFERENCES

Air Quality Expert Panel (AQEP). 2005. Particulate Matter in the United Kingdom. DEFRA.

Buzorius, G., Hameri, K., Pekkanen, J., Kulmala, M. 1999. Spatial variation of aerosol number concentration in Helsinki city. Atmos Environ. 33, 553-565.

Gee, I. L., Raper, D. W. 1999. Commuter exposure to respirable particles inside buses and by bicycle. Sci Total Environ. 235, 403-405.

Gómez-Perales, J. E., Colvile, R. N., Fernández-Bremauntz, A. A., Gutiérrez-Avedoy, V., Páramo-Figueroa, V. H., Blanco-Jiménez, S., Bueno-López, E., Bernabé-Cabanillas, R., Mandujano, F., Hidalgo-Navarro, M., Nieuwenhuijsen, M. J. 2007. Bus, minibus, metro inter-comparison of commuters' exposure to air pollution in Mexico City. Atmos Environ. 41, 890-901.

Gulliver, J., Briggs, D. J. 2005. Time-space modelling of journey-time exposure to traffic-related air pollution using GIS. Environ Res. 97, 10-25.

Gulliver, J., Briggs, D. 2004. Personal exposure to particulate air pollution in transport microenvironments. Atmos Environ. 38, 1-8.

Hitchins, J., Morawska, L., Wolff, R., Gilbert, D. 2000. Concentrations of submicrometre particles from vehicle emissions near a major road. Atmos Environ. 34, 51-59.

Holgate, S. T., Koren, H. S., Samet, J. M. & Maynard, R. L. (ed). 1999. Air Pollution and Health. San Diego, California: London Academic Press.

Kaur, S., Clark, R. D. R., Walsh, P. T., Arnold, S. J., Colvile, R. N., Nieuwenhuijsen. 2006. Exposure visualisation of ultrafine particle counts in a transport microenvironment. Atmos Environ. 40, 386-398.

Kleinman, M. T., Hamade, A., Meacher, D., Oldham, M., Sioutas, C., Chakrabarti, B., Stram, D., Froines, J. R., Cho, A. K. 2005. Inhalation of concentrated ambient particulate matter near a heavily trafficked road stimulates antigen-induced airway responses in mice. A&WMA. 55, 1277-1288.

Pekkanen, J., Kumala, M. 2004. Exposure assessment of Ultrafine particles in epidemiological time-series studies. Scand J. Work Environ Health. 30(2), 9-18

Tainio, M., Tuomisto, J. T., Hanninen, O., Aarnio, P., Koistinen, K. J., Jantunen, M. J., Pekkanen, J. 2005. Health effects caused by primary fine particulate matter ($PM_{2.5}$) emitted from buses in the Helsinki Metropolitan area, Finland. Risk Analysis.

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COMPARING URBAN PARTICLE EMISSION FLUXES MEASURED ON THE BT TOWER (LONDON) WITH MEASUREMENTS FROM MANCHESTER AND EDINBURGH

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ABSTRACT

Turbulent particle number emission fluxes have been measured directly using the eddy covariance technique in three UK cities as part of the NERC SASUA project (Edinburgh 1999-2001), the NERC CityFlux project (Manchester 2005-6) and the NERC/BOC Foundation REPARTEE project (central London, 2006). These campaigns took place over several different seasons and location types. Analysis of the data indicates that in all seasons and cities the particle number fluxes exhibit a clear diurnal cycle with an early afternoon peak that is closely related to the diurnal sensible heat flux cycle. At some sites there was an additional marked correlation with vehicular traffic activity. There was some dependence of flux upon wind direction, with an observable relationship between high particle number fluxes and areas of heavy urbanisation. The processes that determine variation in particle number fluxes are discussed.

1. INTRODUCTION

Aerosol particles influence many things in the world around us from obvious visibility issues to climate forcing to human health. COMEAP (2001), among others, have acknowledged a noticeable effect of particles on human mortality and morbidity rates. Urban areas have many emission sources of aerosol particulates including densely trafficked roads and dense industrial and commercial zones. As people both live and work in urban areas it is of particular importance to understand the atmospheric dispersion of particles in these areas. Measurements of the number concentrations of aerosols in the urban background and at street level have been performed for large cities in the past (e.g. Wehner & Wiedensohler, 2003, Hussein et al., 2004) but these concentrations are dependent upon the rate at which the urban canopy is ventilated, i.e. the vertical flux from the urban canopy. Urban aerosols may be carried away from the city centre towards suburban residential or agricultural areas, and into the regional background, having impacts on terrestrial environments, the radiative properties of the atmosphere and an influence on cloud formation and rainfall. Dorsey et al. (2002) investigated the process of urban ventilation in the SASUA (Sources and Sinks of Urban Aerosol) project above the busy city of Edinburgh, Scotland by directly measuring particle number emission fluxes from the city centre using the eddy covariance technique (Stull, 1988). CityFlux is a multi-site project of field campaigns conducted by the University of Manchester and Centre for Ecology and Hydrology in Edinburgh. A key element of this project is the direct measurement of particle fluxes using the same technique and similar instrumentation to that of Dorsey et al. (2002) to observe the processes of ventilation of the urban canopy in a different city and over different seasons, in Manchester. London measurements were part of the REPARTEE (Regent's Park and Tower Environmental Experiment) project led by the University of Birmingham. This paper aims to review the basic features of the flux data and compare the Edinburgh, Manchester and London campaigns.

2. METHODOLOGY

In London, measurements were made throughout October 2006 ("Aut06") from a mast atop of the BT Tower. The BT Tower mast was situated at a height of 189 m above ground level and accommodated an inlet to a TSI 3010 condensation particle counter (CPC); the pulse output was logged and combined with data from a co-located Solent R3 sonic anemometer to provide 20 Hz fluxes. The BT Tower, formerly known as The Post Office Tower, is a tall slender cylindrical building in central London (Figure 1). The BT Tower campaign ran concurrently with a particle characterisation measurement site in the centre of Regent's Park, a large parkland area approximately 1 km north-west of the tower. The results from this area are not discussed at this conference but will be published in future papers by the author.

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Figures 1, 2 and 3: London, Manchester and Edinburgh (measurement site denoted by blue circle)

In Manchester, measurements were conducted over three periods: “Sum05” June - August 2005, “Win06” February - March 2006 and “Sum06” May - June 2006. Measurements were made with a similar arrangement utilising a TSI 3010 in Sum05 and TSI 3025a in Win06 and Sum06, using a slender mast on top of Manchester’s sixth tallest building, the Portland Tower, at a height of 90m above street level. The location of Portland Tower is in the heart of the city centre (Figure 2), surrounded on all sides by dense urban fabric and streets with busy traffic. There are four buildings taller than the Portland Tower that lie in the north or north-west fetch between 0.25 and 1 km away. Very little data was recorded in this direction, which may be due to sheltering or flow diversion due to these buildings.

Both the London and Manchester campaign setups were adapted from the system deployed above the city of Edinburgh through October - November 2000 (“Aut00”) using a TSI 3760 CPC. In this campaign the aerosol flux data was obtained from the top of the Nelson Monument, a narrow circular stone tower in the east end of the city centre (Figure 3), at a measurement height of 67m above street level, in an area where the mean building height is 15m. The Nelson Monument is surrounded by heavy urban land, residential areas and parkland; these provide a good contrast between the emission properties of these different types of land cover during different wind directions. For more details of the Edinburgh campaign see Dorsey et al., (2002).

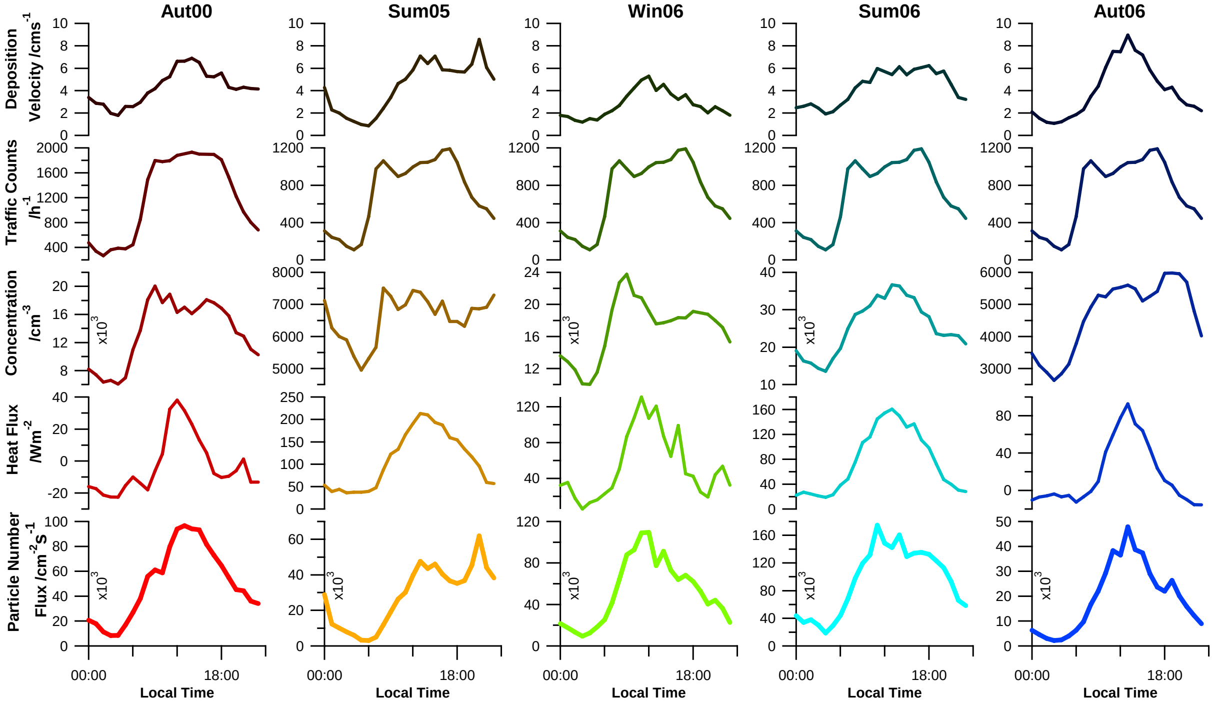
3. RESULTS AND DISCUSSION

An important initial consideration when comparing different seasons is the difference in the meteorological conditions. Table 1 shows the average wind speed and temperatures for each of the periods as well as sunrise and sunset times. On average, the wind speeds measured at Edinburgh and London were higher than in Manchester. This may be due to the BT Tower being twice as high as the Portland Tower and measurements were made in a generally windy period in Edinburgh, as confirmed by local airport met data.

Table1. Meteorological conditions for all campaigns

Campaign	Average Wind Speed ms^{-1}	Average Temperature °C	Sunrise Local time	Sunset Local time
Autumn 00 Edinburgh	6.46	7.1	08:06 to 07:48	17:46 to 16:05
Summer 05 Manchester	4.20	19.5	04:47 to 05:15	21:39 to 21:15
Winter 06 Manchester	5.15	7.3	07:29 to 05:49	17:17 to 18:39
Summer 06 Manchester	4.84	16.1	05:33 to 04:48	20:40 to 21:26
Autumn 06 London	7.90	16.1	07:04 to 06:52	18:34 to 16:36

The main query for these campaigns is how particle number fluxes vary, both temporally and spatially. The last row of figure 4 shows the clear diurnal cycle of particle number flux for all the campaigns. All five campaigns follow a similar flux cycle, rising rapidly in the morning till around midday with a gradual decline in the evening with the lowest dip occurring in the early morning. For Sum05 the particle flux peaks unexpectedly between 21:00 and 22:00 local time. This is an area under further investigation to determine the cause; the peak is related to the occurrence of WNW winds and possible explanations include excess particles released from nearby restaurants or other local sources. The sizes of the fluxes cannot be directly compared, due to different counters being used at different heights. However, Win06 and Sum06 employed identical set-ups with average particle fluxes for each hour in summer typically 1.5 – 2 times those in winter. This is in contrast to Dorsey et al. (2002) who found fluxes reduced in early summer compared to autumn/winter in the SASUA project. The reasons for these discrepancies are under investigation.

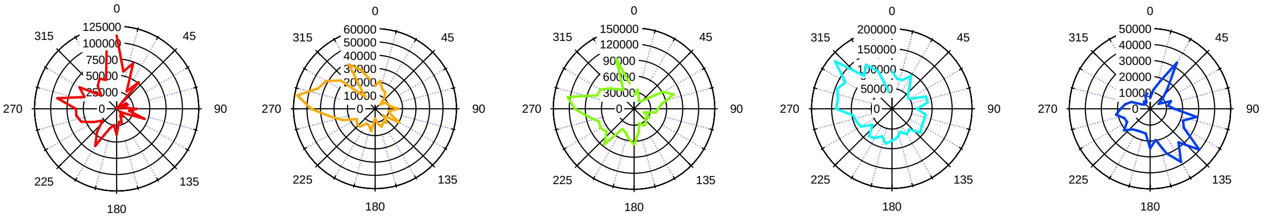


Figures 4: Average diurnal deposition velocity, nearby traffic counts, particle number concentration, sensible heat flux and particle number flux for Edinburgh (Aut00), Manchester (Sum05, Win06 and Sum06) and London (Aut06) campaigns.

The deposition velocity and sensible heat flux, as shown in the first and fourth rows of figure 4, also have prominent diurnal cycles. All three of the Manchester campaigns have generally higher heat fluxes than both Edinburgh and London. This indicates that although all five heat flux cycles are dominated by the cycle of the sun, the Manchester campaigns are also influenced significantly by another factor: the urban heat storage of the city. The measurement point in Manchester was much closer to the surrounding city than in both Edinburgh and London so the influence of the heat radiating from the city appears to have had a much larger contribution in Sum05, Win06 and Sum06 than in Aut00 and Aut06. The most prominent feature of the deposition velocities is that Aut00 has a much more prominent and high peak at 1pm and drops lower than most of the other campaigns at night, most likely due to the increase in wind speeds at this height.

The times of peaks in the traffic for all campaigns have a direct correlation with the concentrations found at the measurement site. This increase is not seen instantaneously in the particle flux: for all campaigns except Aut06 the morning peak in the traffic around 8am is echoed an hour later in the particle flux as a small shoulder before the main large peak. In Aut06 this shoulder is not seen due to the lack of influence of the traffic in the city on the flux at such an elevated height. In all campaigns the heat flux seems to influence the particle flux greatly; all five peaks in particle flux coincide with the peak in heat flux and shoulders in the heat flux are again echoed in the particle flux. These correlations to traffic and heat flux indicate that thermally-generated turbulence alongside turbulent wind shear eddies are more essential than emission production to particle flux levels.

There were low quantities of data in certain directions that had to be considered when looking at flux levels to prevent misguided conclusions. In Aut00 (figure 5a) the highest flux levels appear to have occurred in northerly directions but there is very little data from 330° through north to 160° for Aut00 so this high flux value may not be representative; the more typical peak is in the westerly directions. The low fluxes in E, SE and S winds may be related to the parkland in these source areas (Figure 3). Figures 5b, c and d demonstrate the significantly higher flux in the west-north-west directions over all three campaigns in Manchester. Although the urban fabric is slightly denser in the WNW direction, it is currently unclear as to why fluxes are so much higher from this direction as emission sources in central Manchester are generally even spatially (Figure 2). Aerosol compositional measurements made in the summer 2006 campaign, as well as further micrometeorological analysis, may aid in identifying the cause of this enhanced flux.



Figures 5a, b, c, d and e: Average particle number flux versus wind direction for Edinburgh (Aut00), Manchester (Sum05, Win06 and Sum06) and London (Aut06) campaigns.

Looking at the Aut06 campaign in London it appears that the highest particle number fluxes are found in south-easterly winds, however, this data is biased by very large fluxes recorded over 2 days with atypical meteorology (low nocturnal winds, inversions and high ground-level concentrations). There was very little data available in NW, N and NE winds and so no firm conclusions about the influence of wind direction can be drawn. In conclusion, in all the campaigns there is an observable relationship between high particle number fluxes and areas of heavy urbanisation (city centres). Equally, all wind directions giving comparatively low mean fluxes coincide with residential districts and local parkland.

4. CONCLUSIONS

Particle fluxes have been measured at urban tower sites in three different UK cities by eddy covariance. Similarities include consistent diurnal cycles closely resembling the diurnal cycle in sensible heat flux, peaking in the middle of the day or early afternoon. Dependencies on wind direction have been identified, but potential differences between sites due to height or location cannot be simply interpreted due to in part to differences in instrumentation and the lack of longer-term data needed to cover a range of meteorological scenarios. Nevertheless other supporting datasets not presented here will aid the ongoing programme of analysis.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

COMEAP, 2001. Report on long-term effects of particles on mortality. Committee on the Medical Effects of Air Pollutants. HMSO, London.

Dorsey, J.R., Nemitz, E., Gallagher, M.W., Fowler, D., Williams, P.I., Bower, K.N., Beswick, K.M., 2002. Direct measurements and parameterisation of aerosol flux, concentration and emission velocity above a city. Atmos. Environ. 36, 791-800.

Hussein, T., Puustinen, A., Aalto, P.P., Mäkelä, J.M., Hämeri, K. and Kulmala, M., 2004. Urban aerosol number size distributions. Atmospheric Chemistry and Physics, 4: 391-411.

Stull R.B., 1988, An Introduction to Boundary Layer Meteorology, Kluwer Academic Publishers, Dordrecht, The Netherlands

Wehner, B. and Wiedensohler, A., 2003. Long term measurements of submicrometer urban aerosols: statistical analysis for correlations with meteorological conditions and trace gases. Atmospheric Chemistry and Physics, 3: 867-879.

PM10, PM2.5-BOUND PAHS AND HEAVY METALS IN AN INDUSTRIAL AREA IN NORTHERN GREECE

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ABSTRACT

Ambient PM10 and PM2.5 samples were collected in an industrialized urban area of northern Greece (Thessaloniki). The area is occupied by heavy industry including cement, metallization, electrostatic polishing, lime burning facilities, a stone pit as well as is nearby the ring road of the city which is characterized by heavy local traffic. 16 EPA PAHs and 9 trace elements, associated to ambient PM10 and PM2.5, were examined. The measurements were conducted in two weekly periods during winter and summer seasons. For the PM10 and PM2.5 sampling Teflon filters were used. PAHs were determined by Gas Chromatography coupled to a Mass Spectrometry detector (GC-MS), whereas trace elements by Atomic Absorption Spectrometry (AAS). The results of this study are compared on a seasonal basis giving a well estimated profile regarding the concentrations during the sampling periods.

Keywords: PM10, PM2.5, urban air pollution, polycyclic aromatic hydrocarbons, heavy metals.

1. INTRODUCTION

Industrial activities are the primary suspect when referring to air quality deterioration. Insufficient planning and disordered building resulted in the close proximity of dwellings and industries. This raised great concerns regarding the inhabitant's health and well being. Airborne particulate matter in urban air has been identified as the major concern, especially for the significant effects on human health. A large number of epidemiological studies on particulate matter have highlighted the fact that particles with aerodynamic diameter smaller that 10 μm induces significant health effects (Valavanidis et al, 2006). This due to the adsorption of organic and inorganic substances on the particulate matter, not only on coarse but also on fine particles.

Particles consist of elemental carbon core and absorb a large number of substances, such as heavy metals and various organic and inorganic compounds. Organic compounds are volatile or semi-volatile, such as polycyclic aromatic hydrocarbons (PAHs), phenols etc., material of biologic origin and ions (sulfate, nitrate), reactive gases (ozone, peroxides) and inorganic components (SiO_2, Fe_2O_3 etc.) (Valavanidis et al, 2006). PAHs are widespread semi-volatile organic compounds consisting of two or more benzene rings in linear, angular or cluster arrangements and by definition containing only carbon and hydrogen. PAHs are formed during the incomplete combustion of organic material, such as, coal, oil, wood and gasoline fuel. Concerns about the levels of these compounds in the environment are well justified since some of them are known to be carcinogens (IARC, 1991).

Industrial facilities, waste incineration and fossil fuel burning have been considered as the primary sources of anthropogenic heavy metals and other trace elements emissions. Trace elements are known to be involved in the generation of reactive oxygen species and hydroxyl radicals. Some of these elements, such as As, Pb, Cd, Ni, Cu, and Cr are interesting due to their toxic effects while others such as Fe, Ca, Ba, and Mn are mainly connected to the resuspended soil (Lopez J.M. et al, 2005). According to WHO guidelines (2000) limit values for As, Ni and V regulated at 1000 ng/m^3 while for Cd and Mn at 5 and 150 mg.m^3, respectively. Under certain conditions these metals can cause damage to significant biomolecules in the lungs (Wiseman et al, 1996).

The purpose of this study is to assess the air quality of an industrial area in the city of Thessaloniki. PM10 and PM2.5 concentrations as well as their PAHs and trace element content were determined at both warm and cold periods in order the seasonal variation to be evaluated.

2. METHODOLOGY

Ambient PM10 and PM2.5 samples were collected from an industrialized urban area at northern Greece (Thessaloniki). Sampling was conducted in two weekly periods during winter (from 22/2 to 29/2/2005) and summer (from 9/4 to 15/4/2004) seasons. Two sampling sites was chosen. Site 1 was located near a heavy trafficked ring road and in small distance from the industrial facilities of Thessaloniki such as a cement and a lime industry. Site 2 was located at the south part of the examined area. Both PM10 and PM2.5 were collected at Site 1 while Site 2 was chosen only for PM10 collection.

PM10 and PM2.5 were determined gravimetrically. Particle- bound PAHs were ultrasonically extracted with dichloromethane and extracts were cleaned up through silica gel cartridges. 18 PAHs were analyzed using Gas Chromatography coupled to mass spectrometry detector (GC-MS). For the heavy metals and trace elements analysis Atomic Absorption Spectrometry was used (AAS).

3. RESULTS AND DISCUSION

The mean concentrations of PM10 and PM2.5 during the summer and winter period as well as the corresponding limit values set by EU (1999/30/EC) are shown in Figure 1. PM10 levels were significantly higher during the summer period exceeding the EU daily limit of 50 $\mu g/m^3$. Similar PM10 values have also been found for the center of Thessaloniki for the years 1997-1998 (Voutsa et al, 2005). Elevated summertime values might be indicative of the great resuspension of soil particles as well as the suspension from the stored piles of the cement industry, while the strong north winds during winter enhanced the dispersion of the particulates. The same seasonality was also observed for PM2.5.

Mean PAHs concentrations on PM10 and PM2.5 for the two sampling seasons are presented in Figures 2 and 3, respectively. Benzo(a)pyrene (BaP) exhibited higher concentrations during winter period for both PM10 and PM2.5 (0.45 ng/m^3 and 0.34 ng/m^3, respectively). A similar pattern was also observed for the total PAHs. This seasonality was expected due to the more intensive emissions from traffic, domestic heating and other combustion sources in the cold period. However, no exceedance of the annual limit value of 1 ng/m^3 (2004/107/EC) was observed. A comparison with relevant data from other urban sites showed that BaP concentrations observed in this study were well within the range of the reported values for the area of Kozani, Greece, (0.12 ng/m^3) in 2001 (Kalaitzoglou M. et al., 2004), while total PAH were similar to those reported for an urban site in UK (Smith D.J. et al, 1996). 4-ring (Fa, Py, B[a]A and Chr) and 6-ring (I[cd]P and B[ghi]P) PAHs distributed mainly on PM10 (18.23% and 29.54%, respectively) as shown in Figure 4. A bimodal distribution was observed for the 5-ring PAHs (BaP, B[a,h]A, B[k]F) with equal partitioning on both PM10 and PM2.5.

Figures 5 and 6 show the mean concentrations of the heavy metals and the other elements detected. As and Se levels were below the detection limit. Fe and Ca presented elevated concentrations during the warm period for both PM10 and PM2.5, indicating the greater resuspension of soil particles during the dry summer months. Similar seasonal variability for crustal elements has also been found at sites located at the northwest part of Greece by Petaloti et al (2006). On the other hand, Ti exhibited greater levels on winter period, a trend that is common for eastern Europe regions (Gullu et al, 2005). Pb, V and Cd are detected only in the winter period with mean concentrations for PM10 (28.02, 29.21 and 1.61 ng/m^3, respectively), close to those observed in an urban area of Athens (Mantis et al, 2005).

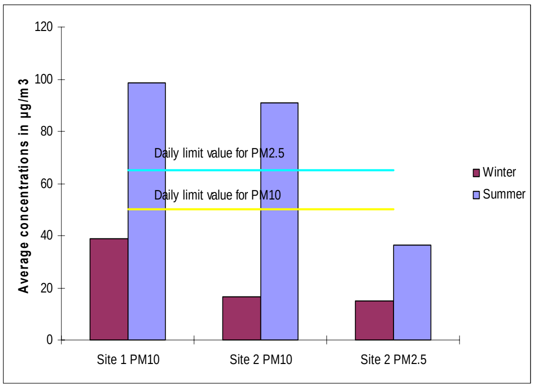

Fig1. Average concentrations of PM10 and PM2.5 in summer and winter period

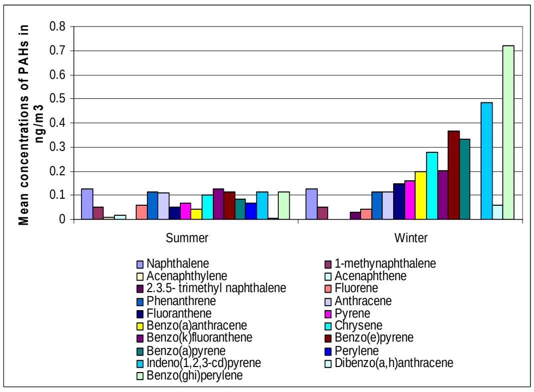

Fig2. Mean concentrations of PM2.5 bound PAHs in both summer and winter period.

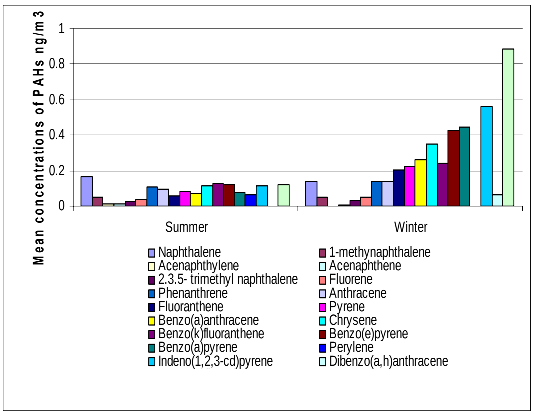

Fig3. Mean concentrations of PM10 bound PAHs in both summer and winter period.

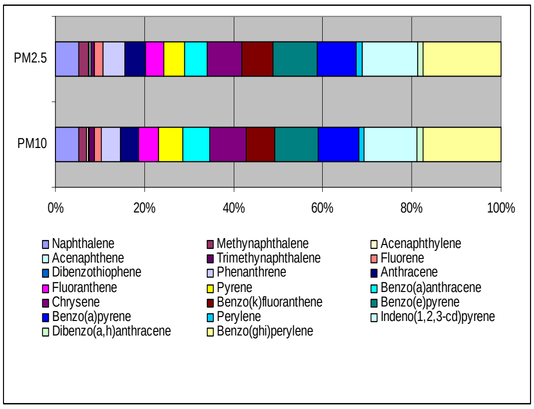

Fig4. Mean profiles of ambient PM10 and PM2.5.

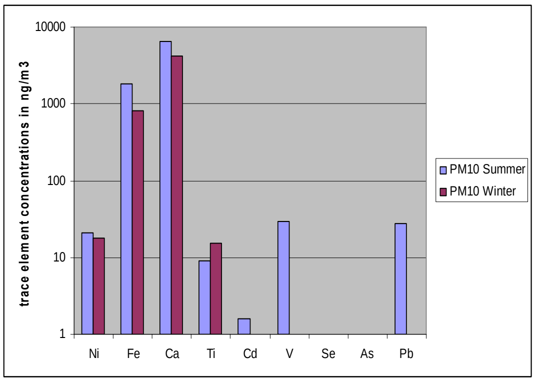

Fig5. Seasonal mean concentrations of selected trace elements in PM10.

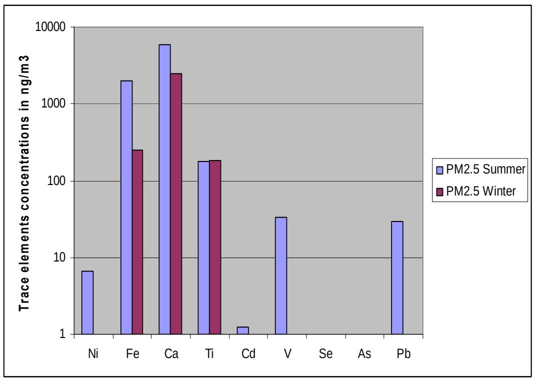

Fig6. Seasonal mean concentrations of selected trace elements in PM2.5.

4. CONCLUSIONS

Summarizing, episodes of high PM10 were found mainly during summer periods exceeding the daily limit value of 50 μg/m^3 same as for the center of Thessaloniki in 1997-1998. These values are mainly associated with vigorous winds during the winter sampling period, enhancing the dispersion of the particulate matter.

In general, particle- bound concentrations are higher in the PM10 fraction for the winter period due to the low temperatures not causing evaporation of the substances. Moreover, BaP concentrations are higher in the winter period for the PM10 and in PM2.5 for the warm period, but in any case, they do not exceed the annual limit of 1 ng/m^3. The contribution of carcinogenic PAHs is greater in coarse and fine fraction during winter period.

Finally, trying to assess the Thessaloniki 's industrial area air quality from inorganic point of view, it can be concluded that this area corresponds to a moderately polluted city with atmospheric trace elements under the current air quality guidelines.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Directive 1999/30/EC of European Parliament for PM10 in ambient air.

Directive 2004/107/EC of the European Parliament and of the council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air.

IARC, International Agency for Research on Cancer. 1987-1991. IARC Monographs on the evaluation of carcinogenic risks to humans, Lyon, vols. 43-53.

Gullu G.H., Olmaez I., Aygun S., Tuncel G. 1998. Atmospheric trace element concentration over the Eastern Mediteranean Sea: Factor affecting temporal variability. Journal of Geophysical Research 1013, 21943-21954.

Kalaitzoglou M., Terzi E., Samara C. 2004. Patterns and sources of particle- phase aliphatic and PAHs in urban and rural sites of western Greece. Atmospheric Environment 38, 2545-2560

Lopez J.M., Callen M.S., Murillo R., Garcia T., Navarro M.V., de la Cruz M.T. Mastral A.M. 2005. Levels of selected metals in ambient air PM10 in an urban site of Saragosa (Spain). Environmental Research 99, 58-67.

Mantis I., Samara C., Kouimtzis Th., Grivas G., Kamouta V., Karamperi A., Protonotarios V., Manalis N., Moutsatsou A., Chaloulakou A., Spyrellis N. (2003) "Chemical composition of PM10 in the atmosphere of Athens, Greece" Proceedings of the 8th International Conference on Environmental Science and Technology. Lemnos island, Greece, 8-10 September 2003.

Petaloti C., Triantafyllou A., Kouimtzis Th., Samara C. 2006. Trace elements in atmospheric particulate matter over a coal burning power production area of western Macedonia, Greece. Chemosphere 65, 2233-2243.

Smith D.J.T and Harrison Roy. 1996. Concentration, trends and vehicle source profile of polynuclear aromatic hydrocarbons in the UK atmosphere. Atmospheric Environment 30 (14), 2513-2525.

Valavanidis Athanasios, Fiotakis Konstantinos, Vlahogianni Thomais, Bakeas B. Evangelos, Triantafillaki Styliani, Paraskevopoulou Vasiliki, Dassenakis Manos. 2006. Characterization of atmospheric particulates, particle- bound transition metals and polycyclic aromatic hydrocarbons of urban air in the centre of Athens (Greece). Chemosphere 65, 760-768.

Voutsa D., Samara C., Kouimtzis Th., Ochsenkühn K. 2002. Elemental composition of airborne particulate matter in the multi-impacted area of Thessaloniki, Greece. Atmospheric Environment 36, 4453-4462.

WHO Air Quality Guidelines for Europe. 2000. WHO regional Publications Eur Ser No. 91. Regional office for Europe, Copenhagen, Denmark

Wiseman H, Halliwell B. 1996. Damage to DNA by reactive oxygen and nitrogen species: role in inflammatory disease and progression to cancer. Biochemical Journal 313, 17-29.

POLAR ORGANIC COMPOUNDS IN THE URBAN ATMOSPHERE OF TWO LARGE CITIES FROM THE NORTH AND SOUTH OF EUROPE

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ABSTRACT

Polar organic species were quantified to characterize the composition of fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) aerosols collected at roadside and background sites in Oporto (Portugal) and Copenhagen (Denmark) during summer and winter campaigns. As a general trend, both cities exhibited roadside average concentrations higher than their correspondent urban background levels. The polar organics were more abundant in the fine fraction, exhibiting a seasonal pattern with high winter concentrations and low summer loads. Aerosols from both cities showed typical distributions of *n*-alkanols and *n*-alkanoic acids in the ranges C_{12}-C_{28} and C_8-C_{28}, respectively. The $<C_{20}$ homologues, usually attributed to kitchen emissions, vehicular exhausts and microbial origins, dominated the fatty acid fraction. Linear alcohols were mainly represented by higher molecular weight homologues from vegetation waxes. Molecular tracer species for wood smoke were found to contribute significantly to the urban aerosol, especially in winter.

1. INTRODUCTION

Most urban atmospheres contain high levels of particulate matter (PM) caused by road traffic and other anthropogenic activities. Besides material damage, atmospheric PM influences radiative forcing of climate and affects human health, contributing to diseases of the respiratory and circulatory systems (Pope et al., 2004) as well as lung cancer.

Most studies on the organic fraction of atmospheric particulate matter have been dedicated to qualitative and quantitative aspects of the apolar or hydrocarbon fraction, particularly on their polycyclic aromatic hydrocarbon content due to their carcinogenic and mutagenic characteristics (Kavouras and Stephanou, 2002; Wang et al., 2006). However, numerous polar organic compounds have been detected in emissions of fine particulate matter from a multiplicity of sources ranging from anthropogenic activities (e.g. power plants, vehicular circulation, meat cooking operations and biomass burning) to natural sources such as biogenic emissions.

To better understand the emissions and atmospheric processes influencing the molecular characteristics of atmospheric PM in urban environments, a comparative analysis of the aerosol organic composition in two size fractions ($PM_{2.5-10}$ and $PM_{2.5}$) was performed in two very different climatic and geographic regions in Europe (Oporto, Portugal and Copenhagen, Denmark). This paper will present the relative strengths of major emission sources, the impact of regional transport on ambient PM levels, the influence of human activities patterns on molecular composition and a comparison between the roadside concentrations of polar organic constituents and at the nearby urban background monitoring sites.

2. METHODOLOGY

To evaluate seasonal traffic contributions two one-month long sampling campaigns were performed, one in winter and another in summer. Two sampling sites were selected (roadside and urban background site), where coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) aerosol particles were daily collected on pre-fired quartz fibre filters with high volume samplers. Samples were extracted with dichloromethane, fractionated into different organic parts according to their polarity and analysed by gas chromatography–mass spectrometry.

3. RESULTS AND DISCUSSION

The major polar organic species present in Oporto and Copenhagen aerosols were *n*-alkanols, sterols, anhydrosaccharides, and *n*-alkanoic, *n*-alkenoic and dicarboxylic acids. These compounds exhibited a seasonal pattern with high winter concentrations and low summer loads. The winter concentration augment could have been associated with higher pollutant emissions, but also with the existence of lower winter temperatures that promoted the reduction of mixing heights and the existence of inversion layers, leading to

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poorer dispersion, diminishing the dilution factors and conducting to an increase of atmospheric pollutant concentrations. As a general trend, both cities exhibited roadside average concentrations higher than their correspondent urban background levels.

To investigate weekly trends in the chemical composition on these polar organic species, the average weekend concentrations were compared with those of working days (Table 1). Although Copenhagen presented no clear distinction between weekend and working days, Oporto in general observed a weekend decrease of polar compounds concentrations, possibly due to emissions from sources with weekly activity patterns such as motor vehicle traffic.

Table 1. Weekend (WE) and working days (WD) total concentrations of polar organic compounds (ng m^{-3}).

Fraction	Site	**OPORTO**				**COPENHAGEN**			
		Summer		**Winter**		**Summer**		**Winter**	
		WD	WE	WD	WE	WD	WE	WD	WE
Coarse	R	39.4	26.2	49.6	40.6	74.3	46.5	97.8	91.1
	UB	27.9	18.4	39.2	44.5	46.0	50.9	34.1	52.1
Fine	R	99.5	83.1	710.0	519.2	67.5	86.6	327.9	454.6
	UB	126.7	97.2	561.4	565.0	112.9	83.8	262.9	343.4

Aerosols from both cities showed typical distributions of *n*-alkanols and *n*-alkanoic acids in the ranges C_{12}-C_{28} and C_8-C_{28}, respectively. The distributions of *n*-alkanols do not differ substantially between summer and winter, nevertheless the very different concentrations observed in each season (Figure 1a). In Oporto and Copenhagen, the majority of the *n*-alkanol mass was concentrated in the fine aerosol fraction, for which a seasonal pattern was observed with increased concentrations and higher carbon preference index (CPI) values in winter. The average of winter/summer concentration ratios was around 2, which may reflect an enhanced microbial component during the colder season since the wax constituents have a less pronounced percentual contribution to the aerosol content in this period of the year. During summer an increment in anthropogenic inputs was observed, thus lowering the global CPI ratios. The homologue that contributed most to this fact was the C_{15}, which has been detected in emissions from charbroilers and meat cooking operations (Rogge et al., 1991). Percentually, the *n*-alkanols wax content of the fine fraction increased from around 30% in winter to 40% in summer for both the Portuguese and Danish samples. Although presenting low concentrations, the coarse aerosol was dominated by the wax components C_{26} and C_{28}, which contributed to the very high CPI values of this size fraction. Since primary emissions, such as leaf abrasion and biomass burning, originate mostly fine particles, the presence of these constituents in larger aerosols may have been related to adsorption processes onto coarse dust particles. The average chain length (ACL) index of *n*-alkanols apparently decreased in winter for the fine fraction, although it has changed only very slightly between periods for the coarse fraction. This suggests that the incorporation processes into the atmospheric particles reflected the major seasonal changes in the wax constitution of the predominant vegetation, occurring mostly in the small aerosol sizes.

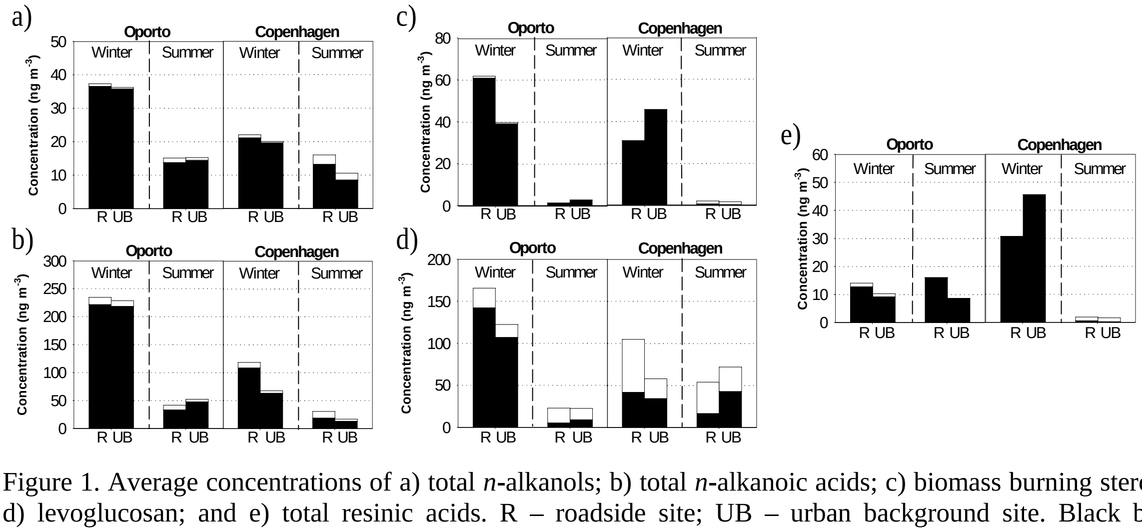

Figure 1. Average concentrations of a) total *n*-alkanols; b) total *n*-alkanoic acids; c) biomass burning sterols; d) levoglucosan; and e) total resinic acids. R – roadside site; UB – urban background site. Black bars correspond to fine fraction and white bars to coarse fraction.

Fatty acids were the most abundant components detected in the polar organic fraction (Figure 1b). Low molecular weight *n*-alkanoic acids, such as palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) were the most abundant constituents in all Portuguese and Danish samples. The dominance of *n*-carboxylic acids $<C_{20}$, especially during the wintertime, with ratios $\geq C_{22}/<C_{20}$ under 1 and C_{max} at C_{16} and C_{18} reflected large microbial contributions, which are usually found in urban aerosols. The average ACL values found both in Oporto and Copenhagen were similar to the fatty acid wax content of conifer vegetation in coastal areas (Alves et al., 2001). The wax portions, although small in total fatty acid contributions, presented the highest concentrations in winter, what was probably due to the higher wax content in dead leaves and also wind abrasion. It has been reported that the dead leaf fatty acid wax content was 5 times higher than the correspondent for the green leaves (Rogge et al., 1991). Oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids are often used as an indication of the aging of the aerosols. The higher ratios of stearic acid to unsaturated C_{18} acids obtained in Oporto during summer indicated the presence of more aged aerosols. Curiously, the fine aerosols from Denmark presented the same pattern, although the coarse fraction exhibited a winter to summer decrease, suggesting particle size emission dependence and atmospheric processing. The $C_{18:0}/C_{16:0}$ ratio is normally used as a qualitative tool for source assessment. In Oporto and Copenhagen, the $C_{18:0}/C_{16:0}$ ratios were generally comprised between 0.5 and 1, with higher winter values, indicating the contribution of cooking operations and road dust (Rogge et al., 2006 and references therein). Nevertheless, a stronger input of vehicular emissions to the fine fraction of the Danish aerosol was observed during summer.

The presence of cholesterol in aerosol samples could be attributable both to meat cooking operations (Rogge et al., 1991) and particles generated by sea spray, deriving from secretions of aquatic organisms (Alves et al., 2006). During summer, both cities presented only cholesterol in the larger particles, supporting the sea spray origin hypothesis, whereas in winter this constituent predominated in the fine fraction with average concentrations close to 2 ng m^{-3}. Two other sterols existent in plant leaves and emitted to the atmosphere via biomass burning, β-sitosterol and stigmasterol, were also detected, mostly in the fine fraction (Figure 1c). The total concentration of these two sterols was much higher in winter than in summer for both cities, reflecting probably the combustion of biofuel in residential stoves.

Three anhydrosugars (levoglucosan, mannosan and galactosan) were identified. Levoglucosan was the most abundant, while galactosan was detected only in some samples. These compounds are formed exclusively via pyrolysis of cellulose and hemicelluloses, making them highly specific tracers for biomass burning. Their average concentrations decreased from winter to summer (Figure 1d), indicating a reduction in the amount of smoke particles. Average ratios of levoglucosan to mannosan of 5-6 and 7-11 were obtained in Oporto for the fine and coarse fractions, respectively, whereas in Copenhagen, the values were in the range of 5 to 8 for the fine aerosol. The coarse fraction presented ratios ranging from approximately 10 during summertime to variable quotients between 11 and 19 in wintertime. Based on average ratios of levoglucosan to mannosan in wood smoke from coniferous trees of 5.4±3.7 (Oros and Simoneit, 2001), the aerosol composition in Oporto was consistent with greater contribution of softwood vegetation. In Copenhagen, it seems that there was a major smoke contribution from coniferous species during the hot season. However, in winter the coarse aerosol seems to have been mainly affected by hardwood smoke, based on literature values of levoglucosan/mannosan ranging from 19-26 (Fine et al., 2004).

Besides sterols and anhydrosugars, resinic acids were other molecular tracers of biomass combustion also detected in the urban aerosol samples (Figure 1e), particularly dehydroabietic and pimaric acids. During the wintertime, these constituents in Copenhagen were about 5 and 2 times higher, respectively for the urban background and roadside stations, in comparison with Oporto. In the Portuguese city, the ratio of dehydroabietic to pimaric acid presented an average value of 5 for both the roadside and urban background stations, remaining constant between seasons. This was in accordance with values between 1 and 8 reported in the literature for organic aerosols from biomass burning of temperate climate conifers (Oros and Simoneit, 2001). In Copenhagen, an average ratio of 4 was obtained for the wintertime, while the summer samples produced values of 9.6 and 15.8, respectively, for the roadside and urban background stations. This variation was indicative of diverse biomass burning sources and/or different atmospheric circulation mechanisms.

Aliphatic dicarboxylic acids in organic aerosols can have several different sources including primary emissions from biomass burning and fossil fuel combustion, as well as photochemical oxidation of organic precursors of both anthropogenic and biogenic origin. In general, both cities exhibited the highest concentrations in fine fraction, except for succinic (C_4) and glutaric (C_5) that in the Copenhagen roadside site were found mostly in the coarse fraction and also in significant amounts in large-size particles of the Oporto and Copenhagen urban background sites. This generic enrichment of fine fraction in dicarboxylic acids suggested a predominance of secondary origin from primary sources (Kubátová et al., 2000). However, the significant amounts of succinic and glutaric acids found in $PM_{10-2.5}$ indicated the existence of some primary sources. Oporto clearly presented higher concentrations in winter for both sites, suggesting a predominance of dicarboxylic acids from primary sources. The most abundant diacid was succinic, followed by azelaic and glutaric. In Copenhagen, there was no significant difference between winter and summer concentrations of the overall dicarboxylic acids, with almost equivalent amounts during both seasons. Succinic and glutaric acids were found again to be the most abundant diacidic species, but azelaic acid concentrations were quite similar to those of sebacic acid (C_{10}).

4. CONCLUSIONS

The seasonal pattern showed that in winter the concentrations of polar organics were higher, probably due to increased anthropogenic emissions and changes in the mixing height of the atmosphere. In Oporto, a weekend decrease in polar compounds was in general observed, but this trend was not noticed in Copenhagen, especially in winter. The *n*-alkanols showed a strong even carbon number predominance with an intense contribution of vegetation waxes. Saturated *n*-fatty acids were the most abundant compounds, showing evidence of vehicular sources, input of cooking operations, road dust and microbial contributions. Unsaturated fatty acids indicated that there were more aged aerosols and/or more degradation of the fatty acids due to atmospheric conditions during summer. Copenhagen, in general, exhibited lower average concentrations of *n*-alkanols and *n*-alkanoic acids. Wood smoke appeared to be an important contributor to the urban aerosols, particularly in wintertime, as a result of local emissions of residential and commercial biomass-burning stoves and fireplaces and/or long-range transport of air masses impacted by biofuel burning. Ratios of several markers of biomass burning suggested a predominance of coniferous smoke in Oporto. In Copenhagen, stronger seasonal differences in these ratios were indicative of distinct biofuels being burned or different atmospheric transport processes. A series of dicarboxylic acids with both primary and secondary origin were detected with a distribution over the two size fractions, suggesting the existence of condensation phenomena onto large pre-existing aerosol particles, redistribution from fine to coarse fraction due to the semi-volatile nature of these compounds, or the emission for the coarse diacids fraction of primary biological particles.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Alves, C., Oliveira, T., Pio, C., Silvestre, A., Fialho, P., Barata, G., Legrand, M., 2007. Characterisation of carbonaceous aerosols from the Azorean island of Terceira. Atmospheric Environment 41, 1359-1373.

Alves, C., Pio, C., Duarte, A., 2001. Composition of extractable organic matter of air particles from rural and urban Portuguese areas. Atmospheric Environment 35, 5485-5496.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterisation of fine particle emissions from the wood stove combustion of prevalent United States tree species. Environmental Engineering Science 21, 705-721.

Kavouras, I.G., Stephanou, E.G., 2002. Particle size distribution of organic primary and secondary aerosol constituents in urban, background marine, and forest atmosphere. Journal of Geophysical Research A 107, 4069-4072.

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J., Maenhaut, W., Roberts, G., Artaxo, P., 2000. Carbonaceous aerosol characterisation in the Amazon Basin, Brazil: Novel dicarboxylic acids and related compounds. Atmospheric Environment 34, 5037-5051.

Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracers in organic aerosols from biomass burning. Part 1. Temperate climate conifers. Applied Geochemistry 16, 1513-1544.

Pope, C.A., Burnett, T.R., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., Godleski, J.J., 2004. Cardiovascular Mortality and Long-Term Exposure to Particulate Air Pollution - Epidemiological Evidence of General Pathophysiological Pathways of Disease. Circulation 109, 71-77.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1991. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. Environmental Science and Technology 25, 1112-1125.

Wang, G., Kawamura, K., Lee, S., Ho, K., Cao, J., 2006. Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. Environmental Science and Technology 40, 4619-4625.

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DISPERSION OF FINE AND ULTRAFINE PARTICLES NEAR AN URBAN MOTORWAY: COMBINING MODELLING AND EXPERIMENTS

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ABSTRACT

Particle number size distributions (diameter <1 µm) were measured for two months at three sites near the A100 urban motorway in Berlin, Germany. The motorway carries 190 000 vehicles per working day. At roadside the particle size distributions showed a number maximum between 20 and 60 nm clearly related to motorway emissions. The average total particle concentration at roadside was 28 000 cm^{-3}. Within distance 80−400 m from the motorway the particle number concentration was around 10 000 cm^{-3} on average. A dispersion model ASAM (All-Scale Atmospheric Model) was applied to a micro-scale urban environment to evaluate the dilution pattern of the exhaust particles. The method of inverse modelling was used by combining particle measurements and simulations as well as traffic counts to derive emission factor for an average vehicle driving on an urban motorway. The estimated emission factor was $(1.7\pm0.5) \times 10^{14}$ # veh^{-1} km^{-1} which is comparable to factors reported by other studies.

1. INTRODUCTION

Clear connections have been found between ambient particular matter (PM) and adverse health effects in humans (Pope and Dockery, 1999). Some epidemiological evidence has been obtained that relates respiratory disease with ultrafine particles (<100 nm) (Oberdörster et al., 1995; Peters et al., 1997). Traffic-related aerosols have adverse health effects because they contain significant amounts of organic toxins (PAHs) and insoluble soot. Traffic-derived aerosols have become the major source of anthropogenic aerosol particles in urban areas and as a result a large part of the human population is nowadays exposed to them.

Vehicle traffic causes a wide spectrum of particles. While coarse particles are emitted directly through break wear and indirectly by road dust re-suspension, fine particles (diameter <1 µm) are primarily emitted in the form of combustion engine exhaust. Most of the particle number in vehicle emission is in the ultrafine particle size range (<100 nm). New particles are also formed downstream the exhaust pipes, when hot exhaust gas cools down and leads to nucleation and condensation of unburned fuel compounds. The existence of these newly formed particles has been confirmed by many roadside measurements of particle size distributions (e.g., van Dingenen et al., 2004; Hussein et al., 2004). In order to capture the full impact of traffic-generated particles on the environment, atmospheric experiments near traffic sources are required, combined with an assessment of particle dispersion and transport as well as aerosol dynamical processes.

Once particles leave the vehicle's exhaust pipe, they will disperse in a complex manner. Wind and associated turbulence moves and disperses the particles. In an open topography these effects will rapidly decrease pollutant concentrations downwind the traffic source. In an urban topography with obstacles, such as densely aligned buildings, the air exchange and dilution is more complicated. Many studies have dealt with the simplistic configurations of urban landscapes, such as street canyons, for which relatively accurate descriptions of pollutant dispersal have been developed and experimentally been verified (Berkowicz, 2000; Vardoulakis et al., 2003). In the case of more irregular topographies, three dimensional fluid dynamics models have been applied to describe pollutant dispersal (Schlünzen et al., 2003; Wissink et al., 2005).

In this work, we report on traffic counts, particle size distribution measurements downstream an urban motorway and the related micro-scale dispersion modelling, which is aimed at verifying the observed spatial particle distribution effects and deriving fleet emission factor for the Berlin urban motorway traffic under realistic driving conditions.

2. METHODOLOGY

The Berlin urban motorway A100 field experiment PURAT 2 (Particles in the Urban Atmosphere) was conducted between July and September 2005 for 10 weeks. Measurements were carried out in the district of Berlin Westend (52º31´N, 13º17´E), an area 7 km west of Berlin's city centre featuring multi-storey residential buildings. The motorway carries on average 190 000 vehicles per working day on six lanes with the proportion of heavy traffic of 7 %. The traffic of the motorway was monitored continuously using an optical counting system. This system is able to distinguish passenger cars from light and heavy duty vehicles according to the length of each car.

Submicron aerosol particle size distributions were measured simultaneously at three sites with different distances and directions from the motorway. Friedhof measurement site was situated in closest proximity to the traffic source, only four meters away from the motorway on its west side. Taxi measurement site was located 80 metres to the east of the motorway, therefore serving as a site more downstream of the source than Friedhof. Wasserwerk measurement station was situated at a distance of 400 m east from the motorway and designed to be an urban background station. Taxi site was equipped with a Twin Differential Mobility Particle Sizer (TDMPS) covering a particle diameter range between 3 and 900 nm, while Friedhof and Wasserwerk stations were equipped with Scanning Mobility Particle Sizers (SMPS, TSI model 3080). The particle size range covered by SMPS was 10−500 nm. The auxiliary measurements included meteorological parameters (wind speed and direction, temperature, air pressure, relative humidity) and NO_x concentrations. Wind data from Berlin Tegel airport was utilized as an indicator of large scale wind situations. Tegel airport is situated 4 km away from Westend area.

The micro-scale atmospheric model ASAM (All-Scale Atmospheric Model) (Schlünzen et al., 2003; Hinneburg & Knoth, 2005) was used to simulate the dispersion and dilution of the inert particles in the near surrounding of the measurement sites. The three-dimensional fluid model was applied to a region of 500 m × 500 m with vertical extension of 100 m.

3. RESULTS AND DISCUSSION

In the proximity of the Berlin urban motorway the particle number concentrations were occasionally on a relatively high level. At Friedhof the total particle concentration exceeded 100 000 cm^{-3} in many occasions, while the average total particle concentration for the whole measurement period was 28 000 cm^{-3}, varying between 1 200 −168 000 cm^{-3}. At Taxi the average particle number concentration was 11 000 cm^{-3} (range 1 700−70 000 cm^{-3}). Wasserwerk site was characterised with the particle concentration of 9 000 cm^{-3} on average and varying in the range of 1 800−60 000 cm^{-3}. The average particle number size distribution at Friedhof had a wide peak between 20 and 60 nm indicating the emissions from the motorway. At Taxi site the number size distribution was quite similar to Friedhof while at Wasserwerk the maximum number occurred for larger particle sizes between 70−100 nm. At Wasserwerk the size distribution is shifted to larger sizes compared to the other sites probably due to particle growth during the transport from the motorway. Even though the total particle concentrations were on the same level at the field sites, Wasserwerk has more nature of an urban background site because the amount of accumulation mode particles (120−400 nm) is clearly higher than at Taxi, where nucleation (10−40 nm) and Aitken (40−120 nm) mode particles dominate.

According to the traffic counts A100 motorway carries on average 190 000 vehicles per working day and 140 000 vehicles on weekend per day. The average traffic speed changes between 75−95 km/h depending on the time of day and traffic volume with higher speeds occurring at night time. Occasional long-lasting traffic jams with clearly lower driving speeds (20−40 km/h) were also observed.

The daily variation of the traffic volume is 800−12 000 vehicles/h on working days. Strong periodicity of the traffic source leads to clear diurnal variation of the particle number concentration (Fig. 1). During working days the morning peak clearly indicates the contribution from the traffic source. In the afternoon concentrations typically decrease even though the traffic contribution stays high. The decrease is probably caused by changes in meteorology: in the afternoon the air is well mixed and better dilution conditions exist because of e.g. higher wind speed and mixing layer height. As a consequence the concentrations dilute faster during daytime. The diurnal patterns of the total particle concentrations measured at Taxi and Wasserwerk are very alike but the amplitude of the daily variation is much smaller than at Friedhof.

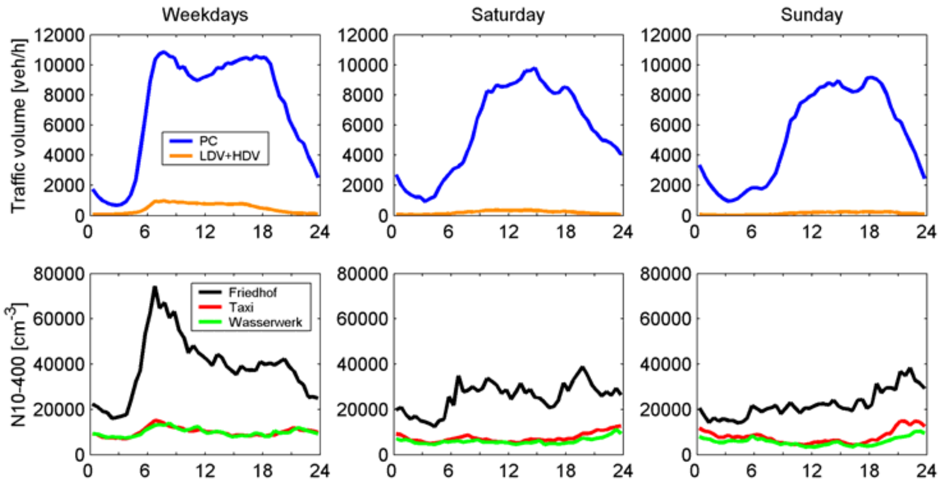

Figure 1. Diurnal variation of the traffic volume and total particle number concentration (10−400 nm) on working days, Saturdays and Sundays. PC=passenger cars, LDV+HDV=light+heavy duty vehicles.

The obstacle resolving dispersion model ASAM was able to reproduce the dilution and spatial distribution pattern of traffic-related particles under different wind sectors that were suggested by the experiments. According to the model simulations the highest particle concentrations appear at roadside site when wind blows from west or north (Fig. 2). Western winds yield high concentrations because on the leeward side of the multi-storey buildings form vortexes which circulate the air over the motorway. Experimental results showed that particle concentrations were on their highest level when wind blew from north along the motorway.

Previously presented datasets were combined in order to determine emission factors for motorway traffic in Germany. The method called inverse modelling relates experimentally determined roadside particle increment concentrations, traffic volumes as well as simulated dilution and dispersion characteristics. Particle number concentrations of the Taxi site were used as an indicator of the urban background air to separate the traffic source contribution from the background levels. Particle increment concentrations for Friedhof data was derived by subtracting the particle concentrations measured at Taxi site from the corresponding Friedhof data. The emission factor indicates how many particles are emitted by the vehicle fleet per kilometre driven under given driving conditions. The fleet emission factor obtained was $(1.7\pm0.5) \times 10^{14}$ particles km^{-1} for an average vehicle driving on an urban motorway. The value represents typical German motorway traffic mixture during working day on summertime. The evaluated emission factor is in good agreement with other studies conducted for comparable driving conditions. For example in Queensland, Australia (Jamriska and Morawska, 2001) emission factor of 1.75×10^{14} particles veh^{-1} km^{-1} has been determined for urban highway traffic. The emission factor typical of urban street canyon conditions in Copenhagen was estimated to be $(2.8\pm0.5) \times 10^{14}$ particles veh^{-1} km^{-1} (Ketzel et al., 2003). Further analysis will include the separate determination of emission factors for passenger cars and light and heavy duty vehicles. The preliminary results indicate that light and heavy duty vehicles emit 30−40 times more particles than passenger cars.

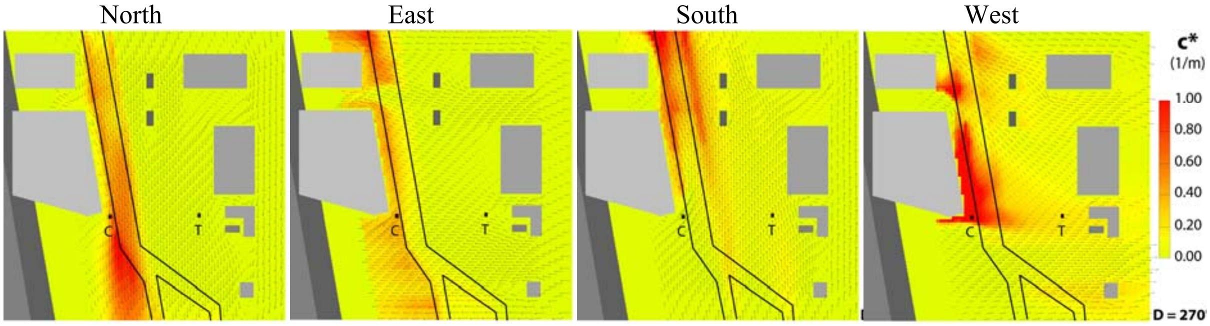

Figure 2. Model simulation results in the main wind directions presented as normalized concentrations c*. Model domain size is 500×500 m. Measurement stations are marked with letters C=Friedhof and T=Taxi.

4. CONCLUSIONS

A two month data set with simultaneous measurements of particle size distribution near an urban motorway as well as related small-scale dispersion simulations was presented. The particle size distributions measured at roadside of A100 were clearly related to motorway emissions. An interesting finding was that the total particle number concentrations were quite equal at Taxi and Wasserwerk sites even though the sites are situated at distances of 80 m and 400 m away from the motorway. The result reveals that the most effective dilution of exhaust particles with the underlying background air takes place in the first 50 meters downstream the traffic source. This was also verified with ASAM dispersion model calculations.

Inverse modelling was applied to derive particle emission factors for the vehicles driving on an urban motorway in Germany. The results of experimental particle number concentrations, dilution simulations as well as traffic counts were combined in the emission factor calculations. Emission factor per average vehicle was estimated to be $(1.7\pm0.5) \times 10^{14}$ # veh^{-1} km^{-1} which is comparable to other studies presented in the literature for similar kind of driving conditions.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Berkowicz, R. 2000. OSPM−a parameterised street pollution model. Environmental Monitoring and Assessment 65, 323-331.

Hinneburg, D. and Knoth, O. 2005. Non-dissipative cloud transport in Eulerian grid models by the volume-of-fluid (VOF) method. Atmos. Env. 39, 4321-4330.

Hussein, T., Puustinen, A., Aalto, P., Mäkelä, J., Hämeri, K. and Kulmala, M. 2004. Urban aerosol number size distributions. Atmos. Chem. Phys. 4, 391-411.

Jamriska, M. and Morawska, L. 2001. A model for determination of motor vehicle emission factors from on-road measurements with a focus on submicrometer particles. Sci. Total Environ. 264, 241-255.

Ketzel, M., Wählin, P., Berkowicz, R. and Palmgren, F. 2003. Particle and trace gas emission factors under urban driving conditions in Copenhagen based on street and roof-level observations. Atmos. Env. 37, 2735-2749.

Oberdörster, G., Gelein, R., Ferin, J. and Weiss, B. 1995. Association of particulate air pollution and acute mortality: Involvement of ultrafine particles? Inhal. Toxicol. 7, 111-124.

Peters, A., Wichmann, H.E., Tuch, T., Heinrich, J. and Heyder, J. 1997. Respiratory effects are associated with the number of ultrafine particles. Am. J. Respir. Crit. Care Med. 155, 1376-1383.

Pope, C.A. and Dockery, D.W. 1999. Epidemiology of particle effects. Air Poll. Health 31, 673-705.

Schlünzen, K.H., Hinneburg, D., Knoth, O., Lambrecht, M., Leitl, B., Lopez, S., Lüpkes, C., Panskus, H., Renner, E., Schatzmann, M., Schoenemeyer, T., Trepte, S. and Wolke, R. 2003. Flow and transport in the obstacle layer: First results of the micro-scale model MITRAS. J. Atmos. Chem. 44, 113-130.

Van Dingenen, R., Raes, F., Putaud, J-P., Baltensperger, U., Charron, A., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.C. et al. 2004. A European Aerosol Phenomenology − 1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmos. Env. 38, 2561-2577.

Vardoulakis, S., Fisher, B.E.A. and Pericleous, K. 2003. Modelling air quality in street canyons: a review. Atmos. Env. 37, 155-182.

Wissink, A., Chand, K., Kosovic, B., Chan, S., Berger, M, Chow, F. K. 2005. Adaptive Urban Dispersion Integrated Model. Proc. 86th American Meteorological Society Annual Meeting Atlanta, UCRL-PROC-216813.

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ULTRA-FINE PARTICLES FROM TYRE AND PAVEMENT INTERACTION

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ABSTRACT

The ultra-fine airborne particles (particles less than 100 nm) in the ambient air are generally originating from combustion processes and atmospheric reactions. During road wear studies on a road simulator, studded winter tyres were identified to generate considerable amounts of ultra-fine particles. At the Swedish National Road and Transport Research Institute (VTI) a road simulator (PVM) was used to study the characteristics of wear particles. Apart from the expected wear particle size ranges (>1 µm), an ultra-fine (<100 nm) fraction with a number maximum around 20–40 nm was found for studded tyres. No ultra-fine particle emission was detected from friction or summer tires. The composition of the emitted particles is assumed to be winter tyre fillers and softening oils, which differ from summer tyres. For a given tyre the velocity and thereby the tyre temperature was the most significant parameter that affected the amount of generated particles.

1. INTRODUCTION

Wear particles from road pavements, tyres, brakes and road maintenance strongly contribute high concentrations of inhalable particles in many road and street environments (Luhana et al., 2004). In Sweden, these episodes normally occur during dry periods in winter and spring and is mainly caused by road wear from the use of studded tyres and winter gritting (Kupiainen et al., 2003). Wear particles from pavement wear normally range from 1 µm and coarser (Dahl et al., 2006). Tyre wear particles are in some references referred to as bimodal, with a coarse fraction > 7 µm and a fine fraction < 100 nm (Fauser, 1999).

The characteristics, formation processes, emissions and health effects of wear particles are currently a research issue since relatively little is known and the spatial and temporal differences seem considerable. Numerous studies have shown that the concentration of inhalable particles (PM_{10}) in ambient air is associated with mortality and different kinds of respiratory health problems in the population (Schwartz et al. 1996; Schlesinger 2000). Meta analyses indicate that coarser fractions of PM_{10} seem stronger related to respiratory disease while the finer fractions tend to be stronger related to cardiovascular disease and mortality (Brunekreef and Forsberg, 2005). However, the mechanisms and properties that make particles more or less toxic are poorly understood.

In this study a road simulator has been used to study and sample wear particles from pavement and tyre wear without the influence from other ambient particles (exhaust particles, pollen, fibres etc.). Previous studies in the road simulator (Dahl et al., 2006) showed that except for mineral PM_{10} particles, also ultra-fine particles formed during wear tests. These particles are thought to originate from the tyres, why new experiments have been conducted to try to confirm these findings.

2. METHODOLOGY

At the Swedish National Road and Transport Research Institute (VTI) a circular road simulator was used to generate wear particles (Figure 1). Particle sampling in the simulator hall makes it possible to sample pure wear particles, with very low contamination from ambient particles. In the experiments, sub-micron particles from tyre wear of three tyre types (summer, friction and studded) on a typically durable pavement (stone mastic asphalt with quartzite and maximum stone size 16 mm) were studied. The particle generation is described in the paper by Gustafsson et al. (2007:1) in the current proceedings. Coarser particle fractions are described in Gustafsson et al. (2007:2). Size distributions from 10 - 500 nm were studied using SMPS (scanning mobility particle sizer).

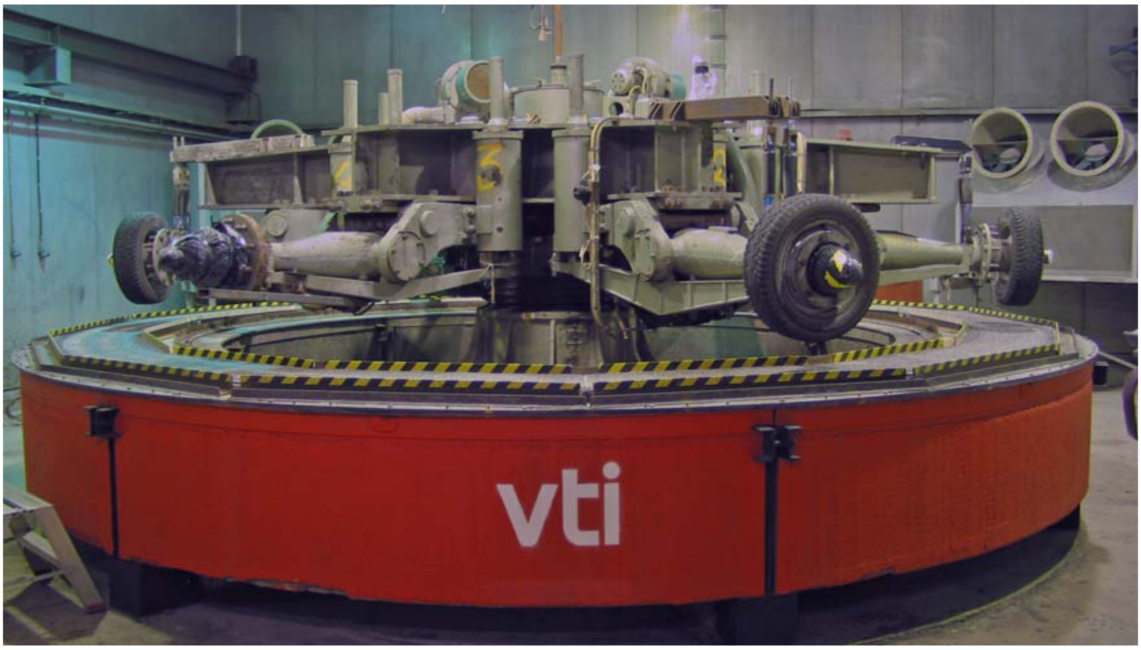

Figure 1. The VTI circular road simulator.

Figure 2. Tested tyre types. From left to right: summer, friction (non-studded winter) and studded tyres.

3. RESULTS AND DISCUSSION

Time series for number concentration of particles from the three different tyres are shown in Figure 3. While summer and friction tyres result in very low concentrations, the studded tyres cause formation of ten of thousands ultra-fine particles per cm^{-3}. Number size distributions for summer, friction and studded tyres are shown in Figure 4. The results show a very obvious peak of ultra-fine particles during the studded tyre test. At all speeds a number concentration peak appears at about 20–50 nm. The number concentration increases with speed. On the contrary neither friction nor summer tyres seem to produce this particle mode. The mode around 100 nm probably consists of background particles. For this mode number concentration is reduced with increasing speed for friction and summer tyres, indicating turbulence induced dilution and deposition.

Since pavement and environmental conditions for all tests are equal it seems very likely that the ultra-fine mode originates in the studded tyres. Their heterogeneous morphology (Figure 5) indicate that they originate both from thermal degradation of carbon reinforcing filler material (soot agglomerates) and the volatilisation of softening oils in the ultra-fine mode.

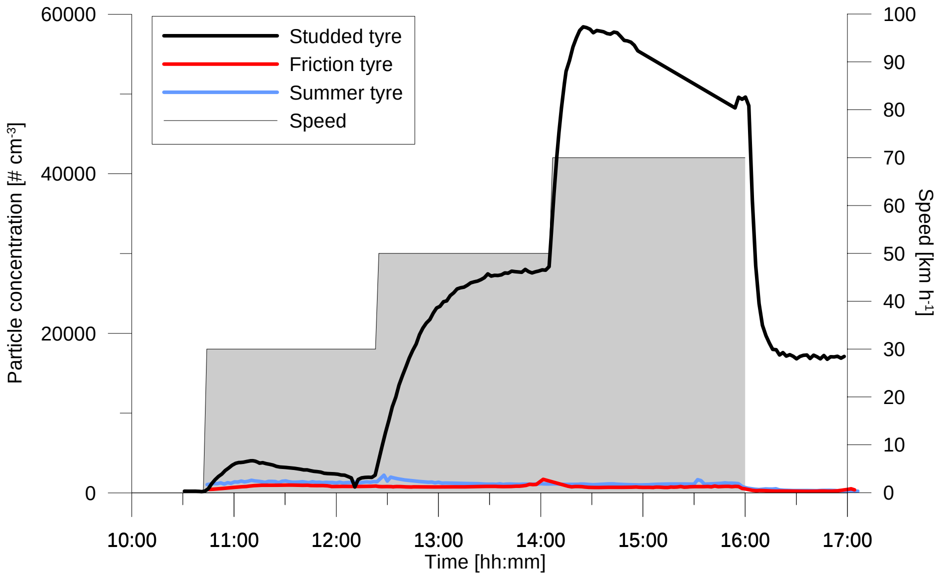

Figure 3. Time series of particle number concentration of particles measured by SMPS system caused by summer, friction and studded tyres at three different speeds.

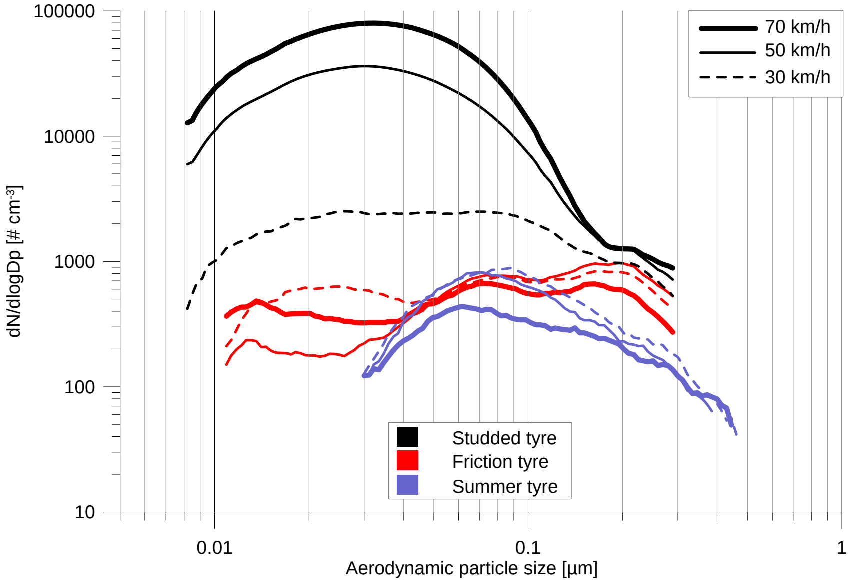

Figure 4. Number size distributions of particles measured by SMPS system caused by summer, friction and studded tyres at three different speeds.

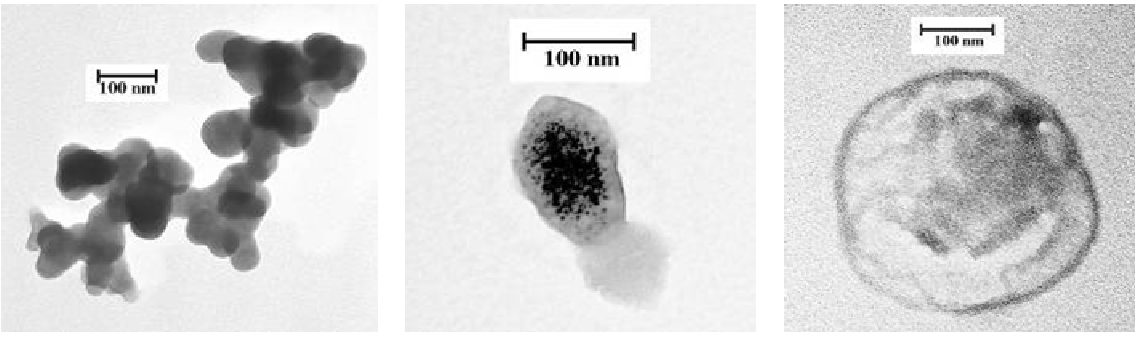

Figure 5. Sub-micron particles formed during wear between studded tyres and pavement. TEM micrographs from Dahl et al. (2006).

Differences in tyre rubber composition are a probable cause to the differences in formation of ultra-fine particles. Winter tyres have softer rubber composition to stay soft during cold weather conditions. Friction tyres are have softer rubber mixes than studded tyres. Summer tyres on the contrary become very hard during cold conditions and instead have rubber composition adjusted to give good friction in higher temperatures. Also the thread patterns differ (Figure 2). Winter tyres have sipes to increase friction on snow, while summer tyres lack sipes. Sipes might both produce particles due to increased tyre surface friction but also act as a sink for particles due to the increased surface.

4. CONCLUSIONS

- Ultra-fine particles form from studded tyre wear of pavement, but does not seem to form from summer and friction tyre wear.
- The origin is likely to be reinforcing filler and volatilisation of softening oils.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Brunekreef, B., Forsberg, B. 2005. Epidemiological evidence of effects of coarse airborne particles on health. Eur Respir J 26, 309-318.

Dahl, A., Gharibi, A., Swietlicki, E., Gudmundsson, A., Bohgard, M., Ljungman, A., Blomqvist, G., Gustafsson, M. 2006. Traffic-generated emissions of ultrafine particles from pavement–tire interface, Atmospheric Environment 40: 1314–1323.

Fauser, P. 1999. Particulate Air Pollution with Emphasis on Traffic Generated Aerosols. Risø National Laboratory, Roskilde, Danmark, p. 151.

Gustafsson, M., Blomqvist, G., Dahl, A., Gudmundsson, A., Jonsson, P., Swietlicki, E. 2007:1. Factors influencing PM_{10} emissions from road pavement wear. UAQ 2007 Proceedings.

Gustafsson, M., Blomqvist G., Ljungman, A., Lindbom, J., Gudmundsson, A., Dahl, A. and Swietlicki, E. 2007:2. Characteristics and inflammatory potential of wear particles formed in a road simulator. UAQ 2007 Proceedings.

Kupiainen, K., Tervahattu, H., Räisänen, M. 2003. Experimental studies about the impact of traction sand on urban road dust composition. Science Of The Total Environment 308, 175-184.

Luhana, L. Sokhi, R., Warner, L., Mao, H., Boulter, P., McCrae, I., Wright, J., Osborn, D. 2004. Measurement of non-exhaust particulate matter, Deliverable 8 from 5th Framework Programme Project "PARTICULATES - Characterisation of Exhaust Particulate Emissions from Road Vehicles", European Commission, Directorate General Transport and Environment.

Schlesinger, R. 2000. Properties of ambient PM responsible for human health effects: coherence between epidemiology and toxicology. Inhalation Toxicology 12 (Supplement 1), 23-25.

Schwartz, J., Dockery, D.W., Neas, L.M. 1996. Is daily mortality associated specifically with fine particles? Journal of the Air and Waste Management Association 46, 927-939.

PARTICULATE AIR POLLUTION IN TRANSPORT MICROENVIRONMENTS

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ABSTRACT

To understand the dynamics of particulate matter inside trains and public cars, an investigation was carried out during 2004 – 2006.For air conditioned rail coaches the concentration of PM10 was ranged between 20 µg/m^3 to 47 µg/m^3 followed by a concentration of 3 µg/m^3 to 17 µg/m^3 for PM2.5 and 2 µg/m^3 to 10 µg/m^3 for PM1. On the other hand, in non air conditioned coaches, the concentration of PM10 rose up to 95 µg/m^3. Inside the car most of the particulate matter was recorded in PM 10 fractions (17µg/m^3 - 47µg/m^3) during both morning and evening journeys. However, during a particular week PM 2.5 and PM1 were also rose up to 40 µg/m^3 and 38 µg/m^3 due to high back ground levels. A good correlation was found between PM 2.5 and PM1 in both train (r^2 = 0.92) and car morning (r^2=0.94) and evening (r^2=0.88) journeys irrespective of any condition.

1. INTRODUCTION

Most epidemiological studies have provided a significant body of evidence to associate particulate matter (PM) with chronic and acute respiratory problems. The exposure to particulate air pollution has been found to be closely linked to an increase in daily mortality and hospital admissions (Tony, 1995). In the developed world people spend most of their times indoors (home, offices, schools,, restaurant, etc…) and they are exposed to various amounts of particulate air pollution depending upon the microenvironment. Apart from all these outdoor and indoor microenvironments, the in transit microenvironment is also important to calculate the total exposure to particulate matter. Although the time spent in this microenvironment is low t the concentration of particulate pollution could be high. It has been reported that a peak exposure of less than 1 hour is most relevant in terms of health effects (Michaels and Kleinman, 2000) and repeated exposure to elevated levels of air pollutants leads to chronic health effects (Schwartz, 2000).
The advancement in transport modes in the last few decades has resulted in increased mobility of people and a large proportion of the working population spend a significant time commuting. The information regarding the exposure of the commuter to particulate air pollution is potentially important but studies of journey time exposure to particulate matter are relatively rare. Most of these studies have focused on exposure of PM in motorized transport or bicyclists. In UK, a study conducted in London by Adams et al., (2001), found that mean personal exposure to PM 2.5 in buses, cars and bicycles were approximately double that of the concentration at an urban background fixed site monitor. Gee and Raper (1999) measured an average of more than 10 times background levels of PM4 inside buses in Manchester, UK. Cyclists on the same route had exposures averaging twice background levels. The higher exposure to RSP (Reparable suspended particle) while commuting by bicycle on urban route compared to a suburban route was documented by Bevan et al. (1991). An investigation of PM10 exposure in buses and cars in Munich in Germany has revealed that PM10 in these vehicles was 1.7-4 times higher than those at static outdoor stations (Pramal and Schierl, 2000). In another study with taxi drivers in London, PM inside the taxi was higher than outdoor levels (Pfefier et al., 1991). Most recently Gulliver and Briggs (2004) compared personal exposure to particulate matter during walking and in car suburban journeys in winter. A high correlation was found for PM 10 between both modes but not for PM2.5 and PM1. However, both (PM2.5 and PM1) were higher inside the car than those for the walker and at the fixed curbside monitor.

Data on particulate matter inside trains is rare and only a few studies have been reported. A study conducted by Leutwyer et al, in 2002 on suspended particulate matter in railway coaches in Switzerland compared PM10 levels in smoking and non smoking cabins and revealed levels of 950µg/m^3 in smoker cabins as compared to 210µg/m^3 in nonsmoking cabins. In another study to compare PM 2.5 between smoking and nonsmoking rail coaches in Italy, Invernizzi et al., (2004) found a dramatic increase in PM 2.5 in smoking coaches (250 µg/m^3), as compared to 15 µg/m^3 in nonsmoking coaches. For nonsmoking conditions in railway coaches, an investigation in Hong Kong (Chan et al., 2002) measured concentrations of 50µg/m^3 for PM10 and 39µg/m^{3}for PM 2.5. Seaton et al., (2005) assessed the hazards associated with exposure to dust on the London Underground. Their study showed that concentrations of PM2.5 at the platform were 270 - 480 µg/m^3 against to 130 – 200 µg/m^3 inside the driver's cabin.

In the United Kingdom, rail is acknowledged as a highly efficient mode of transport and around 4,000 train units carry an equivalent of 10% of the country's passengers journeys as against 81,000 buses of varying types and 16 million cars for the remainder (Anonymous, 2006). However, with regards to the particulate matter inside railway coaches, no study has been reported yet. Hence the present study was carried out to;

1) to measure mass concentration of PM10, PM2.5 and PM1 inside railway coaches in trains around the UK.
2) to measure the exposure of passengers to PM10, PM2.5 and PM1 inside cars.

These finding will not only help to understand the nature of exposure towards PM in these modes of transportation but also will provide the base line information for future studies.

2. METHODOLOGY

2.1. Field Work Design.

To have complete idea of dynamics of particulate matter inside trains, an investigation was carried out during 2004 – 2006. Four train companies serving all around the UK were selected and multiple journeys were made on them throughout this period. These included, One Railway, GNER, Northern and Southern. All the rail tracks were electrified and the coaches were air-conditioned, except Northern Railways (non air conditioned). On the other hand, measurement inside the car was carried out on a route in a typical town of South East England (Colchester). Two journeys were made in one day using the same route – one in morning and other in evening.

2.2. Instrumentation and Sampling Methods

The mass concentration of particles was monitored using two different GRIMM analysers i) Model 1.108 ii) Model 1.101 (Grimm Aerosol Technik GmbH, Ainring, Germany) The GRIMM monitors had a sensitivity of 1 particle/ liter with a reproducibility of ± 2% and flow rate of 1.2 L/minute. All the samples were taken at respiratory levels and sampling location was carefully selected to be free of any obstructions. In the train the sampling location was on table in front of the passengers while in thecar it was placed on the front seat adjacent to driver at a desirable height. The sampling was continuous and at an interval rate of 1 minute. A record of time of travel and number of passenger was also kept.

3. RESULTS AND DISCUSSION

3.1. Mass Concentration in Trains

In general, high concentrations of PM were found in non air conditioned coaches as compared to air conditioned coaches. For air conditioned rail coaches the concentration of PM10 was ranged between 20 µg/m^3 to 47 µg/m^3 followed by a concentration of 3 µg/m^3 to 17 µg/m^3 for PM2.5 and 2 µg/m^3 to 10 µg/m^3 for PM1. These findings are in good agreement with those of Chan et al. (2002). They reported an average concentrations of 50µg/m^3 for PM10 in air-conditioned rail coaches.. On the other hand , in non air conditioned coaches, the concentration of PM10 rose to 95 µg/m^3 followed by 14 µg/m^3 to 30 µg/m^3 and 6 µg/m^3 to 19 µg/m^3 for PM2.5 and PM1, respectively(Fig. 1).

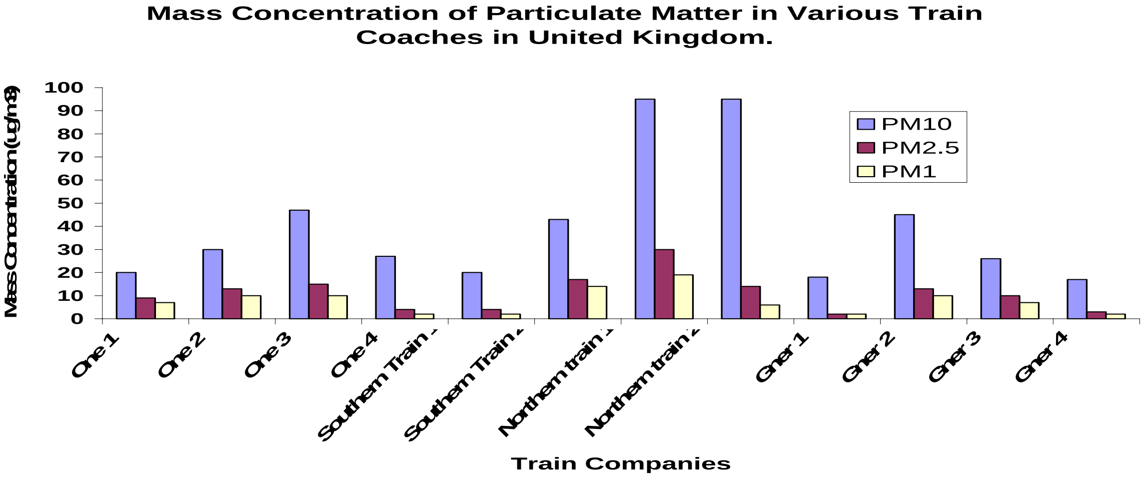

Figure 1. Particulate matter inside the rail coaches in United Kingdom.

However the relationship among PM10, PM2.5 and PM1 revealed that PM10 always stayed well above PM2.5 and PM 1. This shows that resuspension of PM within the coaches was significant. Any open windows in non air conditioned coaches, caused turbulence and resulted in high PM levels. This is reflected in Northern train data (Fig. 1). PM 2.5 levels were well correlated with PM1 (r^2=0.92), no matter which category of train (Fig. 2).

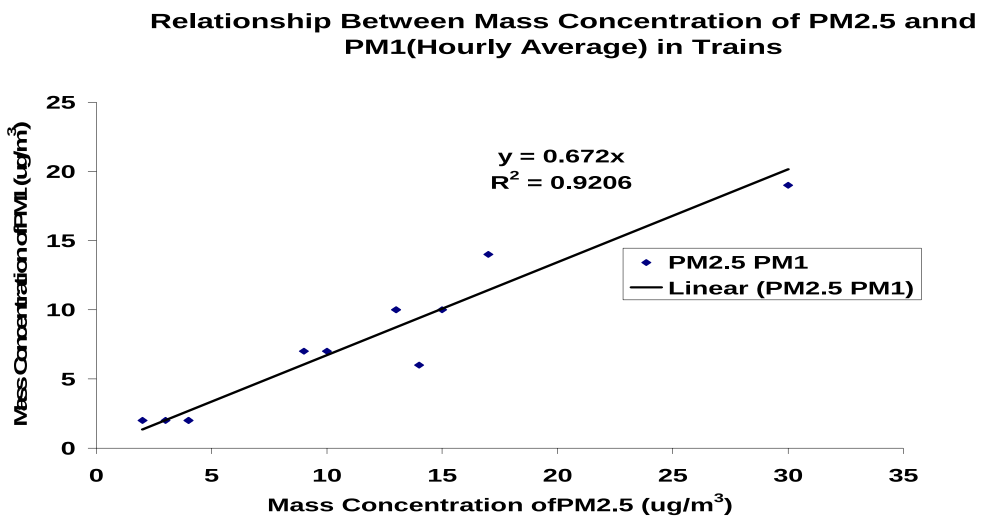

Figure 2. Relationship of PM2.5 to PM1 in trains.

3.2. Mass concentration in car

The mass concentration of particulate matter in the car was generally related to time of journey, which in turn was linked to traffic congestion. Most of the particulate matter inside the car was recorded in PM 10 fraction (17 µg/m^3 - 47 µg/m^3) during both morning and evening journeys. PM 2.5 and PM1 were 4 µg/m^3 - 7 µg/m^3 and 2 µg/m^3 - 3 µg/m^3, respectively (Fig.3). High amounts of PM10 were observed during busy times, while PM2.5 and PM 1 stayed normal. However, during a particular week PM 2.5 and PM1 were also rose up to 40 µg/m^3 and 38 µg/m^3. A comparison of these measurements to a local fixed site monitoring of PM revealed that PM 2.5 was very high all around the south east of England. A good correlation between PM2.5 and PM1 was documented for both morning (r^2=0.94) and evening (r^2=0.88) journeys.

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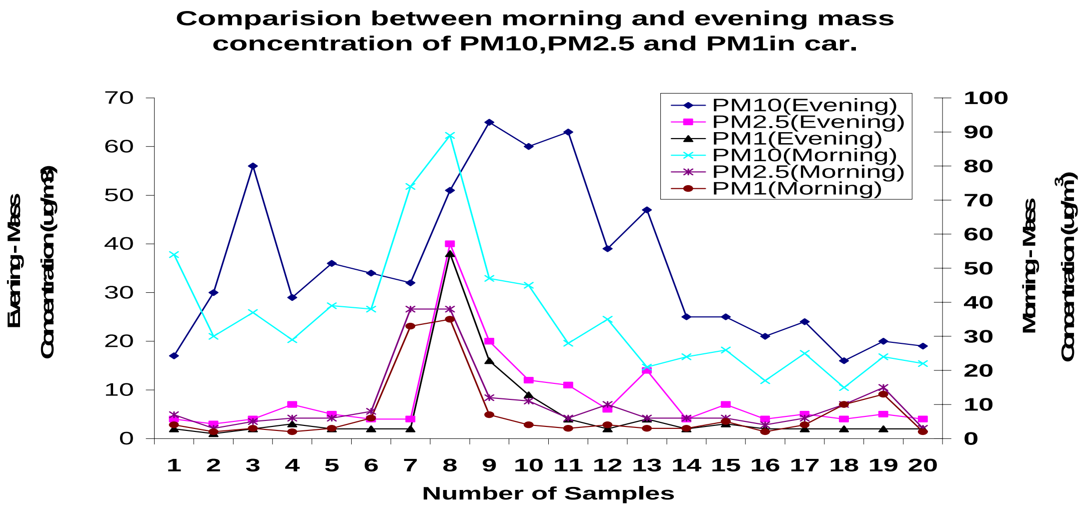

Figure 3. Summary of morning and evening PM concentrations in car.

4. CONCLUSION

In general mass concentration of particulate matter in air conditioned trains rails and in car microenvironments were almost the same (20 ug/m^3 - 47 ug/m^3 for PM 10). High PM levels were found in non air conditioned rail coaches and during busy times in road traffic. Particulate matter is influenced by traffic density and the ventilation system of vehicle.

5. REFERENCES

Adams,H.S., Nieuwenhuijsen, M.J., Colvile, R.N., McMullen, M.A.S. and Khandelwal,P. 2001. Fine particle (PM2.5) exposure levels in transport microenvironments, London, UK. The Science of the Total Environment, 279, 29-44.

Anonymous, (2006). Railway engineers forum response to the Liberal Democrat Consultation. Paper No. 84 on Climate Change.

Bevan, M.A.J., Proctor,C.J., Baker – Roger, J. and Warren, N.D.1991.Exposure to carbon monoxide, respirable suspended particulates and volatile organic compounds whilst commuting by bicycle. Environmental Science and Technology, 25, 788 – 791.

Chan., L.Y., Lau, W.L., Lee, S.C. and Chan,C.Y. 2002. Commuter exposure to particulate matter air pollution in public transportation modes in Hong Kong. Atmospheric Environment 36. 3363-3373.

Gee, I.L. and Raper, D.W. 1999. Commuter exposure to respirable particles in buses and by bicycle. The Science of the Total Environment, 235(1-3),403-405.

Gulliver, J. and Briggs, D.J. 2004. Personal exposure to particulate air pollution in transport microenvironments. Atmospheric Environment 38, 1-8.

Invernizzi, G., Ruprecht, A., Mazza, R.,De Marco, C and Boffi, F. 2004. Transfer of particulate matter pollution from smoking to non smoking coaches: the explanation for smoking ban on Italian trains. Tobacco Control 13, 319-320.

Leutwyler, M., Siegmann, K. and Monn, C. 2002. Suspended particulate matter in railway coaches. Atmospheric Environment, 36, 1-7.

Michaels,R.A. and Kleinman, M.T. 2000. Incidence and apparent health significance of brief airborne particle excursions. Aerosol Science and Technology. 32(2), 93-105.

Pfeifer, G.D., Harrison, R.M. and Lynam,D.R. 1999. Personal exposure to airborne metals in London Taxi drivers and office worker in 1995 and 1996. Science of the Total Environment, 235(1-3), 253-260.

Pramal,G. and Schierl, R. 2000. Dust exposure in Munich public transport – A comprehensive 4 yr survey in buses and trams. International Archives of Occupational and Environmental Health, 73 (3), 209 – 214.

Schwartz, J.2000. Is their harvesting in the association of airborne particles with daily deaths and hospital admissions? Epidemiology, 12(2), 55-61.

Seaton, A., Cherrie, J., Dennekamp, M., Donaldson,K. Hurley, J.F. and Tran, C.L. 2005. The London Underground: dust and hazards to health. Occupational Environ. Med. 62, 3555 – 362.

Tony, R. 1995. Weighing the health risk of airborne particulates. Environmental Science and Technology. 29,360A-364A.

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IMPACT OF RESIDENTIAL WOOD COMBUSTION ON CARBONACEOUS AEROSOLS

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ABSTRACT

Carbonaceous aerosol particles were measured in a residential area with wood combustion during wintertime in Northern Sweden. The mean and standard deviation mass concentrations are 4.4 ± 3.6 μg m^{-3} for organic carbon (OC), and 1.4 ± 1.2 μg m^{-3} for elemental carbon (EC). The average PM_{10} total mass concentration is composed of 48% particulate organic matter (POM), 11% EC, and 41% corresponds to other inorganic compounds. Particles with diameter smaller than 1 μm accounted for 73% of the total PM_{10} concentration. Analysis of particle size distributions suggests that wood combustion is the dominant contribution to the particle concentration at night, and during the day only when temperatures are below -20 °C. The very high correlation between black carbon (BC) mass concentrations and particle size distributions (number and mass concentrations) indicates that most of the particles might come from combustion sources.

1. INTRODUCTION

Carbon-containing particles are an important fraction of the fine mode of the atmospheric aerosol and are mainly composed of elemental carbon (EC) and organic carbon (OC). Both OC and EC are emitted by combustion of fossil fuels and biomass burning while OC can also be produced by secondary sources. Wood burning has been considered as an alternative energy source in Sweden to reduce the usage of fossil fuels and nuclear power, and to not increase the CO_2 emissions according to the Kyoto protocol. However, an increase in the carbonaceous aerosol concentration may give raise to adverse side effects, such as visibility reduction, soiling of surfaces in urban areas, global warming and could also be a risk factor for human health. The purpose of this research is to study the aerosol particles when residential wood combustion (RWC) is the dominant particle source under cold winter conditions. This work is primarily focused on the characterization of the carbonaceous aerosol particles.

2. METHODOLOGY

The field study was conducted in Lycksele (64° 55'N, 18° 72'E, 240 m a.s.l.; population 8600) which is located 590 km North of Stockholm. The measurements were carried out in the residential area of Forsdala in the winter 2005/2006. A differential mobility particle sizer (DMPS) was used to determine the particle size distribution between 25 and 606 nm. Twelve-hour integrated samples of EC and OC were collected with a sequential sampler equipped with a 10 μm inlet impactor, and analyzed using the NIOSH 5040 thermal-optical transmission (TOT) method. Two filter-based absorption instruments were employed to determine black carbon (BC) mass concentrations: a commercial aethalometer (series 8100, Magee Scientific Inc.) operated with a PM_1 sample inlet, and a custom-built soot particle absorption photometer PSAP with no pre-cut size device (Krecl et al. 2007, submitted). Total mass concentrations were measured with a Filter Dynamics Measurement System (FDMS, series 8500 Rupprecht & Patashnick Inc.) for PM_{10} and with a Tapered Element Oscillating Microbalance (TEOM 1400a, Rupprecht & Patashnick Inc.) for PM_1. The weather during the sampling period was typical of the winter season, with snow-covered ground and daily mean temperatures between -27.1 °C and 3.6 °C. The daily mean wind speed was 1.7 m s^{-1} for the whole period and the prevailing wind directions were north (21%), northwest (21%) and southeast (21%). These meteorological measurements were carried out at 13 m above ground level and ~2 km from the aerosol sampling site.

3. RESULTS AND DISCUSSION

3.1 Carbonaceous Measurements

Half-day integrated EC and OC mass concentrations together with total PM_{10} mass concentrations in Lycksele are displayed in Figure 1a. A large variation in OC, EC, and total PM_{10} concentrations is observed during this period. In two occasions, on the nights of 6 and 12 February, EC and OC concentrations exceeded 5 μg m^{-3} and 17 μg m^{-3} respectively. Glasius et al. (2006) reported hourly maximum concentration values of 4 μg m^{-3} for EC and 12 μg m^{-3} for OC concentrations at a Danish site with RWC for rather different temperature conditions. The EC and OC time series also showed a large variability. Their measurements were performed with an Ambient Carbon Particulate Monitor that collected particles in the 0.14-10 μm diameter range whereas all particles with diameters < 10 μm were measured in this study. Particles with diameters smaller than 0.14 μm can have an important contribution to the BC mass concentration depending on the location and BC source (Hitzenberger and Tohno, 2001). The mean and standard deviation mass concentrations are 4.4 ± 3.6 μg m^{-3} for OC, and 1.4 ± 1.2 μg m^{-3} for EC. The average PM_{10} total mass concentration is composed of 48% particulate organic matter (POM), 11% EC, and 41% corresponds to other inorganic compounds. The concentration of POM was estimated by multiplying the OC mass concentration by an average organic molecular weight per carbon weight of 1.4 (Turpin and Lim, 2001). Particles with diameter smaller than 1 μm accounted for 73% of the total PM_{10} concentration in Lycksele.

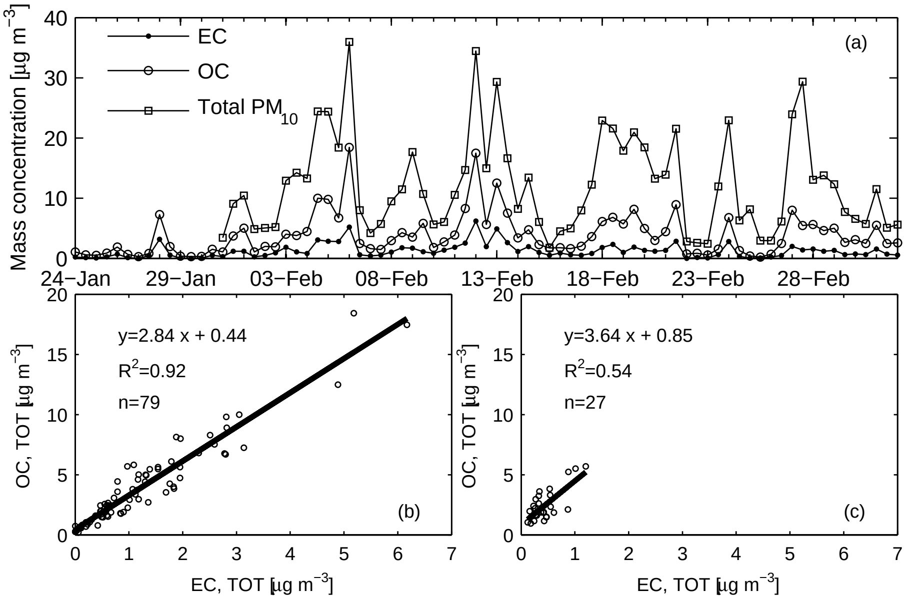

Fig. 1. (a) Twelve-hour integrated values of OC, EC and total PM_{10} mass concentrations in Lycksele, 23 January to 4 March 2006. Date labels are at 6:00 LT. Linear correlation between OC and EC mass concentrations: (b) in Lycksele for the same period, (c) at a background site in Stockholm, 12-hour integrated values, 12-26 April 2006. The solid line represents the least squares line regression. The number of samples *n* and coefficient of determination R^2 are also shown.

The origin of the carbonaceous particles can be qualitatively estimated from the relationship between OC and EC concentrations. Figure 1b shows the linear correlation between EC and OC mass concentrations in Lycksele for the same period. The linear model explains 92% of the data variability, indicating that the major fraction of OC and EC are emitted by a dominant primary source (Turpin and Huntzicker, 1995). Carbon measurements carried out at a urban background site (roof level) in Stockholm by using the same technique presented lower concentrations than in Lycksele. The linear correlation between EC and OC in Stockholm (R^2=0.54, Fig. 1c) is lower than in Lycksele when only EC values lower than 1.3 μg m^{-3} were selected (R^2=0.75, not shown). Further research has to be conducted to determine wether the different correlation coefficients between EC and OC mass concentrations in Lycksele and Stockholm can be explained by different emission sources, meteorological conditions, and formation of secondary organic carbon aerosols in Stockholm.

Aethalometer and PSAP measurements were matched in time with the EC mass concentrations obtained from the TOT method to determine the site specific mass absorption cross sections. The yielded values are 13.4 m^2 g^{-1} for the aethalometer and 20.09 m^2 g^{-1} for the PSAP. These mass absoprtion cross sections are used to convert the absorption coefficients into BC mass concentrations. Fig. 2 shows the linear relationship between hourly PSAP and aethalometer BC mass concentrations. Since both aethalometer PSAP measurements were normalized with respect to EC mass concentrations, any difference observed between them might be due to sampling or instrumental differences such as uncertainties in flow measurements, sample spot area, signal to noise ratios. The different cut-off size of the sampler inlets is not expected to contribute to the observed differences because most of the RWC aerosol is characterized by diameters less than 1 μm (Glasius et al., 2006).

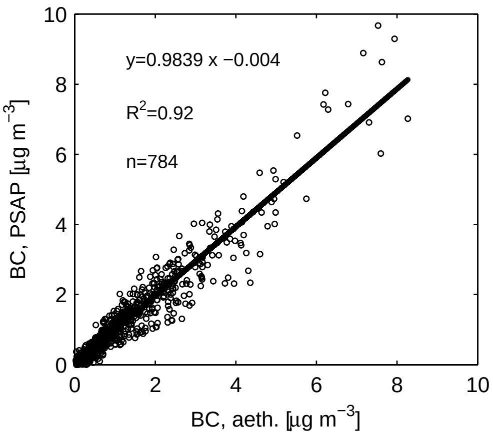

Fig. 2. Linear correlation between hourly average PSAP and aethalometer BC mass concentrations. Measurements were carried out in Lycksele between 30 January and 9 March 2006. The number of samples *n* and coefficient of determination R^2 are also shown.

3.2 Particle Size Distributions

Particle size distributions classified by the associated air tempertaure are presented in Fig. 3. Particle concentrations increase with decreasing air temperature for both daytime and nighttime periods. When temperatures are above -20 °C during daytime the distributions are shifted towards smaller diameters and appear more as a traffic source profile. At night, the average particle number concentration peaks at ~65 nm diameter D_p, and the size distribution shape agrees with the average wood combustion profile (Hedberg et al., 2002). This suggests that wood combustion is the dominant contribution to the particle concentration at night, and during the day only when temperatures are below -20 °C. When temperatures are above 0 °C, particle concentrations are very low, being typical of Scandinavian background sites (Tunved et al., 2005).

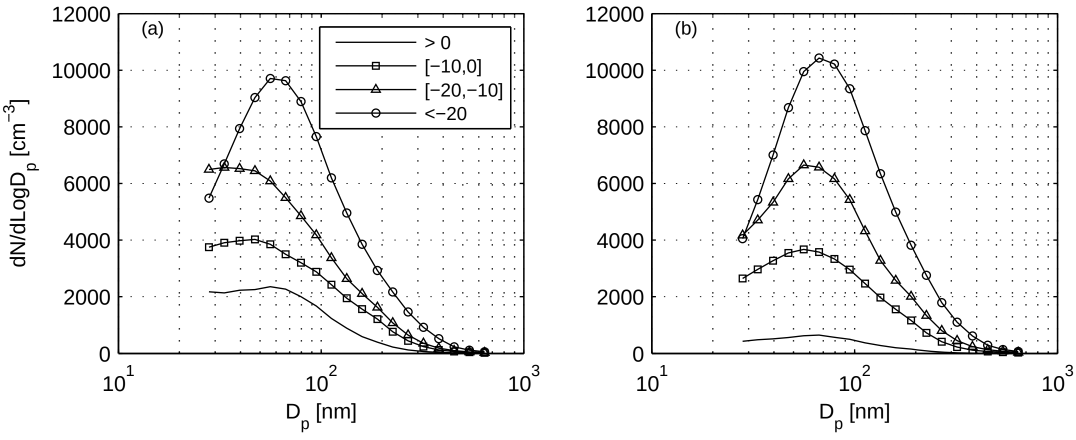

Fig. 3. Average particle size distributions in 10-degree temperature intervals for Lycksele, 30 January to March 10, 2006. (a) daytime (6:00 to 18:00 LT). (b) nighttime (18:00 to 6:00 LT).

3.3 Correlation between Particle Size Distribution and BC Concentration

Fig. 4a displays the correlation coefficient *R* between hourly BC mass concentrations (PSAP) and particle number concentration per channel (DMPS) as a function of D_p. Number concentration of particles in the accumulation mode, especially between 100 and 300 nm, presents a very high correlation with BC mass concentration. Since BC is emitted by combustion of fossil fuel and biomass burning, most of the particles might come from combustion sources. Particle mass concentrations were derived from hourly particle size distributions assuming spherical particles with density 1.5 g cm^{-3}. The average cumulative fraction of the derived mass concentrations as a function of particle diameter is presented in Fig. 4b. It can be seen that 90% of the mass is due to particles with D_p >100 nm whereas 57% of the mass is due to particles with D_p >300 nm. This means that the correlation between BC mass concentrations and particle size distribution is high by both particle number and mass for particle diameters between 100 and 300 nm. The correlation between 12-hour averages of derived mass concentration and measured total PM_{10} mass concentration is high (*R*=0.86).

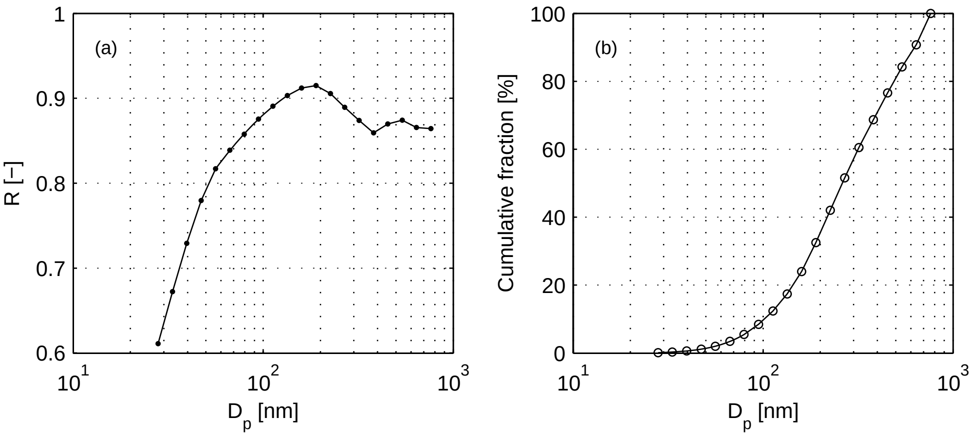

Fig. 4. (a) Linear correlation between hourly BC mass concentrations (PSAP) and particle number concentration per channel (DMPS). The correlation coefficient *R* is displayed as a function of the particle diameter D_p. (b) Cumulative fraction of mass concentration derived from particle size distribution as a function of D_p. Measurements were performed in Lycksele from 30 January to 10 March 2006.

4. CONCLUSIONS

This study indicates that most of the particles might come from combustion sources. Residential wood combustion has a large impact on particle number concentrations at night, and during the day only when temperatures are below -20 ^{o}C. Results shown in Fig. 1 might suggest that the chemical and optical properties of the carbonaceous aerosol are different in Lycksele compared to Stockholm. Further research has to be conducted to determine wether the different correlation coefficients between EC and OC mass concentrations in Lycksele and Stockholm can be explained by different emission sources, meteorological conditions, and formation of secondary organic carbon aerosols in Stockholm. Secondary OC aerosol formation will be estimated following the procedure proposed by Turpin and Huntzicker (1995). This difference in optical properties may have significant impact on radiative calculations.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Glasius M., Ketzel M., Wåhlin P., Jensen B., Mønster J., Berkowicz R., Palmgren F., 2006 Impact of wood combustion on particle levels in a residential area in Denmark. Atmos. Environ. 40, 7115-7124.

Hedberg E., Kristensson A., Ohlsson M., Johansson C., Johansson P.Å., Swietlicki E., Vesely E., Wideqvist U., Westerholm R., 2002. Chemical and physical characterization of emissions from birch wood combustion in a wood stove. Atmos. Environ. 36, 4823-4837.

Hitzenberger R.,Tohno S., 2001 Comparison of black carbon (BC) aerosols in two urban areas- concentrations and size distributions. Atmos. Environ. 35, 2153-2167.

Krecl P., Ström J., Johansson C., 2007 Field comparison of a custom-built particle soot absorption photometer and a commercial aethalometer performed in a residential area during the wood combustion season in Sweden. Submitted to Atmos. Environ.

Tunved P., Nilsson E. D., Hansson H.-C., Ström J., Kulmala M., Aalto P., Viisanen Y., 2005 Aerosol characteristics of air masses in northern Europe: influences of location, transport, sinks, and sources, J. Geophys. Res. 110, D07201, doi:10.1029/2004JD005085.

Turpin B.J., Huntzicker J.J., 1995 Identification of secondary organic aerosol episodes and quantification of primary and secondary aerosol concentrations during SCAQS. Atmos. Environ. 29, 3527-3544.

Turpin B.J., Lim H.-J., 2001 Species contributions to $PM_{2.5}$ mass concentrations: revising common assumptions for estimating organic mass. Aerosol Sci. Technol. 35, 602-610.

Impact of a vegetation-covered urban brownfield on ambient particle concentration

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ABSTRACT

Unused areas in shrinking cities are often covered by vegetation. Within this study the impact of these vegetation-covered brownfields on particle concentrations is investigated. Concentrations of PM and coarse particles were measured on a former marshalling yard in Berlin during the vegetation period 2006.

Concentrations of particles within the brownfield show higher temporal fluctuations than spatial differences. Compared to a roadside measurement site coarse opaque particle concentrations are clearly reduced within the brownfield. Also a dependency on particle size could be found. Whereas PM-concentrations are spatially homogenous and not influenced by different vegetation structures, differences occur in the spatial distribution of coarse particles. Particles with diameter greater than 12 µm showed the highest concentration gradients.

1. INTRODUCTION

While over centuries cities were growing in Europe, several cities suffered losses in population during the last decades. This phenomenon of shrinking cities is characteristic of many post-industrial countries, e.g. England and the USA. It is especially pronounced in the eastern part of Germany, where a decline in population can be found in many regions, mainly due to economic structural change after German reunification.

Since the process of shrinkage is mainly caused by deindustrialisation, shrinking cities are characterised by vacant areas, which were formerly used by heavy industry. There are also vacancies in housing and buildings of social and technical infrastructure. These unused areas often become brownfield sites. They are mainly covered by different kind of vegetation and therefore act as habitats for a diversity of biocoenoses. Hence, they play an important role in the urban ecosystem. But the vegetation on such brownfields not only interacts with other organisms. It has also an impact on other parts of the urban environment, e.g. the pedosphere and the atmosphere.

It is well known that plants act as filter for coarse particulates. Especially trees and shrubs can capture road dust (Farmer 1993). Hence, brownfields may have the potential to contribute to lower particle concentrations in cities and therefore improve urban air quality relating to particle pollution.

In this study, particle concentrations on a vegetation-covered brownfield site were measured to assess the influence of vegetation on particle distribution on the brownfield. The main focus was placed on differences in the behaviour of different particle sizes.

2. METHODOLOGY

2.1. Sampling site

Particle concentrations were measured on an urban brownfield formerly used as a marshalling yard during the vegetation period in 2006 (Figure 1). The brownfield is located in the Southeast of Berlin, Germany. It has an average width of 300 m and a length of roughly 3 km. It is bordered on its northeast side by a busy six-lane road with a traffic flow of about 50.000 vehicles per day. To the southwest small industries and various types of unused brownfields are dominating. On both longitudinal sides of the site there are active railway lines - three on the northeast side and one on the southwest side - used by regional passenger trains.

To quantify the effect of different types of vegetation on the particle distribution, two transects with different vegetation were placed perpendicular to the road. One transect is dominated by annual herbaceous plants (S2 to S4 on Figure 1) whereas trees and shrubs grow along the second transect (S5 to S7). The most frequent tree species are the Norway Maple (*Acer platanoides*) and the Black Locust (*Robinia pseudoacacia*).

2.2. Particle sampling

Along each transect, three passive Sigma-2-samplers (VDI-Guideline 2119/4) were placed to collect particles on transparent adhesive slides. A seventh sampler was located nearby the road (S1). Each sampling period was one week; particles were collected in a height of 2 m above ground.

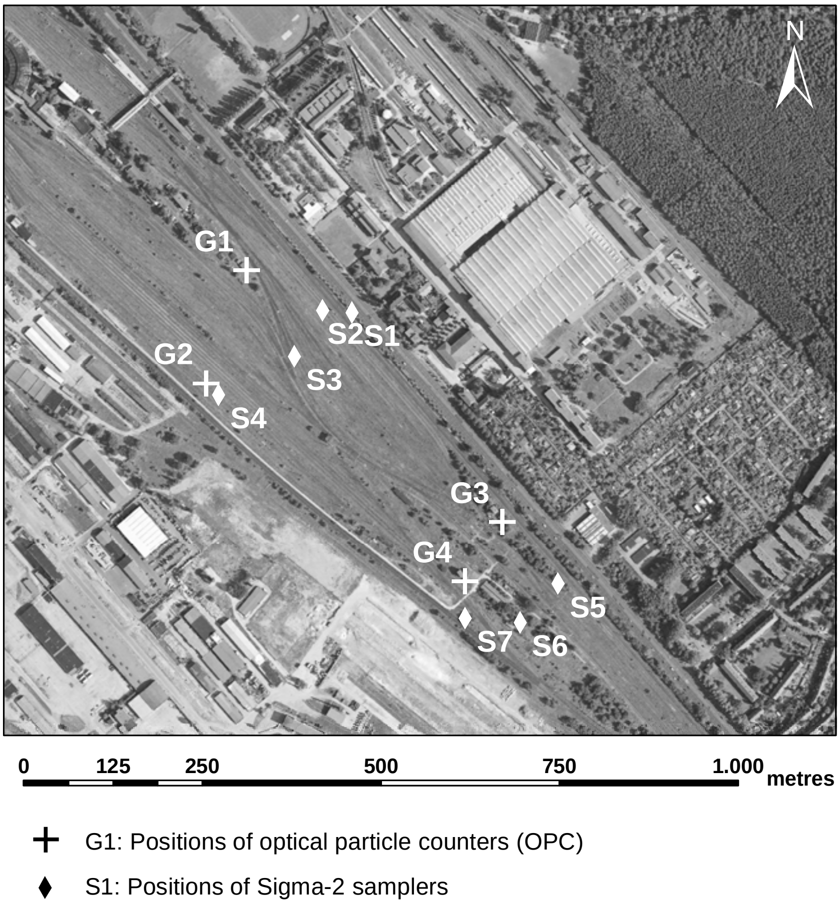

Figure 1. The sampling site on an aerial photograph (original orthophoto scale 1:10 000, photo was taken in August 2004)

Particles are detected on the slides by the use of a light optical microscope. With this technique, coarse particles in the range between 3 and 96 µm can be distinguished. It is also possible to measure transparent and opaque particles separately. Details of this method can be found in VDI-Guideline 2119/4. Particle analyses were conducted by the German National Meteorological Service (DWD).

To gather particle data with higher time resolution and to determine particles smaller than 3 µm, PM_{10}, $PM_{2.5}$ and PM_1 were measured continuously with two optical particle counter (Grimm Environmental Dust Monitors #107). Concentration data were recorded as 10-minute averages; the particle inlet was placed 2 m above ground. The four measurements sites (G1 to G4 on Figure 1) were restricted to locations with access to permanent power supply. Both particle counters were switched every two weeks to another location. Defects of the monitors resulted in gaps in the concentration data.

3. RESULTS AND DISCUSSION

Figure 2 shows the course of coarse particle concentration at the seven sites. The corresponding mean values are given in table 1. The lowest concentration on a one-week basis was 4.6 $\mu g \cdot m^{-3}$ (measured at S4), the highest 73.4 $\mu g \cdot m^{-3}$ (measured at S1). The highest average concentration could be found at position S1, the lowest at position S6. From previous measurements during January and February 2006 at seven positions along the road it could be inferred that S1 is a representative site for that road. Hence, high particle concentrations at S1 reflect the local influence of the road as a particle source. But there is a steep gradient of particle concentration nearby the road. At S2 already, approximately 20 m from the edge of the road, concentrations are in the range of those measured at the other sites within the brownfield.

Figure 2 also indicates that concentrations vary more with time than they do in space. There is a high correlation between the various sites. The strongest can be found between S3 and S4 ($R^2 = 0.94$), the weakest between S1 and S7 ($R^2 = 0.66$). Temporal fluctuations of particle concentrations in Berlin can be mainly

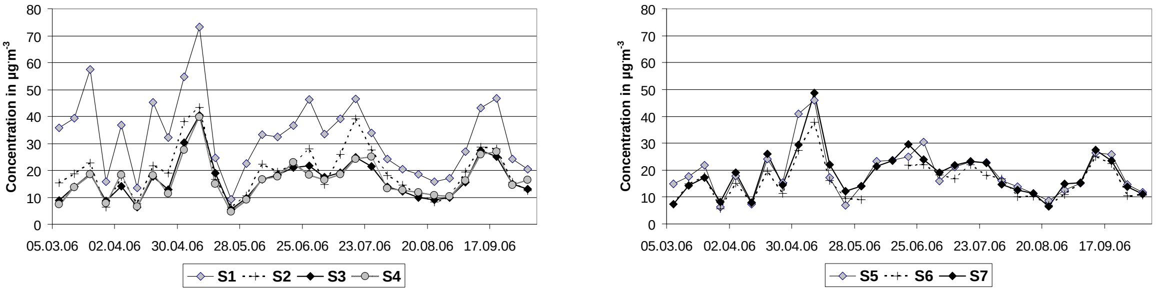

Figure 2. Concentration of coarse particles (3 – 96 µm) between 8 March and 11 October 2006 collected with Sigma-2-samplers

Table 1. Concentration of coarse particles (3 – 96 µm) between 8 March and 11 October 2006 collected with Sigma-2-samplers. Figures are given in µg·m^{-3} as mean values ± standard deviation

Position	S1	S2	S3	S4
Transect 1	32.9 ± 14.5	19.6 ± 9.5	16.7 ± 7.6	16.7 ± 7.4
Position	S5	S6	S7	
Transect 2	19.1 ± 9.0	15.8 ± 7.2	18.7 ± 8.6	

explained by meteorological conditions, especially by different weather types (Wolf-Benning et al. 2005). A comparison of PM-concentrations with wind directions shows, that high PM_{10}-concentrations on the brownfield are associated with winds from Southeast, whereas westerly winds cause only minor PM_{10}-concentrations.

Table 2 shows that there are no significant differences of PM-concentrations at the four positions G1 to G4. Variations between different sites are within the range of parallel measurements the same site (G2, last two rows in table 2). Temporal differences are by far greater than spatial differences. Hence, particles smaller than PM_{10} are homogeneously distributed within the brownfield. This uniform distribution was also reported from another roadside urban green (Langner & Meurer 2004). No effect of different vegetation types on PM-concentrations could be found.

There are not only spatial differences within the bulk concentrations of coarse particles. Fractions of opaque and transparent particles show different shifts (figure 3). Compared to the roadside position S1, opaque particles are more reduced than transparent particles within the brownfield. Opaque particles can be used as tracer for anthropogenic emissions like soot and wear of tyres (Schultz 1989). This can also be considered as an indicator that particles emitted from the nearby road have only a minor influence on particle concentration on the brownfield. The lower reduction of transparent particles may be partly explained by resuspension of soil particles from the brownfield itself.

For both the opaque and transparent particle there is a tendency of decreasing ratios with increasing particle size. Particles between 24 and 48 µm show the largest reduction of concentration compared to the roadside site S1. Together with the PM-data it can be therefore concluded, that only particles with diameters larger than 12 µm show significant differences in their spatial distribution.

Table 2. Mean PM-concentrations during four parallel measurements at different positions between July and September 2006. Figures are given in µg·m^{-3} as mean values ± standard deviation

Position	PM_{10}	$PM_{2.5}$	PM_1
G1	17.6 ± 10.9	11.3 ± 6.8	9.2 ± 6.2
G2	18.3 ± 13.1	11.7± 7.4	9.6 ± 6.5
G3	22.1 ± 13.2	11.9 ± 5.9	9.5 ± 5.5
G4	22.8 ± 22.3	11.2 ± 5.7	8.8 ± 5.2
G2	15.6 ± 10.0	11.0 ± 7.8	9.0 ± 7.2
G3	15.8 ± 7.8	11.2 ± 7.2	9.0 ± 6.9
G2	22.6 ± 15.5	16.7 ± 11.5	14.4 ± 10.7
G2	22.9 ± 14.9	16.3 ± 10.8	13.5 ± 10.4

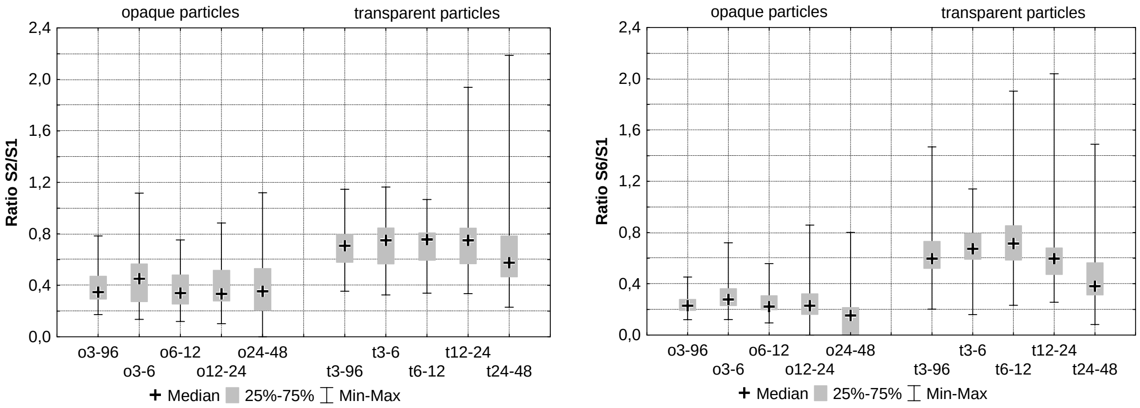

Figure 3. Coarse particle concentrations at S2 and S6 compared to S1. Ratios are given for opaque and transparent particles and different particle sizes (in µm)

4. CONCLUSIONS

Concentrations of particles within the brownfield show higher temporal fluctuations than spatial differences. Compared to a roadside site concentrations of coarse opaque particles are clearly reduced within the brownfield. Also a dependency on particle size could be found. Whereas PM-concentrations are spatially homogenous and not influenced by different vegetation structures, differences occur in the spatial distribution of coarse particles. This leads to the conclusion that vegetation on brownfields does not actively contribute to lower PM-concentrations in urban areas. But their might be an indirect effect on PM-concentrations since brownfields are places with reduced anthropogenic particle emission.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Farmer, A.M. 1993. The effects of dust on vegetation - a review. Env. Pollution 79, 63-75.

LANGNER, M., MEURER, M. 2004. Distribution of PM_{10} and $PM_{2.5}$ on a roadside urban green. J. Aerosol Sci., Abstracts of the European Aerosol Confernce, Budapest, S83-S84.

Schultz, E. 1989. Größendifferenzierende Messung der Partikeldepositionsrate. Staub – Reinhaltung der Luft 49, 113-118.

VDI-Guideline 2119/4. 1997. Measurement of particulate precipitations – Microscopic differentiation and size fractionated determination of particle deposition on adhesive collection plates Sigma-2 sampler - Beuth Verlag. Berlin, Köln.

Wolf-Benning, U., Draheim, T. Endlicher, W. 2005. Particulate matter and nitrogen dioxide in Berlin’s air – spatial and temporal differences. Die Erde 136, 103-121.

PM_{10}, $PM_{2.5}$ AND BLACK CARBON MEASUREMENTS IN RIGA

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ABSTRACT

In the current project in Riga, the capital of Latvia during six years several campaigns of Black Carbon (BC) sampling was arranged using a laboratory made particle sampler and Black Carbon Monitor. BC mass concentrations and variations were studied operating and comparing devices with different measuring principles. Using Dichotomous sampler airborne particles were collected in two fractions of 2.5 - 10µm and up to 2.5µm sizes. Samples of coarse (PM_{10}) and fine ($PM_{2,5}$) airborne particulate matter fractions collected from April to December, 2006 were studied. How it was expected PM_{10}, $PM_{2,5}$ and BC concentration levels depend on season and correspondent meteorological parameters. Mutual comparing of BC measuring devices is in an acceptable agreement. Comparing BC concentrations of airborne particles sampled by the laboratory – made and industrially produced sampling systems, approve the possibility to use a low cost laboratory – made sampler in the air monitoring and controlling system.

1. INTRODUCTION

The atmosphere around and above us contains not only gases, but millions of tonnes of solid mater, which have a grate influence on the climate change, on the atmospheric energy budget and on human health. Black carbon (BC) is an important contribution to this load, giving 5-14% of the mass of this particulate matter (PM) in different areas (Ramanathan and Crutzen). BC is the most efficient component of atmospheric aerosol that absorbs in visible spectral range and this is comprised of elemental carbon (EC) and some organic carbon (OC) species and carbonaceous species are the least understood and most difficult to characterize of all aerosol chemical components (Petzold and Schonlinner). More constantly in terms of air quality, BC is considered as a component of PM_{10} (up to 10µm in diameter), but research results certify that BC more often belongs to fine ($PM_{2.5}$, up to 2.5µm) and ultrafine (particles smaller than 1µm) modes which have longer residence time. It can be validated by presence of BC for instance in the Arctic stratosphere and in other places far away from most known sources.

The direct and indirect ways by which BC affects climate have been proposed. BC scatters and absorbs solar radiation so that an increase in BC reduces the solar radiation that reaches the ground (Krishnan and Ramanathan). BC also alters atmospheric heating rate, humidity and even the microphysics of clouds (changing droplet size) (Johnson et al). Although there are still settled uncertainties in the BC influence to climate, apparently both - climate and health impact of atmospheric BC is clearly important. Ultrafine particles among them BC have a larger potential to cause different inflammation than their larger counterparts on a mass – for – mass basis due to their larger surface area. Smaller particles are able to penetrate the lung lining, enter the blood, they can accumulate in liver and other organs, ultrafine particles have direct effect on nervous system. In vitro toxicology studies have displayed that wood, smoke and BC particles are better initiators for the producing of free radicals (Knaapen et al). Urban air pollution induces cardiovascular and lung diseases such as asthma, chronic obstructive pulmonary disease and lung cancer, but a significant correlation also exists between particle mass concentration and cardiovascular disease (Tainio et al).

Sampling locations and time. In the current project airborne particles were sampled in the central part of Riga. There are possible different pollution sources, namely intense traffic, railway, tram park, River Daugava with the estuary in the Baltic Sea, industry and a region of private houses with individual heating system. At first sampling place was chosen on the first lower roof of Latvian Environmental, Geology and Meteorology Agency (LEGMA) 15m above ground level. Sampling campaign was arranged during October 2000 and the results are described by Viksna et al. In this research work the sampling place was chosen at the Department of Chemistry, University of Latvia. Initially only a laboratory made sampling instrument was used with sampling head at 8m height level, 1m from the wall of building during different time periods from 2002 up to now. In the beginning of 2006 Black Carbon Monitor and Dichotomous PM_{10}/ $PM_{2,5}$ sampler were attained with approximately the same sampling place.

2. METHODOLOGY

Laboratory-made BC sampler. The sampler made to fit reflectometer –the (BC)-sampler is a laboratory-made device. It consists of a pump and a flow monitor, temperature and humidity sensors and a tube that ends with a funnel which is placed in vertical direction with the wide end facing downwards. Between the funnel and the pump a filter holder of brass has been installed with a diameter of the exposed filter area matching that of the reflectometer used for determination of BC contents. The sampling place is equipped with two such samplers. One of them is arranged with the cyclone which is segregating and sampling particles smaller than 1µm. The flow throught the sampler was set at 16,7 L/min. Different filters were used for sampling of airborne particles (Metricel ® Membrane filter GN-6, 37mm, 0.45µm, Gelman Sciences; Membrane filter Tissuquarz 25000RT-UP, 47mm, Gelman Sciences).

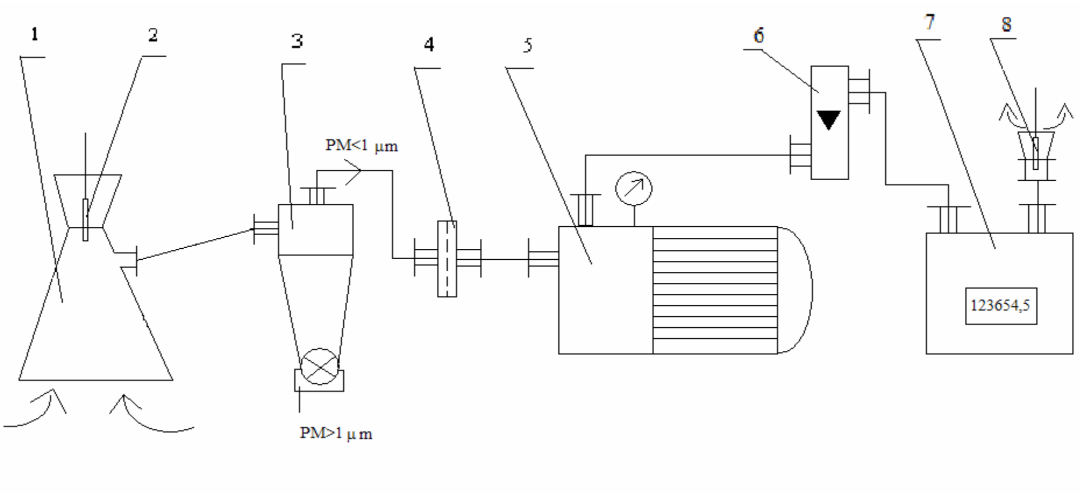

Fig. 1. Laboratory-made BC sampler

1- Sampling tube, 2,8- temperature and humidity sensors Easy Control GIR/GIA, 3- cyclone BGI inc., 4- filter holder, 5- air pump, 6- rotameter, 7- air flow monitor.

The Black Carbon Reflectometer FH 62 I-R. The operating principle of a reflectometer is known as the “black smoke method”. A light source shines its light on aerosol particles on filter and the reflected light is measured by photo diodes located in a black housing. The reflectometer used in the present work (Reflectometer (Black Carbon Detector) for the Particulate Monitor, FH62I-R, Environmental Monitoring ESM Andersen Instruments).

The Smoke Stain Reflectometer M43D. The first stage in calculating the ambient concentration of black smoke is to measure the darkness of the smoke stains obtained from the sampler. This instrument emits a steady light onto the smoke stain, which is reflected back from smoke stain to a photo- sensitive element. The electrical response is then amplified to procedure a meter reading. This instrument has a measuring head, which comprises a source of light (a tungsten lamp) and a photo-sensitive element (a selenium disc). The head fits into a detachable mask which consists of a locating ring with a metal plate. The mask covers all the working area of the element except for an aperture 1,25cm in diameter, through which the stain is measured. A standard gray and white tile is supplied for reflectometer calibration purposes.

The Black Carbon Monitor Carusso/MAAP5012. This monitoring instrument Carusso serves to determine the fraction of elemental carbon suspended in the ambient atmosphere. The principle of determination is based on a combination of the reflectometer method at certain defined scattering angles and the transmission. This method includes multiple-scattering effects into the analysis of the aerosol-filter system and is therefore aiming on a reduction of the uncertainties of the measured aerosol absorption coefficient and the black carbon mass loading of the filter sample.

Dichotomous PM$_{10}$/PM$_{2,5}$ Sampler. The Andersen Instruments Inc. dichotomous sampler is a low-flow rate (16,7L/min) sampler that divides the air stream passing the 10μm inlet into two portions that are filtered separately. Particles are collected via total sampler inlet and separated into fine (< 2,5μm) and coarse (2,5-10μm) fractions on separate 37mm diameter Teflon$^{®}$ filters (Pall Corporation, Teflo ^{TM} W/Ring, 37mm, 2.0μm) by a virtual impactor. Particle-laden air passing through the fractionating inlet of the dichotomous sampler is forced to take a sharp turn upon entry. Because of their greater mass (inertia), most large particles cannot make this turn into the cap and continue to move in their original direction. After passing through the inlet, the air containing inhaleable particles is forced to pass through an acceleration jet and then around a lower jet having a lower velocity air flow. Most of the fine particles do not follow the high velocity flow stream and are captured on the fine particle filter. This particular design is called “virtual impaction” because the particles impact on a slowly pumped (1,67L/min) void rather than on a solid plate. The coarse-particle flow is controlled by its flow selector valve, which feeds into the inlet of the pump.

To obtain PM mass, Teflon filters were weighted before and after particulate sampling by analytical balance of Sartorius CP2-P-F. Teflon filters before weighting were kept in close chamber for at least 24 hours with constant temperature and humidity.

3. RESULTS AND DISCUSSION

Black Carbon mass concentration measurements.

During research work all previously described samplers were used and the average monthly BC concentrations during all sampling period from 2000 to 2006 are showed in Fig. 2. The results show that the concentration of black carbon is changing every month. In autumn time BC concentrations were lower than in spring, when there are more sunny days. But in winter the highest concentrations could be explained with weather conditions when circulation of upper air masses is burdened. Obtained results show that concentrations of black carbon decrease during cloudy days and rainy days, which could be explained by particulate wash out.

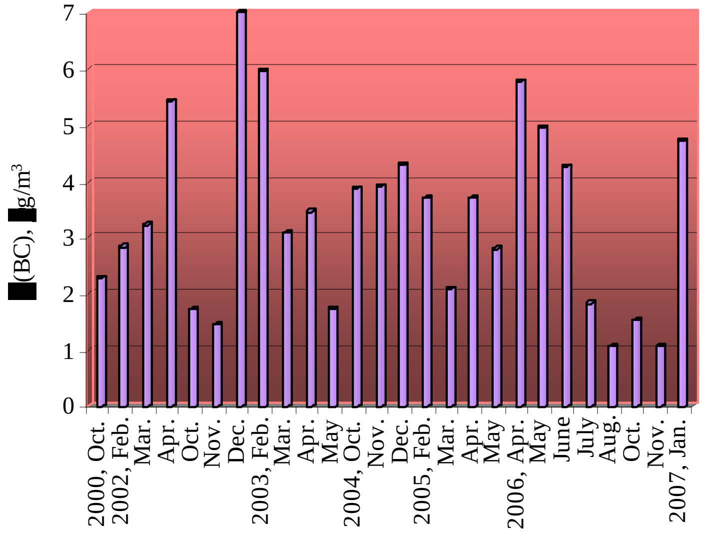

Fig. 2 Monthly average mass concentrations (γ, µg/m^3) of BC in Riga city

The first aim of the present work was to compare results of the concentrations of black carbon obtained by different reflectometers and the second aim of the research work was the clarifying whether laboratory made sampler is proper for BC measurements.

Previously the calibration between two reflectometers FH62I-R and M43D was done. The method of BC determination by the reflectometer FH62I-R is very good developed, whereas by the reflectometer M43D it is complicated and time-consuming. That is why the obtained calibration equation was further used for determination of the BC concentrations by the smokestain reflectometer M43D. Afterwards comparison of BC concentration measurements was done between the reflectometer M43D and the Black Carbon monitor Carusso MAAP/5012 in two different ways. First of all BC samples with different but definite transmission levels in range from 90% to 10% (with different degrees of blackness) were collected by BC monitor and the intensity of reflected light of spots was measured by the reflectometer M43D. The measured results of the transmission and intensity of reflected light were arranged to obtain a calibration curve using the mathematical grouping method. The comparison of BC concentrations measured by BC monitor and calculated using intensities of reflected light for the same samples was the second way to verify the operation of these two instruments with different measuring principles. Concentrations of spots with transmission in the range from 70% to 30% were in good correlation (correlation coefficient=0,92), which is seen in Fig. 3. On the other hand the correlation of achieved BC concentrations out of the mentioned transmission range was unsatisfactory and these concentrations were eliminated.

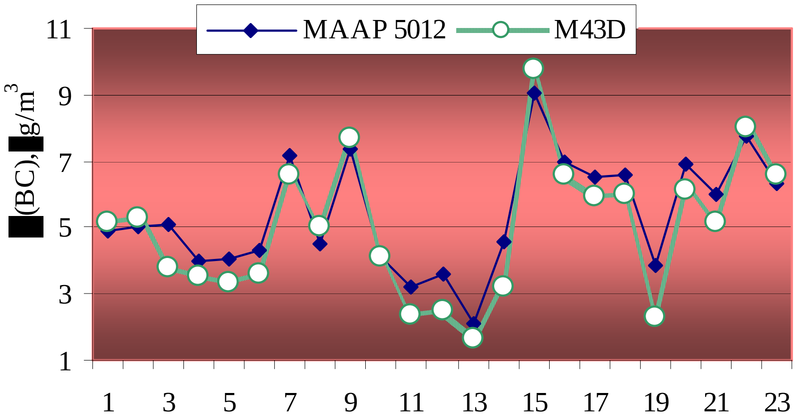

Fig. 3 Comparison of measurement results of mass concentration of BC between two measurement instruments - the reflectometer M43D and the Black Carbon monitor Carusso MAAP/5012

PM_{10} and $PM_{2.5}$ mass concentration measurements.

For the first time $PM_{2.5}$ measurements in Riga were arranged in October 2000 (Viksna et al). In the beginning of 2006 the scientists group of the Department of Chemistry started a longer PM_{10} and $PM_{2.5}$ sampling campaign. PM_{10} and $PM_{2.5}$ mass concentrations during all sampling period are showed in Table 1. At nights particulate matter concentrations are lower, but never the less the limit value for 24h, which is 50μg/m^3 is exceeded in several cases as well as during the day and night time.

Table 1. Arithmetic mean mass concentrations of $PM_{2.5}$ and PM_{10} (μg/m^3), standard deviations (Std), minimal and maximal values.

Month	**$PM_{2.5}$**				**PM_{10}**			
		Std	**Min**	**Max**		**Std**	**Min**	**Max**
March	19,4	4,4	14,0	23,6	17,9	7,7	10,2	25,0
April	25,2	8,9	15,0	40,0	51,0	13,4	31,9	73,1
April (n)*	11,2	0,8	10,7	11,8	19,1	4,4	16,0	22,3
May	20,3	8,9	13,2	37,2	37,3	7,4	27,3	47,7
June	14,7	2,3	12,8	18,6	28,3	9,2	21,5	41,1
July	15,3	1,6	11,6	17,3	26,1	7,9	12,0	41,0
Aug. (n)*	33,9	17,6	17,6	52,6	24,9	14,3	16,5	41,5
Sept. (n)*	19,2	13,7	9,0	38,8	21,3	10,1	14,2	28,4
Dec.	22,9	7,4	14,2	41,5	18,0	7,5	11,0	32,5

*- Sampling was done during night time

Very interesting data are observed if we compare the ratio between BC and aerosol mass. The relative contribution of black particles to fine particle aerosol mass is 10 to 20%, in particular cases even up to 40%. But contribution of BC to coarse particle aerosol mass only 0,2 – 1,4%. It is evident that the fine particles contain the major part of the blackness. That was also certified inspecting the blackness of aerosol particles on filters of Dichotomous $PM_{10/2.5}$ sampler. Mass concentration of BC was 5 to 7 times higher for filter spots with aerosol particles up to 2.5μm.

4. CONCLUSIONS

Comparing the obtained results of aerosol particles sampled by the laboratory-made sampler, BC monitor and Dichotomous sampler, approve that laboratory-made sampler is applicable to use this low-cost sampling device in the air monitoring and controlling system. Thus it is possible to set up several simple sampling systems around the city, to acquire more information about the quality of air and faster identify the air pollution sources and make corrections of results on humidity.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Johnson B., Shine K., Forster P. 2004. The semi-direct aerosol effect: impact of absorbing aerosols on marine stratocumulus. QJR Meteorol. Soc. 130, 1407.

Knaapen A.M., Borm P.J.A., Albrecht C., Schins R.P.F. 2004. Inhaled particles and lung cancer. J. Cancer. 109, 799-809.

Krishnan R., Ramanathan V. J. 2002. vidence of surface cooling from absorbing aerosols. J. Geophys Res.29, (art.no.1340).

Petzold A., Schönlinner M. J. 2003. Multi-angle absorption photometry- a new method for the measurement of aerosol light absorption and atmospheric black carbon. J. Aerosol Science. 35, 421-441.

Ramanathan V., Crutzen P.J. 2003. New directions: atmospheric brown “clouds”. Atmos. Environ. 37, 4033-4035.

Tainio M., Tuomisto J.T., Hanninen O., Aarnoi P., Koistinen K.J., Jantunen M.J., Pekkanen J. 2005. Health effects caused by primary fine particulate matter ($PM_{2.5}$) emitted from buses in the Helsinki Metropolitan area, Finland. Risk Analysis. 25, 152.

Viksna A., Lindgren E.S., Standzenieks P., Jacobsson J. 2004. EDXRF and TXRF analysis of elemental size distributions and environmental mobility of airborne particles in the city of Riga, Latvia X-Ray Spectrom., 33, 414.