SOURCE APPORTIONMENT STUDIES SESSIONS

THE PARTICULATE MATTER PROBLEM IN CYPRUS

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SOURCES OF PARTICLE-PHASE POLYCYCLIC AROMATIC HYDROCARBONS IN A **RESIDENTIAL SITE IN SOUTHERN GERMANY**

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ANALYSIS OF THE ATMOSPHERIC AEROSOL AT SÃO PAULO CITY WITH FINE TIME RESOLUTION

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CHARACTERIZATION OF PM10 EMISSION SOURCES IN THAILAND

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PM10 SOURCE APPORTIONMENTS WITHIN THE CITY OF KLAGENFURT, AUSTRIA

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CHARACTERISATION OF TRACE ELEMENTS IN URBAN ATMOSPHERIC DUST AND THEIR SOURCE APPORTIONMENT IN KOLKATA METROPOLIS, INDIA

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A COMPARATIVE STUDY OF HEAVY METAL CONCENTRATIONS IN ROAD DUSTS DEPOSITED AT THE INDUSTRIAL AREAS

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COMPARISON OF SIZE DISTRIBUTION CHARACTERISTICS OF PARTICULATE MATTER COLLECTED FROM INDUSTRIAL AREAS

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INVESTIGATION OF METAL CONCENTRATIONS WITHIN PM_{10} PARTICLES USING TUNNEL SAMPLING TECHNIQUES

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CHEMICAL CHARACTERIZATION AND SEASONAL VARIATION OF THE IONIC COMPOSITION OF PM 1.0 AND PM2.5 AEROSOLS

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THE DUST UPTAKE CAPACITY OF EUONYMUS JAPONICUS THUNB. LEAF SURFACE AND CAPTURED PARTICLE MORPHOLOGY IN AIR POLLUTED CITY

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THE PARTICULATE MATTER PROBLEM IN CYPRUS

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ABSTRACT

Due to the dry climate in Cyprus Particulate Matter is resuspended from soils and other surfaces. Besides the dry conditions many mines and quarries are distributed over the whole country and many smaller roads are unpaved which are contributing to dust emissions. Within an UNOPS project an illustrative overview over the PM_{10} situation in Cyprus was carried out. It can be recognised that at all traffic and at some residential and urban background sites the actual EU limit values have been exceeded. As an average 17% of the 24h EU limit exceedances are caused by Sahara dust events. The origin of the PM_{10} load has been investigated by factor analysis. Besides the natural events and natural background concentrations the results of the PM investigations identified the traffic as the main anthropogenic pollutant source. The comparison of the PM_{10} concentrations in Cyprus cities with values of other European cities demonstrates the PM_{10} problem in Cyprus and underlines the necessity of abatement strategies.

1. INTRODUCTION

Cyprus with a dry Mediterranean climate with few rainfall and high temperatures has difficulties to comply with the PM_{10} limit values due to transfer of soil dust from rural areas into the cities and inhabited areas and resuspension of particulate matter. From the results obtained by measurements undertaken in Nicosia it was recognized that more than 35 daily PM_{10} averages exceeded the limit value of 50 µg/m³. However, according to the relevant EU Directive where the PM_{10} limits are exceeded owing to concentrations of PM_{10} in ambient air due to natural events (i.e. from dry regions), the Member States are not obliged to implement action plans for these cases. They will inform the EU Commission providing the necessary justification to demonstrate that such exceedances are due to natural events. So, it was very important to investigate within the UNOPS project 'Preliminary Assessment of Ambient Air Quality in Cyprus' (Baumbach and Pfeiffer, 2004) in more detail the natural origin of the PM concentration by means of PM_{10} measurements and analyses. Therefore, the objective of this study is to demonstrate the particulate matter problem in the dry region of Cyprus.

2. METHODOLOGY

2.1 Site description

Cyprus is situated in the eastern part of the Mediterranean Sea. The total area is 9250 square kilometers. It has a Mediterranean climate with long dry summers and soft winters. The hottest months are July and August, with maximum temperatures above 40°C. The average temperature in summer is between 25° and 30°C. Coldest months are December, January and February with average temperatures in the mountains between 3° and 12°C. From October until March an average of 300 mm rain can fall, but in the western region this can be as much as 1100 mm. The three selected study areas are: a traffic-impacted site in the city of Nicosia (General Hospital; 53°22 E, 38°92 N), a residential site in Famagusta (58°51 E, 38°87 N) and a rural background site Agia Marina (50°52 E, 38°77 N).

2.2 Sampling

Gravimetric particulate matter sampling devices with LVS (Low Volume Sampler) are used for PM_{10} sampling. This is in accordance with the reference method defined in EU Directive 1999/30/EC and EN 12341 (1999). The pumped volume flow rate for PM_{10} samples is 2.3 m³/h and the sampling duration is 24 hours. The chosen filter material for PM_{10} measurement is filer type AE 98 Schleicher & Schuell company, membrane filters of cellulose nitrate with a diameter of 47 mm (sampling diameter: 41 mm) and a pore size of 5 µm. It is required by EN 12341 that the filters are equilibrated at 20° C (±1) and 50% R.H. (±5), for 48 hours. This equilibration was performed before the filters were weighed previous to the sample collection and after sampling, before the filter were weighed again with the collected samples.

3. RESULTS AND DISCUSSION

3.1 PM₁₀ level

Figure 1 represents the 24h average PM_{10} concentration in Nicosia traffic and Agia Marina rural background site. The measurements carried out in Nicosia traffic exceed 66 days the 2005 EU daily limit value which results 26% of exceedance (without special events). From the graph it is found that Sahara dust event occurs on 30th of May, 19th of March and 6th of April in both the sampling points in traffic and rural site.



Figure 1. 24h average PM₁₀ concentration in Nicosia traffic site from 05.12.02 to 15.09.03 and in Agia Marina rural background site from 03.11.02 to 16.09.03

Most of the high PM_{10} events are recorded in the period October-May, although several events are also recorded in July to September. The highest frequency of PM_{10} peak events in spring-summer and autumn are probably due to a frequency of Sahara dust events in this period. However for the other periods, the correlation of these peak levels of PM_{10} and gaseous pollutants points towards a dominant anthropogenic cause for most of the exceedances of the PM_{10} limit value. As an average, about 17% of these exceedances (66 events from 386 exceedances), depending on the monitoring sites, are recorded under Sahara dust events.



Figure 2. Comparison of PM₁₀ concentrations of Cyprus cities (2002/03) with other European cities (2001)

Figure 2 presents the comparison of the PM_{10} annual average concentrations in Cyprus cities with values of other European cites. It can be seen that the PM_{10} annual average concentrations in urban traffic areas in Cyprus and even in some residential areas exceed the EU annual limit value of 40 µg/m³. At these and other sites also the EU 24h limit value of 50 µg/m³ is exceeded more than the allowed 35 times. Within the European cities the Cyprus PM_{10} concentrations are ranging in the upper levels. This is partially caused by the high natural background contributions due to the dry soils in this Mediterranean region.

3.2 Particle size distributions

Within a first experiment the size distribution of the airborne particles at the Nicosia traffic site was investigated using a 8-stage Andersen ambient Cascade impactor. The result is shown in Figure 3. The highest portion (33%) is caused by the finest fraction on the back-up filter with particle sizes $< 0.4 \,\mu\text{m}$ aerodynamic diameter. From other investigations at a high traffic site in the German city of Stuttgart it could be demonstrated by Scanning Electron Microscopy (SEM) with energy dispersive X-ray detection (EDX) that this fraction of fine particles consists completely of soot particles (Baumbach et al., 2006). Whether in Cyprus these fine particles are also caused by soot emissions from diesel vehicles has to be proved in further investigations.



Figure 3. Particle size distribution in Nicosia traffic site during 15 - 17.6.06



Figure 4. PM₁₀ source allocation in Nicosia traffic and Agia Marina rural background site without Sahara dust events

3.3 Source identification analysis

A multivariate receptor modeling using Principal Component Analysis (PCA) was applied to the PM_{10} data set for source identification. Enrichment factor analysis was performed in another study (Bari et al., 2005) where the ambient PM_{10} composition was compared with the local soil composition taken as reference. Figure 4 displays the PM_{10} source identification for Nicosia traffic and Agia Marina rural background site without including Saharan dust events. In traffic site seven source types were identified (accounting 83% variance) and these were secondary pollutants with sea-salt (20%), mineral dust resuspended by traffic (16%), local mineral soil (13%), oil and diesel combustion (10%), vehicle abrasion (9%), gasoline exhaust (9%) and unknown source as factor 7 (6%). The rest 17% could not be explained. In the rural background site also seven source types were identified (accounting 82% variance) which were secondary pollutants (19%), local mineral soil I & II (32%), soil from surroundings (11%), sea-salt (8%), waste burning (7%) and oil and diesel combustion (5%) and the rest 18% were not allocated. At the residential site Famagusta 22% could be allocated as traffic induced particulate matter. The other 58% could be identified to be from soil and sea-salt origin.

4. CONCLUSIONS

The major goal of this study was to investigate and assess the particulate matter situation on the Mediterrenean island of Cyprus. It is observed that at all traffic and at some residential sites the EU annual limit value was exceeded. Long range transports of Saharan dust were recorded over urban as well as rural areas with a major frequency in summer and spring periods and about 17% of the 24h limit value exceedances were monitored under these events. The comparison of the PM_{10} concentrations in Cyprus cities with values of other European cities demonstrates the major PM_{10} problem in Cyprus. From cascade impactor sampling highest portion was found in the particle sizes < 0.4 µm. The source identification calculated by Principal Component Analysis shows that the dominant anthropogenic source types affecting the particulate matter composition at Nicosia traffic site were dust resuspension by vehicles, diesel and gasoline vehicles and diffusive and exhaust emissions of traffic. In the rural background site Agia Marina, local mineral soil and sea-salt source types were found to be the largest contributor to PM_{10} which can be considered as being of natural origin.

5. ACKNOWLEDGEMENTS

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SOURCES OF PARTICLE-PHASE POLYCYCLIC AROMATIC HYDROCARBONS IN A RESIDENTIAL SITE IN SOUTHERN GERMANY

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ABSTRACT

Particle-phase polycyclic aromatic hydrocarbons (PAHs) samples were collected from October 2005 to March 2006 at a rural residential site surrounded by forests near Stuttgart in Germany. PAH samples collected on glass fibre filters were firstly extracted using toluene with ultrasonication and analysed by GC/MS. 21 PAH compounds including 16 USEPA priority pollutants were detected and quantified in this study. Total PAH concentrations were in the range 1.7 - 118 ng/m³. It was observed that the combustion derived PAHs and the carcinogenic PAHs were highly pronounced in the winter samples. These results were also compared with the fingerprints of PAH emissions from wood combustion carried out in the test facilities at Stuttgart. To investigate the sources of PAHs in rural residential ambient air, diagnostic analysis of ratios was developed. Positive Matrix Factorization (PMF) modeling was implemented to investigate the sources of PAHs in this residential area.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants and include some of the most carcinogenic materials (IARC, 1984). PAHs are formed during the incomplete combustion of organic matter and fossil fuels (e.g. diesel engines, domestic heating, pyrolysis of coal, oil, wood) and approximately 90% of PAH emissions are estimated to be anthropogenic (Harvey, 1997; Goetze et al., 1991). PAHs are present in both gas and particle phases. Lighter PAHs are formed predominately in the gas phase, whilst high molecular weight PAHs are found mainly in the particle phase. Especially in rural areas, where wood is frequently used for heating seasons, residential wood combusiton is an important source for soot and polycyclic aromatic hydrocarbons (PAHs), mainly in winter. As the study site is situated in a forest area by elevated terrain and subject to strong winter inversions, the burning of wood can be the cause of considerable annoyance and high PM₁₀ concentrations. Therefore, the objective of this study was to identify and quantify the main sources of particle-phase PAHs in such a rural residential site.

2. METHODOLOGY

2.1 Area of study

Dettenhausen is a rural residential town in the district of Tuebingen and situated 19 km south of Stuttgart, capital of Baden-Wuerttemberg state in Germany. It covers an area of 11.02 km^2 with inhabitants of 5389. The residential site is surrounded by topographic features with altitudes of 500 m above sea level.

2.2 Sampling procedures

The sampling period was initiated from 1 November 2005 to 31 March 2006 which is characteristic of the winter time with lower temperatures and higher frequency of surface inversion episodes, limiting the dispersion of pollutants within the atmosphere. The samplings of particulate matter, PM_{10} were carried out using low volume samplers (LVS) in accordance with the reference method defined in EU Directive 1999/30/EC and EN 12341 (1999) and the chosen filters were glass fibre filters (GF, Whatman, 50 mm diameter). The pumped volume flow rate was 2.3 m³/h and the sampling duration was 48 to 72 hrs. According to the specifications of EN 12341, filters were equilibrated in the weighing chamber for 48 hrs under controlled condition to prevent hydration of the filters' surface utilizing an analytical balance and stored in a freezer (-20 °C) until analysis.

2.3 PAH analysis

50 glass fibre PM_{10} filter samples were analysed by Gas Chromatgpraph Mass Spectrometry (GC/MS). A filter aliquot containing half part of filter was spiked with 100 µl PAH isotope labelled standard (16 perdeuterated PAHs according to USEPA) and 100 µl PHTH (d⁴- Dibutylphthalate and d⁴-Benzylbutylphthalate) standards. The filter extraction was performed with adding Toluene for 30 min in an ultrasonic bath. Filter extracts were analysed on a Hewlett Packard 5890 Gas Chromatograph coupled with a HP 5971 Mass Selective Detector

(MSD). The PAHs were analyzed and identified one by one, based on their retention time and respective areas, relating them directly to the isotope labelled standards added to the extracts.

3. RESULTS AND DISCUSSION

3.1 PAH levels

16 species specified by USEPA as priority pollutants which are naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Py), chrysene (Chr), benzo[a]pyrene (BaP), benzo[a]anthracene (BaA), benzo[k]fluoranthene (BkF), benzo[b]fluoranthene (BbF), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) are considered for analysis. Additionally 5 species retene (Ret), benzo[j]fluoranthene (BjF), perylene (Prvl), triphenylene (Tpl) and benzo[e]pyrene (BeP) which were frequently used as reference PAH compounds are detected and quantified. Figure 1 shows the comparison of relative average contribution of single PAH compunds to total PAHs for residential ambient samples and for wood burning in the test facility. The average value obtained for the sum of 21 PAHs in the 50 ambient samples was 22.9 ng/m³, maximum value of 121.4 ng/m³ and minimum value of 1.6 ng/m³. It can be seen that the combustion derived PAHs (contributing 75% of total PAHs) such as Fluo, Py, Chy, BbF, BkF, BaA, BeP, IP and BghiP and the carcinogenic compounds (contributing more than 40% of total PAHs) such as BbF, BkF, BaA, BaP, BjF, DahA and IP are highly pronounced in the winter samples. The compounds Fluo, Py, Ret, BaA, BjF, BeP, BaP and Pryl which were found in the ambient air show similar behaviour with the concentrations obtained from wood burning. The typical compounds for wood burning such as Ret, Fluo, Py, Ant, BaA, BaP, Chr (Ramdahl, 1983; Li and Kamens, 1993; Khalili et al., 1995; Marbach and Baumbach, 1998; Kulkarni and Venkataraman, 2000) show about 70% contribution whereas other compounds like BkF, BjF, BeP, IP and BghiP also show some proportions.



Figure 1. Relative average contribution of PAHs in ambient residential and wood burning samples

3.2 Potential sources of PAHs – Diagnosis of ratios

The use of relative ratios of PAH as confirmation indicators of the source that emits the pollution into the urban atmosphere was suggested by Sawicki (1962). To investigate the origin of PAHs in airborne particulate matter in Dettenhausen, diagnostic analysis of ratios was developed. In this study the mean values of the combustion-related PAHs to the total PAH concentrations (CombPAH/TPAH) was 0.4 which is similar to the ratio obtained from wood combusiton (0.39, Kalaitzoglou et al., 2004). The mean ratios obtained from Fluo/Fluo+Py was 0.5 ± 0.04 approaching the value calculated for gasoline vehicles (0.40, Rogge et al., 1993a), used motor oil (0.36, Sicre et al., 1987) and for wood burning (> 0.50, Yunker et al., 2002). The mean IP/IP+BghiP ratio was 0.40 ± 0.02 indicating emissions from diesel vehicles (0.35-0.70, Rogge et al., 1993b). The wood burning influence can be assessed from the ratio Phe/Phe+Ant with its value 0.9 ± 0.1 is comparable to the value (0.89) indicated in

Kalaitzoglou et al., 2004 as well as the ratio Fluo/Py was 1.1 ± 0.20 can be compared to that reported in the literature (0.9 ± 0.30 , T.Jordan, 2005; 0.8 - 1.0, Freeman and Cattell,1990). Furthermore, the ratios BaA/Chr (1.5 ± 0.35), BaA/BaP (1.6 ± 0.70) and Ret/Ret+Chr (1.76 ± 1.8) are also the characteristic of wood burning (Li and Kamens, 1993; Simcik et al., 1999; Cass et al., 2001). The results obtained from different ratios suggest that the major polluting sources in the rural residential area Dettenhausen during winter were the burning of fuels like wood and oil, diesel and gasoline vehicles. The ratio analysis contríbutes qualitatively to the identification of the main emission sources in the residential area, which are afterwards related to the correlated compounds obtained from Positive Matrix Factorization (PMF) modeling.

3.3 Factor Analysis

In this study PMF was used to analyze the PAH dataset. PMF is a relatively new variant factor analysis technique developed by Paatero and Tapper (1993, 1994) and Paatero (1997). PMF has special features of the use of realistic error estimates to weight the data values and the imposition of non-negativity constraints in the factor computational process. The application of PMF depends on the estimated uncertainties for each of the data values. The uncertainty estimation provides a useful tool to decrease the weight of missing data and data below the detection limit in the solution. The procedure of Polissar et al. (1998) was used to assign measured data and the associated uncertainties as the input data to the PMF. Thus seven PAH sources were identified in the residential area. Figure 2 displays the source profiles as percentages of source and species contributions. Six sources show PAH profiles with strong similarities to particular source types present in the area and the origin of Factor 4 is poorly understood. Factor 1 and 2 are consistent with diesel and gasoline vehicle emissions. According to Zielinska et al. (2004) diesel exhauset gases contained higher amounts of lower molecular weight



Figure 2. PMF modelled percentages of source and species contributions for the residential site. Darker bars highlight identified source tracers.

 $(2 - 4 \operatorname{ring})$ PAHs than exhaust from gasoline; the amount of 5 ring PAHs is comparable and low for both fuels and for gasoline powered vehicles especially higher molecular weight compounds were more abundant. In Factor 1 lower molecular weight compounds (Ace, Acl, Fl, Phe, An, Fluo, Py, Tpl, Ret, Chr) except Nap show higher proportion compared to Factor 2. Thus Factor 1 indicates emission sources from diesel vehicles whereas highmolecular-weight PAHs (IP, BghiP) show the dominance in Factor 2 representing gasoline vehicle emissions. Factor 3 is associated with high contribution of Fluo, Py, Chr, BaA, BkF, BbF, BeP, BaP, IP, BghiP and represents road dust (Harrison et al., 1996; Marynowski et al., 2004). Factor 5 and 7 show strong similarities with source contributions indicating wood burning. Kulkarni and Venkataraman (2000) associated Chr, BaP, Fluo and Py with wood combustion whereas Khalili et al. (1995) identified Ant, Ph, Fluo and Py as tracers for wood combustion. The high contribution of Retene is the suggested tracer for wood burning (Ramdahl 1983; Brenner et al., 1995; Schauer et al., 1996). Factor 6 is enriched in oil burning exhausts. Oil combustion emissions are enhanced in volatile PAHs (Phe, Py, Fluo) with smaller but significant contributions of high molecular weight PAHs like IP, BghiP (Kavouras et al., 2001), as seen in Factor 6. In addition, BkF, BbF, Chr, Tpl and BaA are frequently observed in oil combustion emissions (Rogge et al., 1997). Furthermore, significant levels of Nap, Acl and Flu also identified Factor 6 as oil burning tracer (Larsen et al., 2003). The origin of Factor 4 is poorly understood and is represented as other sources.

4. CONCLUSIONS

The major goal of this study was to identify of the different emission sources of PAHs that have a significant influence on the concentrations of atmospheric particulate matter in the rural residential site Dettenhausen, Germany. The emission sources indentified in this study have resulted from PAH source fingerprints in the literature associated with calculation of PAHs ratios and Postitive Matrix Factorization modeling. Results showed that wood burnig may be assumed to be the main sources of PAHs in the ambient air in the residential site. Among other sources diesel and gasoline vehicle emissions, oil burning and road dust were also identified. To make a quantitative source apportionment, analyses of futher typical tracer organic compounds of corresponding local souce profiles have to be investigated.

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ANALYSIS OF THE ATMOSPHERIC AEROSOL AT SÃO PAULO CITY WITH FINE TIME RESOLUTION

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ABSTRACT. Atmospheric aerosol samples collected every 3 h, from 14 to 18 July 2005, were used to study the sources of particulate matter at the São Paulo City. Samples were collected using a stacked filter system, in order to fractionate the aerosols in their fine and coarse fractions (equivalent aerodynamical diameter, $\phi < 2.5 \mu m$ and $2.5 \mu m < \phi < 10 \mu m$, respectively). The concentrations of particulate matter on both fractions were determined; trace elements contents were also measured on both fractions using PIXE technique. Four sources of coarse particulate (soil, industrial process, fossil fuel burning, and sulphates) and four sources of fine particulate (industrial process, fossil fuel burning, soil, and source of Al and K) were identified using Principal Components Analysis, and meteorological information. The results showed that the high resolution sampling could be a useful tool to provide a good definition of the principal components, despite the relatively limited number of samples used in this study.

1. INTRODUCTION

The São Paulo Metropolitan Region (RMSP) is a complex and peculiar ambient, specially concerning to its atmospheric pollutants. An inventory performed by the local environmental control agency evaluates that 2.3×10^6 t of noticeable pollutants were injected in the RMSP airshed, on 2005 (CETESB, 2006). Nearly 95% of this were accounted to the fleet of 7.2 million vehicles, while the remaining were attributed to the 46.6 thousand industrial units.

The characteristics of its sources are contrasting with other word megacities. By one side is the own Brazilian energetic matrix, composed by 40% of renewable sources, or hydroelectricity, against the word wide 85% average usage of fossil fuels. By another side is the Brazilian range of vehicular fuels, which compositions have been very dynamic. It is the case of ethanol, used as pure fuel, or mixed in the normal gasoline (22%, as antiknock agent) or, either on a fully variable proportion, in the recent flex motors. There is also an increase adaptation of vehicles for Natural Gas and the commercialisation of a mix of diesel and vegetable oils (called bio-diesel).

The atmospheric aerosol represents one of the worst air pollution problems in the region, and has been studied in several works (e.g. Orsini et al., 1986; Andrade et al., 1994; Alonso et al., 1997; Artaxo et al., 1999; Castanho and Artaxo, 2001; Miranda et al., 2002; Bourotte et al., 2005). Nevertheless, the complexity of this area and the dynamics of its source impose the permanent study of atmospheric aerosol's comportment. Its deleterious effects directly affects the life of 19.3 millions inhabitants, distributed over an 8051 km² area (Emplasa, 2006).

2. MATERIALS AND ANALYTICAL METHODS

The sampling campaign started at 0 h of day 14 July 2005 (Thursday) and ended at 24 h of day 18 July 2005 (Monday), given a total of 40 samples, collected every 3 h. The sampling station was settled on the roof of the Institute of Geosciences (23K 032720 7393593 UTM), in the main campus of the São Paulo University. Particles with equivalent average aerodynamical diameter (ϕ) less than 10µm (PM₁₀) were admitted in a staked filter unit proposed by Hopke et al. (1997). The particles were retained on Polycarbonate filters (diameter of 47 mm); first the coarse (2,5µm< ϕ <10µm – PM_{2,5-10}) on filter with 8 µm holes, and after, the fines (ϕ <2,5µm – PM_{2,5}) on filter with 0,4 µm holes. The air inflow was of 16.6 l/min. The weighing of the collected mass was performed with a microanalytical balance, following standard procedures to eliminate electrostatic charging and contamination by suspended particles. One quarter of some of the collected filters, in both fractions, was analysed by PIXE (Particle Induced X-ray Emission; Johansson et al., 1995), given the concentration of chemical elements with atomic number greater than 12.

3. RESULTS AND DISCUSSION

Figure-1A shows the temporal series of the concentrations of fine, coarse and inhalable particulate. The national standards for daily and for annual average concentrations of PM_{10} , 150 and 50 µg/m³ respectively, were not surpassed on those days.

explained by the typical reduction of urban activities on Saturdays and Sundays and, also, by the progressive increase of the wind speed along the experiment (Figure-1C), what facilitates the dispersion of pollutants. The concentration peak by the end of Friday is typical of the chaotic traffic in this day of the week. It could had been intensified by the prevailing N and NNW wind after midday (Figure-1B), bringing directly the emissions of a close 12 tracks avenue (Marginal Pinheiros).

The average concentrations of the trace elements in the filters and the respective standard deviations were determined. Principal Component Analysis (PCA) applied in all the obtained database, revelled four components, for PM2,5-10 and $PM_{2.5}$ either. These results are on Tables 1 and 2 (the highest loads in each component are in boldface), together with the eigenvalues and the explained cumulative variance of the components and, also, the communalities for each chemical element. Missing

The concentrations increased from Thursday till Friday, decreasing during the weekend. That could be



Figure 1. Temporal series for: (A) PM₁₀ concentrations (inhalable), PM_{2.5} (fine) and PM_{2.5-10} (coarse); (B) Wind direction; (C) Wind speed. The time scale is in hours and begins at 0 h, 14 July 2005.

values are filled with the respective average concentration, but elements present in less than 80% of the total number of cases (26) were neglected. The Cr was also eliminated of the PCA in the PM_{2.5-10} analysis because some filters were contaminated with it. At least 82% of the variance were explained by the extracted components, in both cases - fine and coarse particulate.

The first component of the PM_{2,5-10} is identifiable as soil ressuspention. The TCC (Total Coarse Concentration) prevailed on this component, showing a load of 0.85. In the second component, Zn, Cu and Mn could be associated to industrial activities, especially those involving metallurgical process. The significant load of Cl in this component could be attributed to sea salt transported by the E and SE wind, often enhanced by sea breeze, and arriving to the sampling point after pass through the largest industrial area of the RMSP. Nevertheless the association of Cl with industrial sources persists with N and NO wind, when we look to the temporal series of these elements. Pb and Br, relatable to fossil fuel burning define the third component. In that case, the Pb should come from the petroleum mineral composition itself. The fourth component is characterised by S, mainly associated to sulphates.

The first component of the PM_{2.5} may be associated to industrial process, especially metallurgy (Table-2). The Cl could be associated to industrial sources, like in the case of $PM_{2.5-10}$. The second component, grouping Pb, S and TFC (Total Fine Concentration) should be from the usage of fossil fuel (Br was not detected in the fine filters because they were contaminated with it). The majority of TFC is related to this factor (load of 0.63), being coherent with the source inventory for the RMSP (Cetesb, 2006). The third component, with high load of Ti and Ca, may be attributed to the fine fraction of soil ressuspention. The forth component groups Al and K, were expected to be together with soil ressuspention, but in this case arose as an specific unidentified source.

It is remarkable that although the highest load of the TFC be in the second component, it also has significative loads in the other three components, which totalize more than half of its explained variance. Such is an important indication about the $PM_{2,5}$, which has a high association with respiratory diseases. It indicates that controlling actions should take care of all that sources.

Only a few amount of the Cu variance was explained (0.484). It could means that its sources are diffuse, needing to be better evaluated (may be brushes of the many electric motors used on vehicles, home appliances and tools).

Co	oncentration	S		Rotated	l Principal	l Compone	nts	
Average	Deviation	Cases (N)	Comm.	Element	1	2	3	4
(µg/m³)	(µg/m³)							
0.0487	0.037	25	0.937	Ti	0.93	0.23	-0.14	0.01
0.468	0.36	26	0.865	Ca	0.86	0.24	-0.03	-0.05
16.5	9.6	26	0.927	CPG	0.85	0.44	-0.10	-0.01
0.640	0.49	26	0.953	Fe	0.84	0.50	-0.04	0.04
0.00328	0.0022	21	0.783	Sr	0.83	0.256	0.10	-0.12
0.822	0.56	22	0.762	Al	0.72	0.08	0.39	0.30
0.162	0.13	26	0.955	Κ	0.71	0.14	0.04	0.66
1.18	1.4	26	0.583	Si	0.70	0.08	-0.31	0.00
0.0366	0.035	26	0.829	Zn	0.15	0.87	0.23	-0.07
0.00640	0.0063	25	0.784	Cu	0.36	0.80	0.08	0.076
0.0966	0.061	25	0.652	Cl	0.19	0.76	0.18	0.07
0.0174	0.0088	26	0.898	Mn	0.64	0.70	-0.02	-0.01
0.00739	0.0067	26	0.757	Pb	0.04	0.16	0.85	-0.06
0.184	0.083	26	0.792	Br	-0.22	0.20	0.82	0.16
0.0873	0.13	23	0.962	S	-0.13	-0.01	0.06	0.97
0.00342	0.0040	21		Cr				
				Eigenvalues	5.94	3.17	1.79	1.53
				Cumulative	39.6	60.8	72.7	82.9
				Variance				

Table 1. Trace elements concentrations and Principal Components in the PM_{2.5-10} fraction

Tabl	e 2. Trace e	lements cor	ncentration	is and Principal	Compone	ents in the l	PM _{2.5} fracti	ion
Co	oncentration	S		Rotated	l Principal	l Compone	ents	
Average	Deviation	Cases (N)	Comm.	Element	1	2	3	4
(µg/m³)	(µg/m³)							
0.0101	0.0090	26	0.926	Mn	0.95	0.02	0.16	-0.05
0.0304	0.030	22	0.935	Cl	0.91	0.00	-0.09	0.32
0.203	0.15	20	0.927	Fe	0.77	0.07	0.324	0.15
0.0595	0.053	26	0.916	Zn	0.77	0.51	-0.10	0.22
0.285	0.17	26	0.833	S	0.01	0.90	0.06	-0.14
0.0114	0.009	26	0.846	Pb	0.09	0.87	-0.20	0.19
15.2	6.5	26	0.815	CPF	0.37	0.63	0.39	0.36
0.0927	0.074	25	0.837	Ca	0.03	0.00	0.91	-0.03
0.0185	0.012	26	0.879	Ti	0.10	-0.19	0.81	0.43
0.00953	0.011	26	0.484	Cu	0.39	0.30	0.44	0.22
0.267	0.26	21	0.814	Al	0.13	0.01	0.04	0.89
0.185	0.12	26	0.886	Κ	0.26	0.22	0.36	0.80
0.00101	0.0007	15		Sr				
0.654	0.92	20		Si				
				Eigenvalues	3.32	2.41	2.15	2.03
				Cumulative	27.6	47.7	65.6	82.5
				Variance				

No substantive differences were found among the source groups associated to the components in this experiment and those obtained in previous works. Nevertheless, it was evident that the 3 h sampling time

resolution enabled a sharper definition of the elements pertaining to each component, even with a relatively limited number of cases, what, in principle, could make unviable the use of PCA. The components definition was very similar to that obtained by Andrade (1993) and Andrade et al. (1994) in the Spacex experiment (135 samples), using a resolution of 6 h for daytime sampling and 12 h for nigh-time. Other experiment, EIF (137 samples), described by Andrade, 1993, with less resolution (12 h) and performed during summer time, lost some definition of the components. The same could be observed in Castanho and Artaxo (2001) with an experiment conducted with 12 h resolution, in summer time, at the School of Public Health (142 samples collected nearly 8 km farther from our station).

Nevertheless, the increase of the time resolution reduced the collected mass and, in consequence, the capability to detect some trace elements. In that sense it should be desirable better work that compromise between time resolution and detection limit for those elements. In our case, for instance, only one more sampling hour means a mass increase of 25%. Increase in the sampler's airflow also provides a proportional addition in the collected mass, although care must be taken to do not run out of the specifications for the samplers cut off diameters.

4. CONCLUSIONS

The use of PCA in a database collected with high time resolution (3 h) at the RMSP enhanced the components definition and respective groups of sources. Considering the complexity of the megalopolis, such procedure was important to increase the correlation between chemical elements related to a source, or a group of sources. Variability and correlation are bases of the PCA. Therefore, the increase of the time resolution in experiments where the use of PCA is intended, may improve its results. Data base obtained with large time intervals sampling may highly smooth the variability of the ensemble, in such a way that it could compromise the correlation between the elements of a source (or group of sources), even if a large number of samples are available. The sources discriminated in the present study, in the $PM_{2,5-10}$ fraction, and following the amount of explained variance, were: soil ressuspention, industrial process, fossil fuel burning, and sulphates; in the $PM_{2,5}$ were: industrial process, fossil fuel burning). Nevertheless more then half of its explained variability is connected to the other three factors, indicating that air control actions in the fine particulate fraction should take care of all the specified sources.

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SOURCES, CONCENTRATIONS AND DEPOSITION OF HEAVY METALS IN STOCKHOLM

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ABSTRACT

Concentrations of particulate heavy metals in air and precipitation were measured in Stockholm during 2003-2004. Filter sampling were made both in a heavy trafficked street canyon and at roof levels to estimate emission factors and the contribution from traffic to observed concentrations. Average concentrations of cadmium were 50 times lower than the EU directive and for nickel and arsenic 10 and 6 times lower. Higher concentrations were in general observed in the street canyon in comparison to roof levels indicating the influence from road traffic emissions. The local traffic was found to be responsible for 90% of the observed copper concentration at the street canyon site. It is likely that the major source for copper is wear of break linings. Local traffic contribution for chrome, zinc and lead were estimated to be 20 %. Lead concentrations have decreased during 1996 – 2004 due to reduced emissions from wear of brake linings.

1. INTRODUCTION

The concentrations and distribution of heavy metals in urban air is not well known mainly due to lack of measurements in city environments. More detailed investigations, both measurements and calculations, are needed in many European cities in order to compare the levels to the new directive regulating heavy metals in air (2004/107/EG). Vehicle components, pavement material, road equipment, road maintenance activities are important sources of heavy metals in urban environments. Road traffic environment is also one of the most important sources that contribute to human air pollution exposure. Emissions from traffic are due to wear of brakes, tires, road pavement, vehicle components and also due to exhaust emissions. Corrosion of metallic material alongside streets may also contribute to the levels found in air. Particulate metal compounds may be present on different particle sizes and in different chemical forms (e.g. elemental, sulphates or oxides). This may lead to different toxic and carcinogenic effects.

2. METHODOLOGY

Parallel filter sampling of particulate heavy metals was made in a densely trafficked street canyon (Hornsgatan) and at an urban background site at roof level in central Stockholm, Sweden. Weekly samples were collected once per month using Gent samplers (Hopke et al., 1997) with a 10 µm cut-off (PM10). Monthly precipitation samples were also collected during the same period at the roof level site using wet only precipitation samplers with automatic lid to minimize the influence from dry deposition (no data presented in this paper). Filters and precipitation samples were analysed for 15 metals, arsenic, (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), vanadium (V), zinc (Zn), mercury (Hg) and wolfram (W) using ICP/AES (http::www.analytica.se). Hg was sampled and analysed as described by Zielonka et al. (2005).

Road traffic emission factors (g/vehicle kilometres; g/vkm) were estimated using NOx as tracer for traffic emissions:

$$Ef^{Metal} = Ef^{NOx} \cdot \frac{C_{Street}^{Metal} - C_{UB}^{Metal}}{C_{Street}^{NOx} - C_{UB}^{NOx}}$$

Were E_f^{Metal} and E_f^{NOx} is the calculated emission factor for NOx and the metal, respectively, C_{street} and C_{UB} are the measured concentrations at street level and at roof level (urban background), respectively. The total road traffic emissions in Stockholm was estimated by multiplying the emission factors by the total road traffic transports (vehicle kilometres). Based on the emission factors road traffic contributions to the total urban background levels were estimated using a Gaussian air quality dispersion model (SMHI, Airviro; <u>http://airviro.smhi.se/iairviro</u>) (see Johansson et al., 2006). Meteorological conditions were based on a climatology that was created from 10 years of meteorological measurements (15 minute averages) in a 50 meters high mast located in the southern part of Stockholm. The wind field for the whole model domain was calculated based on the concept first described by Danard (1976). The dispersion calculations were performed on a 100 meter resolution (122 500 receptor points). Individual buildings and street canyons are not resolved but treated using a roughness parameter (similar to the treatment used by Gidhagen et al., 2005).

3. RESULTS AND DISCUSSION

Figure 1 shows the observed concentrations. The temporal variations were quite similar for the street and roof measurements for all metals. In general, relatively low levels were found during September, October, February

and March and relatively high levels were found during November – January, April and August. For most heavy metals substantially higher levels were observed in the street canyon as compared to the roof site. The largest difference was found for Cu and Sb, with on average more than 7 times higher levels in the street compared to roof. W, Co, Mn, Zn, Mo and Pb were found to have 4.0, 3.1, 2.8, 2.4, 2.2 and 2.1 times higher levels in the street canyon as compared to the roof site. For As and Cd only a few values were significantly above the detection limit.

In comparison with the target values for year 2013 according to the EU directive for As, Cd and Ni, the levels at the street site were 6, 50 and 10 times lower, respectively. The same type of particulate measurements was made 1995-1996. The only compound with a significant decrease was lead. The reason for the decrease is probably due to the reduction of lead content in break lining during the last decade. Also a slight decrease is observed for cadmium and cobalt, while other metals depicts no or only minor changes in the concentrations since the middle of the 90's (to 2004).



Correlations between the metals are presented in Table 1. Highest correlation for Cu is found for Sb followed by Zn, which indicates that brake wear is an important source for these metals. There is also very high correlation between Cu and Cr and Pb. Wolfram (W) is likely due to wear of studs on studded tires and is highly correlated with V, which may either be due to the association between the wear of asphalt (containing bitumen with crude oil with V) or that both W and V are part of the steel of the studs. Several metals like Cr, Ni, Mo, Co, V and Mn are part of different steel alloys and are therefore correlated. For particle bound Hg there are generally higher levels at the street compared to roof and highest correlations are seen with W and Co.

Emission factors and the total road traffic emission of some of the heavy metals was estimated for the traffic on Hornsgatan based on the concentrations measurements at roof-top and street and using NOx as tracer. Table 2 presents the total road traffic emission factor for Hornsgatan for Cu, Cr, Ni, Pb and Zn. The total emission factor is due to wear of brakes, tires, road pavement and may also partly be due to exhaust emissions. These values are compared with emission factors for brake wear based on metal analysis of break linings, turnover time for break linings and total vehicle transport in Stockholm. Based on analysis of brake lings in 1998 (Westerlund and Johansson, 2002) and 2005 (Hjortenkrans et al., 2006) brake wear emissions have decreased by more than a factor of 10 for Pb; with the emission factor going from 65 to 4.1 μ g/vkm. The values for Cu and Zn is about same as 1998 (the small changes for Cu and Zn are hardly significant due to the large variation in metal contents of different types of break linings (Hjortenkrans, 2006).

As shown in table 2 emission factor for Cu from break wear (based on break lining analyses) is 84 % of the total emission factor as estimated in our study. Break wear is probably the largest individual source of airborne Cu in Stockholm. Also for Zn a large part of the emission may be due to break lings wear (50 %). Another important source of Zn may be tire wear. For Cr, Ni and Pb, only 2 %, 16 % and 10 %, respectively, may be due to break wear. Pb is to some extent still present in fuels and motor oil.

Table 1. Correlation between heavy metal concentrations at the street site (Hornsgatan). Values >0,8 are shown as bold.

	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Sn	V	W	Zn	Hg	Hg
													part.	gas
Co	1,00													
Cr	0,73	1,00												
Cu	0,77	0,97	1,00											
Mn	0,96	0,85	0,88	1,00										
Mo	0,44	0,70	0,66	0,58	1,00									
Ni	0,54	0,61	0,62	0,63	0,93	1,00								
Pb	0,77	0,79	0,82	0,84	0,75	0,85	1,00							
Sb	0,82	0,94	0,96	0,92	0,58	0,57	0,85	1,00						
Sn	0,63	0,83	0,78	0,75	0,56	0,55	0,83	0,87	1,00					
V	0,85	0,54	0,58	0,80	0,56	0,71	0,77	0,58	0,45	1,00				
W	0,81	0,29	0,32	0,67	0,25	0,47	0,62	0,42	0,36	0,87	1,00			
Zn	0,93	0,86	0,88	0,94	0,56	0,61	0,87	0,90	0,74	0,84	0,69	1,00		
Hg	0,71	0,12	0,17	0,56	0,11	0,27	0,27	0,23	0,04	0,63	0,78	0,43	1,00	
part														
Hg	0,73	0,41	0,46	0,63	0,13	0,28	0,50	0,46	0,28	0,78	0,75	0,75	0,44	1,00
gas														

The emission factors obtained in our study may also be compared with estimates based road tunnel studies. Mean emission factors in two different Swedish road tunnels were significantly lower for Cu but quite similar for Pb and Zn (Sternbeck et al., 2002). Kristensson et al. (2004) found lower much values for Cr, Ni, Pb and Zn in the Söderleden road tunnel in Stockholm. Laschober et al. (2004) estimated emission factors for a number of heavy metals based on measured concentrations in the Kaisermühlen-tunnel in Austria. For Zn, Cu, Pb and Ni they found 34, 30, 9.5 and 1.8 μ g/vkm, respectively, which all are much lower than the values obtained in our study. Valiulis et al. (2002) also found lower emission factors for Cu, somewhat higher emission factor for Pb and similar emission factor for Zn. The higher value for Pb obtained by Valiulis et al. (2002) in Estonia, compared to both our study and Sternbeck et al. (2002) from Sweden and also the Austrian study by Laschober et al (2004) may be due to differences in Pb content in the vehicle fuels or motor oils.

It is to be expected that metal emission factors for break linings will vary depending on the traffic conditions. Our measurement site is quite close to a road traffic crossing and a slightly sloping road may lead to increased emissions due to break wear. Laschober et al. (2004), Allen et al. (2001), Sternbeck et al. (2002) and Valiulis et al. (2002) have found higher emissions of Zn, Pb, and Cu at sites with stop and go conditions as compared to sites with lower traffic and presumably less braking manoeuvres. Based on the emission factors as obtained from measurements at street and roof level, the contribution from road traffic was calculated for the Greater Stockholm area (35 km x 35 km) using the Gaussian air quality model. The contributions to the total measured concentrations of Cu, Cr, Zn, Pb, W, Hg(p) and Ni at roof level was 91 %, 23 %, 20 %, 16 %, 10 %, 10 % and 4 %, respectively. Due to lack of background (rural) measurements it is difficult to determine the total urban contribution ot the levels. Based on background data from southern Norway most of the Cu and 60 % to 70 % of the measured Ni, Cr and Zn are due to local sources, but it is difficult to know if these background measurements are representative for rural air outside Stockholm.

4. CONCLUSIONS

Heavy metal emission from road traffic has been estimated based on parallel filter sampling in a densely traffic street and at a roof-top site in central Stockholm. Using NOx as tracer emission factors have been estimated and compared with emission factors for brake linings and emission factors found in road tunnel studies. For Cu and Zn brake wear is likely very important for the emissions as indicated by comparing with estimates based on brake wear analysis and verified by high correlations between these metals and with Sb. Metals such as Cr, Ni, Mo, Co, V and Mn are part of different steel alloys and are therefore also correlated. For these metals road tunnel studies as

compared to outdoor street canyon environments. Most of the Cu in Stockholm is due to wear of brake linings of local traffic.

Table 2. Emission factors for some heavy metals based on measured concentrations at street and roof level in central Stockholm. Also shown are emission factors for break wear estimated based on analysis of break linings and estimates of the total traffic transport in Stockholm. Unit μ g per vehicle-kilometer.

Me- tal	Break wear 1998 ¹⁾	Break wear 2005 ²⁾	Total emission factor This study	Fraction of total emission due to wear of brake linings ³⁾	Kaisermühl en-tunnel (Austria, 2002) ⁴⁾	Tingstad Lundby tunnels (Gothenburg, Sweden, 1999/2000) ⁵⁾	Gelezinis Vilkas tunnel (Vilnius, Estonia, 2000) ⁶⁾	Söderleden road tunnel (Stockholm , Sweden, 1999) ⁷⁾
Cu	470	460	542	84 % (2005)	30	Tingstad: 172 Lunby: 147	159	214
Cr	0.84	-	41	2 % (1998)	-	-		0.14
Ni	1.0	-	6.5	16 % (1998)	1.8	-		0.14
Pb	65	4.1	41	10 % (2005)	9.5	Tingstad: 36.9 Lundby: 35.1	54	4.8
Zn	118	131	261	50 % (2005)	34	Tingstad: 205 Lundby: 239	206	24
W			15	-	-	-		

¹⁾ Westerlund och Johansson (2002), assuming that 35 % of the wear gets airborne according to Garg et al. (2000). ²⁾ Estimate based on break lining analysis 2005 by Hjortenkrans et al., (2006). ³⁾ Fraction of total emissions due to brake wear based on Hjortenkrans et al., (2006) for 2005 and Westerlund and Johansson (2002) for 1998. ⁴⁾ Laschober et al. (2004) ⁵⁾ Sternbeck et al. (2002) ⁵⁾ Valiulis et al. (2002) ⁷⁾ Kristensson et al. (2004)

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CHARACTERIZATION OF PM10 EMISSION SOURCES IN THAILAND

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ABSTRACT

 PM_{10} (Particulate Matter smaller than 10 microns) levels in Thailand as well as many other countries far exceed acceptable safe level. In controlling PM_{10} , it is most effective to target the most important sources. Profiling or characterization of chemical compositions of PM_{10} from emission sources provides important information for understanding the emission sources and identifying their contribution to the ambient PM_{10} level.

Air quality deteriorates as a result of urbanization and industrialization at the expense of encroaching on agricultural land and woodland and at the same time turning the remaining agricultural land into emptied unproductive lands. The emission sources evolve and change and exert their influence on the air quality.

In this study, mobile sources, industrial sources and area sources were sampled for PM_{10} emission and analyzed for chemical compositions. The mobile sources included 6 types of vehicles: 2-stroke and 4-stroke motorcycles, gasoline vehicles with and without catalytic converter and heavy-duty and light-duty diesel vehicles. The vehicles were tested on chassis dynamometers using driving cycles developed specifically for Bangkok.

Stack sampling was conducted for factories in 9 industries including power plant using heavy fuel oil, industrial boiler using biomass, industrial boiler using coal, wood industry, plastic industry, ceramic industry, iron and steel industry, and industrial waste incinerator.

Area sources included soil and road dust.

The PM_{10} samples were analyzed for elemental compositions both metallic and non-metallic such as Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, K, Mg, Na, Ni, P, Pb, Po, Pt, S, Se, Si, Sb, Sc, Ti ,Te, V, Zn, organic carbon and elemental carbon and ionic species including NH_4^+ , Na^+ , K^+ , Cl^- , NO_3^- and $SO_4^{2^-}$.

The assembled source profiles of PM_{10} provide a valuable database for understanding the PM_{10} sources and conducting source apportionment of PM_{10} as a way to identifying source contribution of PM_{10} in ambient air and developing PM_{10} control strategy.

Keywords: PM₁₀; source profile; emission source; chemical composition; Thailand

1. INTRODUCTION

 PM_{10} (Particulate Matter smaller than 10 microns) levels in Thailand as well as many other countries far exceed acceptable safe level. In controlling PM_{10} , it is most effective to target the most important sources. Profiling or characterization of chemical compositions of PM_{10} from emission sources provides important information for understanding the emission sources and identifying their contribution to the ambient PM_{10} level.

Air quality deteriorates as a result of urbanization and industrialization at the expense of encroaching on agricultural land and woodland and at the same time turning the remaining agricultural land into emptied unproductive lands. The emission sources evolve and change and exert their influence on the air quality.

In Thailand, source profile of total suspended particulates (TSP) was investigated by the Japan International Cooperation Agency (1991) on "The Study on the Air Quality Management Planning for The Samutprakarn Industrial District in The Kingdom of Thailand". They conducted source profiles of soil dust and road dust in Samutprakan province and characterized chemical compositions of fuel gasoline. Radian (1998) conducted source profiles of soil dust and road dust in Bangkok and source profiles of the emission from vehicle exhaust gas such as heavy-duty diesel vehicle, light-duty diesel vehicle and motorcycle and major emission sources such as steel mill and power plant. Wangkiat, A. (2002) conducted source profile of biomass burning and light-duty diesel vehicle.

In this study, a total of 17 emission sources comprising mobile sources, industrial sources and area sources were sampled for PM_{10} emission and analyzed for chemical compositions. The emission source profiles were used in the source apportionment study of particulate matter in Samutprakan province (Pollution Control Department, 2006).

2. METHODOLOGY

2.1 Source samplings

The mobile sources included 6 types of vehicles: 2-stroke and 4-stroke motorcycles (MC2 and MC4), gasoline vehicles with and without catalytic converter (GVWC and GVNC) and heavy- and light-duty diesel vehicles (HDDV and LDDV). The vehicles were tested on chassis dynamometers at the Pollution Control Department's emission testing laboratory using driving cycles developed specifically for Bangkok Metropolitan Region.

Industrial stack PM_{10} samples were obtained isokinetically. The nine industrial emission sources included power plant using heavy oil, industrial boiler using saw dust, industrial boiler using palm shell, industrial boiler using coal, wood factory, drying process using natural gas, ceramic factory, steel mill, and industrial waste incinerator.

Area sources included soil and road dust. Soil samples were collected upwind and downwind within 500 meters of 4 air quality stations and along 5 major roads in Samutprakan province (Figure 1). Soil samples were air dried and combined into composite samples of soil and road dust. Each composite sample was dispersed in a wind tunnel to be collected by personal pump with PM_{10} cyclone.

2.2 Analysis of chemical components

The PM₁₀ samples were collected on both teflon and quartz filters. Quartz filters were preconditioned at 550° C for 1 hour before sampling. Samples on quartz filters were analyzed for organic and elemental carbon. Teflon filters were analyzed for elemental compositions both metallic and non-metallic such as Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Cu, Fe, I, K, Mg, Na, Ni, P, Pb, Pt, S, Se, Si, Sb, Sc, Ti, Te, V and Zn and water soluble ionic species including NH_4^+ , Na^+ , K^+ , Cl^- , NO_3^- and $SO_4^{2^-}$.

a) Elemental components

 PM_{10} on teflon filters were analyzed for elemental components by X-ray Fluorescence, XRF-EDS (Oxford ED 2000) at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

b) Water soluble ionic species

After XRF analysis, PM_{10} on teflon filters were dissolved by deionized water. The samples were analyzed for negative ionic species : CI^{-} , NO_{3}^{-} and SO_{4}^{2-} by ion chromatograph (Dionex, ICS 2500), positive ionic species : Na^{+} and K^{+} by AAS and NH_{4}^{+} by Indophenol method at the Department of Environmental Engineering, Chulalongkorn University.

c) Organic and elemental carbon (OC and EC)

 PM_{10} on quartz filters were analyzed for OC and EC by a CHNS/O analyzer (Perkin Elmer PE 2400 series) at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

3. RESULTS AND DISCUSSION

3.1 Chemical Compositions of PM₁₀ from Mobile Sources

All vehicles were tested on chassis dynamometer to collect particulates on Teflon and Quartz filters. The major chemical compositions of all 6 types of vehicles were organic carbon and elemental carbon as shown in Table 1. The results are compared to the OC/EC ratio from other studies in Table 2.

Both MC2 and MC4 emitted OC higher than EC. The OC/EC ratio of MC2 is 4.3, while that of MC4 is 2.2. Both gasoline vehicles GVNC and GVWC also had OC/EC ratio equal to or greater than 1 at 2.7 and 1, respectively. On the contrary, both LDDV and HDDV emitted elemental carbon higher than organic carbon. The ratio of OC/EC in LDDV and HDDV were 0.2 and 0.3, respectively.

The study by Radian (1998) in Thailand showed OC/EC ratio of motorcycles was 10, LDDV was 0.3 and HDDV was 4.4. Several studies in U.S.A. showed the ratio of OC/EC in the exhaust gas of diesel engines vary from 0.31-1.21 and in gasoline engines vary from 2.14-18.6. The results from this study agree with the previous studies done in U.S.A.

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Figure 1. Sampling Locations in Samutprakan Province

Table 1. The major chemical compositions (% mass) of various emission sources

Emission Sources	Chemical fraction	Chemical fraction
X7-14-1	>10%	1-10%
Venicles		
2-stroke motorcycle	OC, EC	Cr, Fe, Ni, Ce
4-stroke motorcycle	OC, EC	V, Cr, Fe, Co, Ni, Cu, Zn, Te, Ba, Ce
Gasoline w/o cat.	OC, EC	Cr, Fe, Ni
Gasoline with cat.	OC, EC	Cr, Fe, Ni
LDDV	OC, EC	Cr, Fe, S, Ni
HDDV	OC, EC	Cr, Fe, Co, Ni
Industries		
Boiler using wood waste	K, EC	Si, P, Fe, S, Ca, SO_4^{2-} , Cl ⁻
Boiler using coal	SO_4^{2-}	
Power plant using fuel oil	OC, SO_4^{2-} , EC	V, Fe, S, Ni, Ce
Drying process using natural gas	OC	Fe, $SO_4^{2^-}$, Cl^-
Incinerator	OC, EC	Fe, Ce, SO_4^{2-} , Cl ⁻
Steel mill	Fe, Zn	K, OC, EC, Cl ⁻
Ceramic factory	-	Al, Si, Fe, K, OC, EC
Wood factory	Cl	Ba, Ce
Area sources		
Soil dust	OC, EC	Si, Cs
Road dust	-	Si, OC, EC

	OC/EC ratio							
Types of vehicles	This study	Radian (1998)	Wangkiat					
			(2002)					
2-stroke motorcycle	4.3	10.0	-					
4-stroke motorcycle	2.2	-	-					
GV w/o cat.	2.7	-	-					
GV with cat.	1.0	-	-					
LDDV	0.2	0.3	0.1					
HDDV	0.3	4.4	-					

Table 2. Comparison of OC/EC ratio emitted from vehicles to other studies in Thailand

3.2 Chemical Composition of PM₁₀ from Industrial Sources

The chemical fraction of various types of industries had major species varied according to fuels and raw materials used in the processes (Table 1). The chemical fractions with greater proportion than 10% are as follow, the industrial boiler using wood waste (saw dust and palm shell) had potassium at 15.1-16.7%, the industrial boiler using coal had sulfate at 48.9%, industrial boiler using fuel oil had elemental carbon at 42.6%, sulfate at 22.9% and organic carbon at 10.4%, incinerator had elemental carbon at 22.8% and organic carbon at 22.2%, steel mill had zinc at 18.6% and iron at 16.0%. Drying process using natural gas had organic carbon at 21%, which may come from the chemical products. Wood factory emission has chloride element at 14%, which came from its specific process.

3.3 Chemical Composition from Soil and Road Dust

The major components of soil dust were organic carbon at 24.9%, elemental carbon at 14.5%, silica at 1.6% and cesium at 1.1%. The major components of road dust were organic carbon at 9.4%, elemental carbon at 5.6% and silica at 1.2%.

4. CONCLUSION

The assembled source profiles of PM_{10} provide a valuable database for understanding the PM_{10} sources and conducting source apportionment of PM_{10} as a way to identifying source contribution of PM_{10} in ambient air and developing PM_{10} control strategy not only for Thailand but for other developing countries. The full report (Pollution Control Department, 2006) provides full details of the 17 emission profiles resulted from this study.

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PM10 SOURCE APPORTIONMENTS WITHIN THE CITY OF KLAGENFURT, AUSTRIA

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ABSTRACT

Within the framework of the European funded LIFE Project KAPA GS, launched in summer 2004, it is intended to perform PM10 source apportionments within the city Klagenfurt (Austria). From November 2004 to November 2005 a dense network of twelve monitoring stations for PM10, PM2.5 and PM1 was installed in Klagenfurt. The GRAMM/GRAL model system is used for the calculation of the wind fields and the dispersion. A model validation was performed on basis of monitored PM10, PM2.5, PM1 and NOx concentrations. The results are used to evaluate the effects of action plans before they are set into force.

1. INTRODUCTION

In many regions in Austria the topographical situation and the meteorological conditions result in high PM10 concentration values. Permanent violations of PM10 air quality (AQ) standards call for action plans to reduce the PM10 emissions. In order to evaluate the effects of action plans before they are set into force a combined emission-dispersion tool has been developed within the framework of the Project KAPA GS. This approach has been applied to the city of Klagenfurt, which is a city of 90.000 inhabitants and approximately 150.000 including suburbs and commuters. Its location in a basin on the south side of the Alps results in wintertime in long periods with strong inversions combined with calm winds. These unfavourable dispersion conditions lead to a relatively high PM10 burden. The annual mean values are met on all air quality monitoring locations, but the threshold value for PM10 as daily mean value is exceeded frequently. In 2005 84 violations were registered at one of the monitoring stations (seeTable 1).

Air quality monitoring station	year	max. daily mean value	No. of days > 50 µg/m ³	annual mean value	
		$[\mu g/m^3]$	[]	$\left[\mu g/m^3 ight]$	
Koschatstraße	2005	86	31	26	
	2004	84	34	27	
Völkermarkter Straße	2005	123	84	39	
	2004	116	80	38	
	2003	99	74	38	
	2002	127	58	37	

Table 1: PM10 concentrations during the years 2002 to 2005

2. METHODOLOGY

Based on a new traffic model for Klagenfurt, traffic emissions were calculated with the program NEMO (Network Emission Model), which combines a detailed simulation of the fleet composition and of the emission factors and applies it to a road network (Rexeis et al. 2005). In NEMO the emission factors of the HBEFA 2.1 (Umweltbundesamt 2004) are used and can be applied to a road network considering also different road types and varying slopes.

The revised emission inventories of domestic heating and industry were implemented in the simulations for the spatial distribution of PM10. Therefore the prognostic wind field model GRAMM (Öttl 2000) and the Lagrangian particle model GRAL (Öttl et al. 2003) were applied. This model system was developed especially for the application to dispersion situations with low wind speeds in complex terrain.

The input data consists of different source types with different release characteristics. As a consequence it is necessary to simulate these different kinds of sources like line sources, point sources and tunnel portals,

simultaneously. GRAL fulfils these requirements and the following parameters are taken into account for the individual source types:

- Point sources: location (3D): Source strengths, exit velocity, temperature differences, diameter.
- Line sources: location (3D, also bridges): Widths, source strengths, heights of noise barriers.
- Area sources: Same as line sources.
- Tunnel portals: Location (3D), source strengths, exit velocity, temperature differences, traffic influence on tunnel jet.

Quality assurance of the modelling system GRAL is guaranteed by permanent validation activities using data from field experiments. Currently 18 different data sets for tunnel portals, point sources, line sources and built-up area are used for the model evaluation, such as Prairie Grass, Indianapolis, INEL, Elimaeki, Goettingerstrasse, Hornsgatan, etc. Many of the modelling results have been published in peer-reviewed journals (e.g. Oettl et al. 2001, Oettl et al. 2003).

3. **RESULTS AND DISCUSSION**

A model validation was performed on basis of monitored and calculated (Figure 7) NOx concentrations and showed a good correlation. Figure 1 shows the contributions of the different source categories in Klagenfurt for the annual mean values at two different PM10 monitoring stations. Primary traffic exhaust emissions contribute roughly 10% to the total observed PM10 concentrations at the kerbside station, and approximately 5% at the urban background site. The calculated PM10 concentrations are shown in Figure 2. Outside the city centre the contribution is less than 1µg/m³ except near major roads. The non-exhaust traffic emissions contribute approximately 25% to the total observed PM10 concentrations at the kerbside station, and 15% at the urban background site (Figure 3) and have broader dispersion band due to higher emission factors. Domestic heating seems to be the second largest source for primary PM10 with a contribution of roughly 10% (Figure 4) and has the biggest extension in terms of covered area. Industry contributes only approximately 6-7% to the total observed concentrations in Klagenfurt (Figure 5). The results are also available for the winter mean value, the number of exceeding days and the maximum daily mean value. Interestingly, the city seems to contribute only approximately 50% to the total observed concentrations even at kerbside stations, which calls for measures to reduce PM10 emissions not only within cities but also at regional scales. Short and long term measures are taken into account. The short term measures are based on traffic restrictions which shall be implied as soon as $50 \,\mu g/m^3$ (daily mean value for PM10) are exceeded for more than 5 consequent days. In this case one of the main streets (Völkermarkter Straße) will be closed for traffic. Figure 8 shows the result of the simulation. Long term measures are based on actions which should result in long term changes of the emission situations. As an example the effects of upgrading of old heating facilities on the PM10 concentrations are shown. In the near future approximately 600 households which use currently wood, coal and oil shall be connected to the district heating system. Figure 9 shows the result of the simulation. Further investigations within this project include analysis of non-exhaust emissions from vehicles by two-point PM10 observations at a major road. The main focus here is to identify possible reduction potentials concerning different winter sanding policies.



Figure 1: Contribution of the different sources to the PM10 concentrations in Klagenfurt



Figure 2: annual mean PM10 concentrations - traffic exhaust



Figure 4: annual mean PM10 concentrations – domestic heating



Figure 6: annual mean PM10 concentrations – all sources



Figure 3: annual mean PM10 concentrations - traffic non-exhaust



Figure 5: annual mean PM10 concentrations – trade and industry



Figure 7: annual mean NOx concentrations – all sources



Figure 8: Impact of the closure of one main street on the PM10 concentration (daily mean value)



Figure 9: Impact of local upgrading of domestic heating systems on PM10 wintertime mean value $[\mu g/m^3]$

4. CONCLUSIONS

The results of the emission and dispersion modeling agree well with the measured concentrations and the chemical analysis. The model chain offers the possibility to calculate air quality inventories on basis of different source types with different emission characteristics with a very high resolution. The results can be used to evaluate the effects of action plans before they are set into force. The analysis in Klagenfurt showed that emissions from traffic and domestic heating are dominating, but the background concentration accounts for at least 50 % of the measured concentrations. The main reasons are the formation of secondary particles and the transport of particles from outside the calculation domain. In the near future calculations with a chemical-transport-model will be performed to get more knowledge about the regional background.

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AIR QUALITY LEVELS IN THE BASQUE COUNTRY (SPAIN): SOURCE CONTRIBUTION AND METEOROLOGY INFLUENCE

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ABSTRACT

With the aim of developing Air Quality Action Plans in the Basque Country (Spain), we have studied the levels and characteristics of the pollutants included in Directive 1999/30/EC. The work is focused to the identification of pollution sources and the influence of meteorology in local air quality levels. Between 2003 and 2005 eight regions exceeded the limit values of PM_{10} . Also, one of these did not attain the annual limit value of NO_2 due to intense urban traffic. The results show that there is not a clear trend in the annual mean concentrations of PM_{10} and NO_2 in most of the measuring sites. However, the critical aspect is the number of exceedance of the 24-hour limit value of PM_{10} since the annual mean value of this pollutant is usually met. Depending on the region, urban traffic, industry, activity at ports and urban construction works have been identified as the main sources of PM_{10} . In general, the levels of PM_{10} in the Basque Country are highly conditioned by local to regional meteorology. Complex topography and the sea influence, develop air mass movements along the valleys usually decoupled from the general synoptic situation.

1. INTRODUCTION

Air quality is one of the most important environmental problems that people have to face. In many sites pollutant concentration have decrease since a few decades ago, but still much work has to be done if the new air quality standards are to be met. Recent studies (Apheis, 2005) have shown that there is an important relation been air quality and health. Actually, 350,000 cases of premature death per annum have been estimated in Europe due exposure to actual particulate matter (PM_{10}) levels, and 21,500 cases of hastened death due to ozone (O_3). So more efforts are needed to reduce the impacts of air quality.

Directive 1999/62/CE refers to the necessity of developing Air Quality Action Plans in the areas where the limit values of air pollutants are not met (Directives 1999/30/CE, 2000/69/CE, 2004/107/CE). In this sense, to improve air quality it is necessary to understand the reasons that caused high levels of pollutants. The development of a clear diagnosis of the air quality allows the application of specific and accurate actions that should lead to a cleaner atmosphere.

The Basque Country (Spain) has improved air quality since a few decades ago. In December 1977, Bilbao metropolitan area (25x10 km.) was declared zone of polluted atmosphere. Inside this area there were many heavily polluting industries (one refinery, two oil-fired and one coal-fired thermal generating stations, one iron and steel works, sulphuric and nitric acid manufacturing plants, ...). Since then many industries have closed or have adapted to new and less polluting technologies. Also the change in fuel helped improving the situation. In 2000, the declaration of polluted atmosphere was laid off (Acero, 2005).

Nowadays, levels of PM_{10} are exceeding the limit values in eight regions of the Basque Country. Also, one of these (Bilbao metropolitan area) did not met the NO₂ standards due to high urban traffic. Together with the local characteristics of meteorology, the growth of traffic has become the main problem for urban air quality. On one hand diesel engines emit fine fraction of particulate matter ($PM_{2.5}$), and on the other, both gasoline and diesel vehicles produce gases (NO_x , VOC) that contribute to the generation of secondary particulate matter. An extra emission of PM_{10} due to traffic has to be considered (brakes, resuspension of road dust, ...) which can be as important as the emission from the engine. Also, certain areas in the Basque Country are influenced by industry (iron and steel, cement and energy generating activities), port activities and urban construction works.

2. METHODOLOGY

Previous to the definition of specific actions to improve the atmospheric situation in the Basque Country, a diagnosis of the air quality was developed in each of the eight regions with exceedance of the limit values. Since particulate matter (PM_{10}) is the main problem in air quality in the Basque Country, the diagnosis in each region was focused to this pollutant trying to evaluate its main characteristics. However other pollutants

were also analysed using them as trace substances related to certain sources (NO_x for traffic, SO_2 for refinery, metal concentrations for steelmaking and foundaries). The aspects analysed in each diagnosis were: Emission Inventory (industry, traffic, domestic), air quality levels, influence of the meteorology, and identification of the principal sources.

To analyse the characteristics of particulate matter (PM_{10}), the evolution of levels were studied taking into account different time variables (day, week and month evolution). The influence of wind speed and direction in air pollutants was used to identify sources by relating levels of concentration between different pollutants. Also, levels of metals in PM_{10} helped identifying sites with influence of iron and steel activities. The comparison of all the results in different measuring sites (not only the ones with exceedance) became helpful to identify pollution sources.

To elaborate the diagnosis of air quality, data from years 2002 to 2005 were analysed. All the statistical calculations were done using hourly data of different pollutants. These were available through the Air Quality Network of the Basque Government. The analysis of the composition of particulate matter were carried out by the Health Department of the Basque Government and University of the Basque Country.

3. RESULTS

3.1. Air quality levels and meteorology influence

Annual mean levels of PM_{10} do not present a clear trend between years 2002 and 2005. In comparison with rural sites (Valderejo, Izki, Mundaka, Pagoeta), levels registered in urban stations are much higher (at least, concentrations are double). However, not all the urban sites (background and traffic) exceed the annual limit value (40 μ g/m³) and on the whole the values measured are not as high as in other Spanish and European cities (>45 μ g/m³). One of the reasons that favour lower annual PM₁₀ concentrations is the frequent rain precipitation in the north of Spain.



Figure 1. $-PM_{10}$ annual mean values in several Figure 5 fites of the Basque Country values values in several values of the Basque Country values in several values in several Figure 5 fites of the Basque Country values in several Figure 5 fites of the Basque Country values in several Figure 5 fites of the Basque Country values in several Figure 5 fites of the Basque Country values in several Figure 5 fites of the Basque Country values in several Figure 5 fites of the Basque Country values in several Figure 5 fites of the Basque Country values 5 fites of the Basque Country values 5 fites of the Basque Country values 5 fites 5 f

Figure 2. – Number of exceedance of PM_{10} limit value in several sites of the Basque Country

Hopelessly, considering Directive 1999/30/CE, the number of exceedance of the 24-hour limit value of PM_{10} , presents a problematic situation. Every year since 2002 many urban stations have registered more than 35 exceedance (discounting days of African dust intrusions). The reason of this situation is that the 24-hour limit value might be stricter than the annual mean value. Globally, in Spain it has been demonstrated that the number of exceedance of 24 hour limit value is not equivalent to the annual mean value of PM_{10} (Querol, 2004). Despite the north of Spain presents a different climatology than the central and south part of the Iberian peninsula where dry soils many influence PM_{10} resuspension and air quality levels, results particularized to the Basque Country still present the same conclusion (Figure 3). An annual limit value of $40\mu g/m^3$ corresponds to a percentile 90th of 68 $\mu g/m^3$ (not 50 $\mu g/m^3$ as the actual 24 hour limit value). Taking this into consideration, more sites would have met the air quality standards.

The situation of air quality levels in the Basque Country is characterized by the local to regional meteorology influenced in an important way by complex terrain and sea-land interactions (Millan, 1987). Winds at surface levels are usually decoupled from the synoptic situation at higher levels in a way that air masses adapt to the topography following the direction of the valley. In stable situations, sea-land breezes are developed. The intensity of these regional phenomena depends on the solar radiation, and on the air and sea-water temperature. Especially in autumn but also in winter, these atmospheric conditions favour the accumulation of pollutants moving up and down the valley in daily cycles with little possibility for dispersion. In summer, higher solar radiation develops intense sea breezes that can influence far land-inside, helping the renovation of the air masses in the valleys. So despite the frequent rain precipitation (compared to rest of the Iberian

peninsula) that produces an important 'cleaning' of the atmosphere, the meteorological characteristics in the region are the reason why high 24-hour values of PM_{10} are registered, specially during autumn and winter.



Figure 3. – Relation between annual mean values of PM_{10} and the percentile 90th. Data from years 2002, 2003, 2004

3.1. Temporal variation and characteristics of PM₁₀ levels

Daily variation of PM_{10} and NO_x can be used as indicators of the influence of traffic on air quality. Generally two peaks of these pollutants can be found matching the hours with higher traffic. Many urban sites present PM_{10} and $PM_{2.5}$ peaks one or two hours later than NO, indicating the formation of secondary particulate matter from primary emissions or simply the transport of polluted air masses. Weekly variation of PM_{10} have also proved the influence of traffic in different urban stations, showing a general reduction in concentrations during the weekend (Figure 5).





Figure 4. – Daily variation of PM_{10} in an urban site Figure

Figure 5. – Weekly variation of PM₁₀ in urban sites

In general there is also a relation between rain precipitation and the monthly mean values of PM_{10} . Months in the same season of the year with low precipitation rates present higher PM_{10} levels than other months with higher rain precipitation. Thus, rain acts as an agent that cleans the air masses accumulated in the valleys.



Figure 6. $-PM_{10}$ concentration ($\mu g/m3$) represented by wind direction; a) june-july, b) november-december

Due to the characteristics of meteorology inside the valleys, the wind direction and velocity has shown to be an important reference to identify the origin of air pollution. The different characteristics of meteorology during the year (more intense sea breezes during the summer time) involves different movements of pollutants and so the impact of sources many vary (Figure 6). The diagnosis of the eight regions with exceedance of the limit vales of PM_{10} has shown that the iron and steel industry has an important effect in the air quality where these activities take place. Levels of metals are much higher (Table 1) than those considered normal values in Spain (Querol, 2004). In this sense it has to be considered that around 50% of this type of activities in Spain is placed in the Basque Country. But there are also many other big industries (energy generating plants, chemistry plants, refinery, ...) and other smaller ones that on the whole emit important quantities of pollutants (NO_x , SO_2) to the atmosphere where they can transform to secondary particulate matter. All these important economic activities and the strategic location of the Basque Country inside the Iberian Peninsula (natural way to cross the Pyrenees), make roads have a very high number of heavy duty vehicles circulating with medium and long distance trips. This traffic has to be added to the intense circulation of vehicles in urban areas.

Metal (ng/m ³)	Durango	Mondragon	Olaberria	Bilbao	Basauri	Normal range in Spain ⁽¹⁾
Cr	10,5	4.5		15	19	1-8
Ni	5,8	5,3		10	9,7	2-7
Cd	0,8	0,5		1,6	3	0,2-0,8
Mn	77	32		56	99,5	10-25
Pb	68	28	420	85	98	10-60
Fe	1572	516	2540	795	-	
Zn	-				407	20-100
Cu	23,2	9,7		42	112,1	20-50

Table 1. – Concentration of metal in PM₁₀ in different sites of the Basque Country

⁽¹⁾ Querol, X, 2004

4. CONCLUSIONS

In the study we have analysed the main characteristics of air pollution in the Basque Country focusing on the PM_{10} levels. Nowadays too many sites present exceedance of the 24-hour limit value of this pollutant. However some regions also exceed the annual limit value. This situation many change soon if the new Directive of Air Quality finally considers other standards for the 24-hour PM_{10} concentration. More areas/regions will then meet the limit values in the Basque Country.

The topography and the proximity of the sea define a specific meteorology through the valleys with characteristics that vary during the year. Pollution emitted in one municipality can be accumulated and transported through the valley, interfering the air quality levels in a distant site. Thus, actions in a big area, not just one municipality, are needed if the air quality problem is to be solved.

For PM_{10} there are several sources contributing to the total levels. In big agglomerations the principal source is urban traffic but in medium sized towns (20.000 inhabitants) the industry also plays an important role. The important activity of the iron and steel industry in some parts of the territory (Durango, Beasain, Erandio, Basauri, Azpeitia) contribute to primary PM_{10} , increasing the levels of metals in atmosphere. The results show higher metal values in PM_{10} compared with typical urban locations in Spain. Also, the activities at ports are an important source of PM_{10} in the nearby area (Lezo, Nautica, Zierbena). Finally in certain municipalities an increase of PM_{10} levels has been appreciate during urban construction works, sometimes being responsible for the exceedance of the limit values (Renteria in 2004, Zelaieta in 2003-2004, Barakaldo in 2003-2004).

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IDENTIFICATION OF TRAFFIC-RELATED PM SOURCES AT A HIGH TRAFFIC SITE IN STUTTGART, GERMANY

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ABSTRACT

A novel method was developed for investigating the contributions of the different traffic-dependent sources of PM to the ambient PM_{10} at a traffic site. PM samplings were carried out from two ambient sites by means of eight stage non-viable cascade impactors and PM_{10} samplers in the city of Stuttgart from 12 January to 26 March 2006. The two sampling sites were characterised by different exposure to traffic emissions, enabling the assessment and comparison of PM concentration levels and particle size distributions between the traffic and urban background sites. After sampling, the morphology, composition and mineralogy of PM from the respective impactor stages were determined with Scanning Electron Microscopy (SEM) with an integrated Energy Dispersive X-ray analysis (EDX) system. This method of the size-selective PM sampling coupled with the SEM/EDX analyses was able to identify three potential PM sources as resuspended road dust, urban background dust load, and diesel soot particles.

1. INTRODUCTION

The two European Union air quality guidelines, the framework guideline 96/62/EG and the daughter guideline 1999/30/EG, have been transposed into the German national law by the 22nd Ordinance of the Federal Immission Control Act. The Ordinance stipulates that as per 1 January 2005, the daily mean PM_{10} concentration may only exceed the limit value of 50 µg/m³ 35 days per year, and the yearly average PM_{10} concentration may not exceed 40 µg/m³. However, this PM_{10} limit value is frequently exceeded in many cities which are heavily impacted by traffic. At the heavily trafficked Stuttgart Neckartor, the 24 h limit value of 50 µg/m³ for PM_{10} prescribed by the European legislation was exceeded 160 and 186 times in 2004 and 2005 respectively. In 2005, the PM_{10} annual average value was 51 µg/m³ which exceeded the limit value of 40 µg/m³. As such, the responsible authorities have been requested to adopt appropriate measures in the form of action plans for adherence to the PM_{10} limit values. The problem with PM_{10} exceedances at Stuttgart Neckartor arises predominantly in the months from January until April and September until December. A PM_{10} seasonal pattern can also be observed, with highest concentrations in the winter months and lowest concentrations in the summer.

The contribution of traffic-related PM sources was previously determined by the computation of emissions' propagation from the surrounding PM_{10} sources (UMEG 2005). Another method was suggested by Lenschow et al. (2001), with which the PM_{10} contribution from traffic (local effect) could be determined from the differences of PM and its chemical components between the local influence of traffic on the adjacent street and the urban background station. However, the emissions attributed from exhaust and abrasion could not be differentiated here. More detailed PM_{10} source apportionment method could also be determined by chemical analyses of the PM_{10} samples and by comparison of the dust composition from different emission sources. As this source apportionment method is based on statistical results, numerous PM_{10} samples are required before any recognition to possible emission sources can be made. The factor analysis or the positive matrix factorising could be used for such statistical method (John and Kuhlbusch, 2004; Baumbach and Pfeiffer, 2004). However, this method is costly due to the required laboratory instrumentation and the final results are not always clear. In this paper, an attempt was made to investigate the contributions of the different traffic-dependent sources of PM to the ambient PM_{10} at the traffic site of Stuttgart Neckartor.

2. METHODOLOGY

2.1 Site Description and Sampling Period

Size-fractionated particle samples were collected from two ambient sites in Stuttgart during the early months of 2006. The two ambient sites were the Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW) measurement station in Stuttgart Neckartor and for comparison purposes the urban background site in Schlosspark. The monitoring instruments were sited beside the 6-lane federal highway B14 with more than 81,000 vehicles passing through per day. The measurements in Neckartor were carried out from 12 January to 26 March 2006. One eight-stage Anderson impactor (Andersen Instruments Inc.,

USA) was installed at the existing LUBW measurement station in Neckartor at 2.50 m above ground level. In order to investigate the direct influence of the local road traffic and to allow an inter-comparison of the traffic caused pollution with the urban background in this area, parallel measurements were carried out in the second measurement site in Schlosspark from 2 to 24 February 2006 with an identical cascade impactor and a low volume PM_{10} sampler (Leckel, Germany). The measuring equipments were deployed at the terrace of a café in a lake, "Cafe im See" in the middle of the park, 180 m to the traffic monitoring station at Neckartor.

2.2 Sampling

A gravimetric PM sampling device with the Low Volume Sampler (Leckel, Germany) was used for PM_{10} sampling. This was performed in accordance with the reference method defined in EU Directive 1999/30/EC and EN 12341 (1999). The volume flow rate for PM_{10} sampler was fixed at 2.3 m³/h and sampled over 24 h as recommended in the EU Directive 99/30/EC. The chosen filter material for PM_{10} measurement was filter type GF10 Schleicher & Schuell company, glass fibre filter with a diameter of 50 mm (sampling diameter: 41 mm). The preparation and weighing of filters were performed according to EN 12341. Gravimetric samplings with cascade impactors were carried out with 8-stage Andersen non-viable ambient particle size samplers (Andersen Instruments Inc., USA). For the particle separation aluminium foils were used as collection plates and glass fibre filters as backup filter. The volume flow rate for the impactors was fixed at 28.3 m³/min and the effective cut-off diameter of the impactor stages were as follows: 0.4, 0.7, 1.1, 2.1, 3.3, 4.7, 5.8, 9.1 and 10.0 µm for particles with the density 1.0 g/cm³. The chosen filter material for backup filter was GF10 Schleicher & Schuell company glass fibre filter with a diameter of 90 mm. The change in weight for each stage in the cascade impactor including the backup filter was determined by weighing apparatus Sartorius MC1, Research RC 210P. The preparation and weighing of backup filters were performed according to EN 12341.

2.3 SEM/EDX Analysis

The morphology, composition and mineralogy of the particles were determined from the aluminium foils of different impactor stages based on individual particle analysis with Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray analysis (EDX). In this analysis, cutouts of the aluminium foils were mounted on sample holders by aid of conductive carbon-pads. Conductive silver was used to contact the non-conductive cutouts of the backup filters with the sample holder. In order to show the morphologies of the respective samples and measurement of single microstructures, a high resolution SEM (ZEISS Crossbeam 1540 XB) was used. Images of nanostructures with magnifications up to 200,000 times were taken. A low acceleration voltage of 2.2 kV was also adjusted to minimise the charge effects of single particles.

The elemental composition of the PM and single microstructures were identified by EDX analysis (Cambridge Stereoscan S90 with Link AN 10000 detector). The EDX-analyser was calibrated by aid of a cobalt standard. The adjusted acceleration voltage during EDX-Analysis was 25 kV. Area analyses with magnification of 300 times as well as point analyses of microstructures were conducted. The spectra were then recorded with a life time of 70 s and a resolution of 10 eV/channel.

3. RESULTS AND DISCUSSION

3.1 Measurements from Cascade Impactors

The mass of PM collected on each respective stage of the cascade impactor was divided by the total sampling volume in order to determine the particle concentration in each size fraction. There are different methods to depict the size distributions of PM load. Here, the respective concentrations of each PM size fraction have been depicted as vertical bars and the concentration range on the y-axis has not been varied to insure comparability. The particle size distributions during the sampling period from 24 January to 3 February 2006 in Stuttgart Neckartor are depicted in Figure 1. High PM₁₀ concentrations exceeding the EU regulated limit values were recorded from both the traffic site at Neckartor and the urban background site in Schlosspark during this period under continuous stable atmospheric conditions. A similar pattern of the particle size distributions (0.7 to 10.0 µm) from Neckartor could be observed here. The concentrations of the finer fractions (smaller than 0.7 µm) were notably reduced starting from 2 February 2006. This could be explained by the agglomeration of these finer fractions into larger particles due to the higher humidity. The coarser fractions from 3.3 to 10.0 µm were also found to be non-existent in Schlosspark from 2 to 3 February 2006. Thus, the origin of these fractions could be attributed to traffic-induced sources. The concentrations of the fractions from 0.7 to 2.1 µm were also observed to be similar from the two samplings sites in Neckartor and Schlosspark during the sampling period. Thus, these two fractions could be regarded as the overall and urban background concentrations.



Figure 1. Particle size distributions at Stuttgart Neckartor and Schlosspark from 24.01 to 03.02.2006

3.2 SEM/EDX Analysis

Four particle size fractions representing the size ranges of 5.8 to 9.0 μ m, 2.1 to 3.3 μ m, 0.7 to 1.1 μ m and < 0.4 µm from the sampling period 24 to 27 January 2006 at Neckartor were selected for the SEM/EDX analyses. Different particle sizes and the formation of agglomerated particles were recognisable for the fraction from 5.8 to 9.0 µm. Blistering clods and cubic, crystalline particles were evident in different places. Small particles were also evident on the surface of larger particles. From EDX analysis, typical traffic induced elements such as sodium, silicon, chlorine, calcium, potassium and iron could be detected in this fraction. Agglomerated particles composing of nearly homogeneous particle sizes were observed for the fraction from 2.1 to 3.3 µm. Floc structures with fractal substructure and large particles coated with small particles were also evident from the SEM analysis. The major road dust elements and some contributions of carbon, oxygen and sulphur originating from background were also detected from EDX analysis. For the fraction from 0.7 to 1.1 µm, integrated matrixes of small plate structures with porous surface could be observed here. Sporadic agglomerations of particles with small plate structures and crystal structures were also visible in this size range. The crystallisation behaviour was promoted by the continuous atmospheric inversion and high humidity during the sampling period. These crystalised samples exhibited high sulphur, oxygen and potassium concentrations together with nitrogen, which could indicate the presence of ammonium nitrate and ammonium sulphate. For the fraction smaller than 0.4 µm, only diesel soot was evident morphologically. Mainly carbon, oxygen and small traces of sulphur were detected by the EDX analysis.



Figure 2. SEM/EDX analysis for particle size range 0.7 to 1.1 µm from 2 to 3 February 2006

SEM/EDX analyses of particle size fractions from Neckartor and Schlosspark over the sampling period 2 to 3 February 2006 were also performed for comparison purposes as shown in Figure 2. Although there were no

significant morphological differences between the samples collected from traffic impacted site of Neckartor and the urban background site in Schlosspark, the EDX analyses detected the presence of nitrogen in the Neckartor samples but not in Schlosspark. The carbon content was also significantly higher at Neckartor than in Schlosspark.

4. CONCLUSIONS

The results from cascade impactor samplings and analyses at Neckartor during high PM concentrations (> 80 μ g/m³) were averaged and depicted in one summarising diagram in Figure 3. The nine fractions can be classified into three groups of potential PM sources:

- The coarse fraction from 2.1 to 10.0 µm: resuspended road dust
- The fraction from 0.7 to 2.1 μ m: background and agglomeration particles with nitrogen and sulphur containing crystals
- The fine fraction smaller than 0.7 μ m: agglomerated diesel soot particles containing traces of sulphur



Figure 3. Average particle size distributions at Stuttgart Neckartor from 10 samplings during high PM_{10} concentration (24 h $PM_{10} > 80 \ \mu g/m^3$)

In the coarse particle fractions of road dust and background, small particles were found on the surface of larger particles. The fractions 0.4 to 0.7 μ m and 2.1 to 3.3 μ m were in transition modes which could be influenced by the neighbouring potential PM sources. Considering PM₁₀ abatement strategies, the coarse road dust fraction could be reduced by appropriate road cleaning measures. The background PM concentration (0.7 to 2.1 μ m) was estimated to be approximately 38 % of the total PM load and these fractions contained the overall and the urban background. Thus, these fractions cannot be directly influenced by direct road cleaning measures at the road site. The reduction potential of PM particles emitted from diesel vehicles could be determined up to 18 % of the PM mass concentration during high concentrations at Stuttgart Neckartor.

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SAMPLING, ANALYSIS AND CHARACTERISATION OF PARTICLES IN THE ATMOSPHERE -SEARCH FOR TRACERS – PART 2

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ABSTRACT

The problematic of this work concerns the origin identification of atmospheric particulate pollutants found in the area of Dunkirk (North of France), a strongly industrialised city, in order to determine physicochemical parameters that could be used as tracers for the evaluation of fallout fluxes. Sampling, analysis and characterisation of point-source and/or diffuse particles emissions were performed in an industrial site and in its surroundings. The organic, metallic and soluble inorganic pollutants were analysed by GC-MS, ICP-MS and IC respectively.

1. INTRODUCTION

The knowledge of the atmospheric pollutants, their origin and their concentrations is essential to assess their impact on environment. The problematic of this work concerns the origin identification of atmospheric particulate pollutants that can be found in the area of Dunkirk (North of France), a strongly industrial city having huge metallurgic (steel, ferro-manganese, ...) and chemical (refineries, petrochemistry ...) activities but also cement plants In particular this study is aimed to determine physicochemical parameters that could be used as tracers of a selected industrial activity (steel making industry) to assess its contribution to the global pollution of the Dunkirk area. In a previous work (Cazier and al, 2005), sampling, analysis and characterisation of point-source particles were performed in the steel-making industrial site. We focused in particular on some specific sectors: a coke work plant, a sintering unit and a steelwork unit. Specific physicochemical characteristics (PAHs ratios, lead isotopic ratios) were defined by GC/MS and ICP/MS analysis and possible organic and mineral tracers were selected.

In the present work, the analysis of the selected sources was completed by ion chromatography to determine the major soluble inorganic compounds. Then, to validate the compounds selected as possible tracers of this industrial activity, twenty diffuse particles samples were collected in the surroundings of the site under specific wind direction. Among these environmental samplings, some were performed, the same day, upwind and downwind of the industrial site studied, in order to exhibit the site influence.

2. METHODOLOGY

Some samples were taken directly at the sources for raw material heaps (iron ores, coal) and dust collecting systems of blast furnace and steelwork. Samplings were also performed in the stacks using an isokinetic sampler equipped with heated probe and filter and in environment using global filtration (80 m³/h) of the atmosphere. Fiberglass filters were used for organic compounds sampling and cellulose filters for metallic and soluble inorganic compounds. The organic compounds were obtained by soxhlet extraction (24 hours with methylene chloride). The extracts were concentrated under nitrogen flux and analysed by GC-MS. For metals, the cellulose filters were treated by microwave digestion using HNO₃ and HClO₄ in 1:2 ratio. The solutions were analysed by ICP-MS. For soluble inorganic compounds the samples were submitted to an ultrasonic extraction with ultra-pure water and water extracts were analysed by Ionic Chromatography.

3. RESULTS AND DISCUSSION

To validate the parameters selected, during the first part of the study, as possible tracers of the industrial activity (Cazier and al, 2005), twenty diffuse particles samples were collected in the surroundings of the site under specific wind direction (steelwork, coke work, sintering and coke oven influences). Among these environmental samplings, some were performed, the same day, upwind and downwind of the industrial site in order to exhibit its influence. Results for some sources and environment samples, and also for upwind and downwind samplings are presented below.

3.1 – Source samples

The organic content of the particles collected on various processes of the plant selected exhibit mainly paraffin, PAH and methylated PAH. Paraffins were well identified in the coke work samples whereas not

found or at trace level in the sintering and steelwork samples. The organic compounds at the coke work unit (cogeners PAHs and associated methyled PAHs) exhibit strong changes as the methylated PAHs disappear all along the combustion process. For the parent PAHs, all of them are detected in the raw materials and coke work samples but only the heaviest ones are found in the hot processes and the sintering unit (mass 252, 276, 302) and PAHs such as coronene appear. Possible organic tracers could be selected using ratios of concentration between specific PAHs : Fla/Pyr, Chry/BaA, BghiP/IND, BaP/BkF and BeP/BkF. Fla/Pyr may be used as tracers for the hot processes of the coke work unit whereas BaP/BkF could be used for the sintering unit. The steelwork unit may be traced by Fla/Pyr or BeP/BkF (Cazier and al, 2005).

The metal analysis exhibited specific characteristics for most of the process samples, being either metallic content profile, metal ratios or lead isotopic ratios : iron ores have high content of Mn and specific Mn/Pb (>200) and Mn/Cu (17-260) ratios ; coals have low content of metals and Mn/Pb<2.2 ; coke work samples have specific profiles ; dust collection system of the steelwork unit have specific lead isotopic ratios and Zn/Cu>10 ; particles collected at the steel casting step have specific profile and metallic ratios : Mn/Pb>20 and 1.9 < Co/Ba < 17 ; sintering has low Zn content and Ba/Cu>1 (Figure 2); blast furnace samples have, as for steelwork unit, Zn/Cu>10, but pig iron pouring particles have also specific Mn/Cu ratio (970-1300) and low amount of Al and blast furnace dust collection system is noticeable by its lead isotopic ratio and Pb/Cd ratio (60-70).

In the present study, the analysis of the sources samples was completed by ion chromatography (IC) to determine the major soluble inorganic compounds. Coke work source samples were not analysed, this unit emitting mostly organic compounds. For the sintering unit, no specific fingerprint can be established, in this case we characterised NH4+ ion which is not detected in the other sources. Specific profile could be found for all other specific sectors. Table 1 summarizes the individual particle composition of different processes of the industrial site investigated. CaCl₂ seems to be specific to the steelwork unit, whereas MgSO₄, K₂SO₄ and CaSO₄ are related to blast furnace activities except for its dust collection system part. The high Ca²⁺ percentage in the steelwork unit can be linked to the addition of CaCl₂ for sulphur removal at this step of the process.

Unit	Sampling place	%Cl	%NO ₃	% SO4 ²⁻	%Na ⁺	% K ⁺	%Mg ²⁺	%Ca ²⁺
Blast furnace	Dust collection system	37	-	6	6	17	1	33
	Pig iron pouring	3	1	43	5	32	-	16
	coal	3	1	11	6	-	37	42
Steelwork unit	Dust collection system	21	3	8	6	5	1	55
	Iron casting	18	11	15	2	1	-	53

Table 1: soluble inorganic compounds in some source samples

3.2 – Samples collected in the surroundings of the site

The close surroundings of the site encompass, in the west part, a ferro-manganese metallurgic site, a cement production unit and a petroleum refinery and at the east site a refinery specialised in lubricant production. The North Sea runs all along the north of the site and the south of the site is strongly urbanised.

Tendencies for the organic compounds (Table 2) show that Fla/Pyr (0,88-1,83) is quite constant whatever influence samples are submitted to (urban or industries (metallurgy or refineries)) which make it unusable as a tracer. The same phenomenon is observed for Chry/BaA (2,9-3,5), BghiP/IND (0,8-1,3) and Pyr/BaP (0,78-1,25). BaP/BkF is about 0,39 to 0,5 when the sample is taken under urban influence and about 0,58 to 0,67 when submitting a global metallurgic influence (steelwork, coke work, blast-furnace), allowing it to be a good tracer.

Table 2: PAHs ratios in diffuse particle samples collected under specific wind direction.

			I		F			T T T T T T T T T T T T T T T T T T T				
Influence		Urban		Coke	work	Blast F	Furnace	Steel	work	Mixed*	ref	ìnery
Sampling date	08/02/05	25/11/04	13/05/05	08/06/04	30/09/04	08/02/05	24/11/04	25/05/04	11/10/05	13/05/05	18/03/05	09/02/05
Fla/Pyr	1.3	1.18	1.46	1.73	1.44	0.88	1.4	1.06	1.27	1.22	1.83	1.11
Chry/BaA	nd	3.47	nd	nd	nd	nd	nd	nd	nd	3.22	nd	nd
BaP/BkF	0.49	0.5	0.39	0.63	0.67	0.48	0.6	0.58	0.63	0.66	nd	nd
BghiP/IND	nd	0.82	nd	nd	1.3	nd	nd	nd	0.97	nd	nd	nd
Pyr/BaP	0.93	2.44	6.4	nd	0.79	0.96	1.13	nd	0.78	1.25	nd	nd
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nd : not detected * mixed sources of the steel making site of interest

These results can be correlated to the ones found in the sources : BaP/BkF of 0,6 to 0,7 mostly represents the coke work unit, where quite high amount of PAHs are found which can strongly contribute to the ratio found in the particles downwind of the steelmaking site. We also observe ratios close from the ones found at the
sources : Fla/Pyr (0,7-1,7), BghiP/IND around 1 for hot processes and >1 for coals, Pyr/BaP >> 1. At the opposite, the Fla/Pyr of 0.35 is never observed whereas expected when having a steelwork unit influence; it may be linked to the low amount of PAHs in the steelwork effluents.

Upwind and downwind samplings have been performed in February and May 2005 under the metallurgic site influence. It can be noticed that similar upwind chemical profiles were obtained in the two cases for soluble ions (Figure 1) and for PAHs ratios (except Pyr/BaP). In February, no contribution of the blast furnace source was observed as no change in PAHs ratios (BaP/BkF stays near 0.49), soluble ions profile (Figure 1) and metal profile is observed. Possible explanations can be the weather conditions or the site influenced air masses altitude compared to the sampling mast height. In May, the influence of the metallurgic industrial site is observed on the aerosol composition : BaP/BkK evolves from 0.39 to 0.66, respectively determined as tracers for urban and metallurgical influence, the concentration levels of Ca^{2+} , K⁺ and SO_4^{2-} increase from upwind to downwind (according to the source's ion analysis, the blast furnace seems to be the most influencing unit) and strong modification of the metal profile is also observed.



Figure 1: Measured weight percentages of ions upwind and downwind of the site

Metal profiles give indications on sources and can also reveal other contribution. For example, samples collected under the sintering unit influence have coherent profile with the source but one of them has higher content of copper that may indicate a steelwork unit contribution (Figure 2).

For metallic ratios, the values determined in the environment are more difficult to correlate to sources values, but specific ratios have been found in the environmental samples and can be used to differentiate the



Figure 2. : profile comparison between source and environment

metallurgic site of interest from the other industrial activities : 1.14 < Pb/Cu < 4.65 and Mn/Cu >2 for the site influence (urban and refineries influences having Pb/Cu <2.5 and Mn/Cu<2) whereas ferro-manganese site influence shows a Pb/Cu ratio around 8, this ratio being around 10 for the cement producer. For cement and ferromanganese site, Ba/Cu>1.3 whereas <1 for all the other influences. Cement site influence exhibit also a Al/Zn ratio of 44 whereas <15 for all the other influences. Concerning the lead isotopic ratios, the ferromanganese site has a very specific signature. For the metallurgic site of interest, the samples performed under urban or refineries influences are either at the edge or different from the Pb isotopic ratios of the site sources. Cement factory signature can't be distinguished from the steelmaking metallurgic site. Other samplings should be done to confirm this last point.

For IC analysis results, ionic species detected in environmental samples are by concentration order : NH_4^+ > $NO_3^->Ca^{2+}>Cl^->SO_4^{2-}>Na^+>Mg^{2+}>K^+$ (table 3). NH_4^+ is the main cationic species found (23-46%), and is only emitted, in our sources, by the sintering unit. Direct comparison with the sources profiles shows that soluble inorganic compositions of the surrounding aerosol strongly differ from the sources. In all cases, the profiles are similar except for sintering unit influence where Ca^{2+} was detected. This last parameter could allow the differentiation of this source. As for PAHs and metals, ratios between soluble ions have been calculated (Table 4). A relationship can be established between the following ratios: Cl^-/NH_4^+ , NO_3^-/NH_4^+ , Ca^{2+}/SO_4^{2-}

Influence	Sampling date	%Cl	%NO ₃	% SO4 ²⁻	%Na ⁺	%NH4 ⁺	% K ⁺	%Mg ²⁺	%Ca ²⁺
	08/11/04	18	23	9	8	33	-	-	9
Blast furnaça	24/11/04	16	16	10	12	23	1	6	16
Blast fulliace	08/02/05	18	23	9	8	33	-	-	9
	11/10/05	7	8	10	3	32	1	2	37
Sintering unit	26/05/03	10	2	1	16	39	5	2	25
	29/05/03	8	4	2	8	46	1	2	29
Coke work	30/09/04	22	25	18		35			
Urbon	08/02/05	21	17	12	2	43			5
Orban	13/05/05	16	17	8	15	32		6	6
Ferro-manganese metallurgic site	13/05/05	16	7	18	15	10	7	9	18
and refinery	09/02/05	8	27	15	6	29	1	3	11

Table 3: weight percentages of total soluble aerosol concentrations in environmental samples

and the sources. When samples are collected under urban activities influence $0,402 < NO_3^- /NH_4^+ < 0,549$, whereas this ratio is upper to 0,66 for the steel industry. For Ca^{2+}/SO_4^{-2-} ratio, the observations are similar, urban (0,429-0,728) and global industrial site influence is established. The Cl/NH₄⁺ ratio seems to be a more specific tracer: aerosols sampled under influence of refinery and cement factory (0,124–0,26), city (0,491–0,497) and steel industry (0,542–0,681)) could be differentiated by ratio values comparison. For the samples collected close to the ferro-manganese metallurgic site, we notice a high Cl/NH₄⁺ ratio value (1,6) which seems to discriminate this metallurgic source from the steel making one. Using these observations, it is possible to define specific ratios and profiles as tracers of specific sources.

 Table 4: soluble inorganic elements ratios under various influences

Influence	Blast furnace	Blast furnace Coke work Metallurgic		Urban	Cement factory	refinery
			activities			
Cl ⁻ /NH ₄ ⁺	0.542-0.681	0.617	1.64	0.491-0.497	0.26	0.124
NO ₃ ⁻ /NH ₄ ⁺	0.666-0.701	0.721	0.732	0.402-0.549	0.525	0.557
Ca ²⁺ /SO ₄ ²⁻	0.926-1.35-1.54	1.618	1.02	0.429-0.728	0.99	0.37

4. CONCLUSIONS

The multi-technique analysis show that the exact profiles and ratios determined in the on-site samples were affected in the environment by mixture with other sources (domestic heat, vehicles ...). However, we exhibit that is was possible to get, in the environment, new specific ratios and profiles resulting from the specific sources (steelwork, coke work, sintering, coke oven, urban, maritime). The samplings performed the same day upwind and downwind of the industrial site of interest showed the source influence. A new approach using organic, metallic and ionic ratios determined in samples collected in the surroundings of the industrial site was then developed in order to determine the aerosols origin. Extensive environmental samplings will undergo to confirm and complete the tendencies observed.

5. ACKNOWLEDGMENTS

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ANALYTICAL METHOD FOR THE DETERMINATION OF SUGARS AS SOURCE INDICATORS OF BIOGENIC ORGANIC CARBON IN ATMOSPHERIC PARTICULATE MATTER.

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ABSTRACT

This study reports a method for the analysis of sugars in atmospheric samples. Fifteen individual sugar standards, including sugar alcohols, anhydrosugars, mono-, di- and tri- saccharides were analysed by gas chromatography- mass spectrometry (GC- MS) after derivatization with BSTFA (N,O-bis-(trimethylsilyl)trifluoroacetamide). Air sampling was carried out using a Hi- Vol sampler at a flow rate of 30 m³.h⁻¹. The particle phase was collected according to four 6 h periods by day over three days. Detection limits varied between 5 μ g.L⁻¹ and 10 μ g.L⁻¹ for all sugars and corresponding to quantification limits between 28 pg.m⁻³ and 56 pg.m⁻³ for 540 m³ of air sampled.

The results on two sampling campaigns (summer and autumn) in Strasbourg (East of France) are presented and discussed.

1. INTRODUCTION

Atmospheric particles contain organic tracers that are characteristic of their sources, their mode of formation and their subsequent alteration during transport downwind. Sugars or saccharides represent the major form of photo synthetically assimilated carbon in the biosphere. In aerosol, the saccharides are comprised of three main groups: primary saccharides consisting of mono- and disaccharides, saccharides polyols (reduced sugars), and anhydrosaccharides derivatives such as mainly levoglucosan (*Medeiros et al., 2006*).

Major amounts of saccharides have been reported to be present in aerosols of certain geographic regions such as South America (Amazonia; Brazil; Chile) and North-western Pacific (Korea; Japan). The saccharides are emitted directly from sources, although they may also be emitted significantly by thermal stripping during burning in wildfires (*Simoneit et al.*, 2004).

In addition, sugars are believed to play an important role in atmospheric chemistry and in the regulation of climate. Biomass burning may affect the climate directly due to their ability to absorb and scatter light, indirectly by altering cloud properties, since they act as cloud condensation nuclei (CCN), and semi directly due to their light absorption properties. The interaction between biomass burning aerosols and clouds may also lead to an increase in stratospheric water vapour content. It is the part of the aerosol which has a significant role in determining its properties as a CCN (*Schkolnik et al., 2005; Graham et al., 2002*).

Existing analytical methods for sugar compounds consist of gas chromatography (GC) and highperformance liquid chromatography (*Wan et al., 2006*). Several detectors coupled with chromatographic methods have been used to quantify sugars and include mainly flame ionization detection (FID) and mass spectrometry (MS) for gas chromatographic analysis; refractive index (RI) detection, pulsed amperometric detection (PAD) and MS for HPLC. Among these methods, MS is the most common methods used. More recently, liquid chromatography (LC) combined with electrospray ionization mass spectrometry (ESI- MS) has been proposed as an useful method for analyzing trace saccharides in complex media (*Cheng et al., 2006*).

In this work, we present a GC- MS method for the separation and quantification of sugars. Due to their high polarity, hydrophilicity and low volatility, saccharides have to be converted into volatilizable and stable trimethylsilyl derivatives. These derivatizations of sugars were performed using N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1 % trimethylchlorosilane (TMCS).

The atmospheric concentration for the particle phase in aerosol samples collected over 2006 during two seasons to Strasbourg (east of France) are presented.

2. METHODOLOGY

2.1 Chemicals and solutions

All the organic solvents were LC grade and were obtained from Prolabo (France).

The sugars standards were supplied from Aldrich and Cluzeau Info Labo (France). Individual standard stocks were made at the level of 1 g.L⁻¹ in dimethylformamide (DMF) and subsequently used to perform a composite standard of 10 mg.L⁻¹. This composite standard was further diluted using DMF to prepare calibration standards solutions ranging between 25 μ g.L⁻¹ and 1000 μ g.L⁻¹.

2.2 Aerosol sample collection and pre- analysis treatment

 PM_{10} atmospheric particulates matters were collected in a typical background urban site in France during August 2006 and November 2006. Samples were collected in four time periods per day (0400-1000, 1000-1600, 1600-2200 and 2200-0400 local time) over 3- day periods on Quartz fibber filter by using a Digitel DA 80 high- volume sampler at a flow rate of 30 m³.h⁻¹. Similar meteorological and climatic condition were chosen for the combination of samples. In addition sample collected during the week were not associated with those collected during the week end.

After sampling, samples were stored in freezer and were extracted as fast as possible for 20 h in a Soxhlet apparatus with a solution of hexane/dichloromethane (50:50, v/v). They were subsequently concentrated by using a rotary evaporator to about 500 μ L.

For the derivatization step, 250 μ L of the extract was transferred to a sampling vial and 100 μ L of BSTFA + 1 % TMCS was added. The reaction vial was hermetically sealed and vigorously stirred for 1 h, at 80 ° C with a magnetic stirrer. 1 μ L of this solution was subjected to GC analysis in the splitless mode (1 min).

2.3 Apparatus and analysis

All measurements were performed using an AS 3000 autosampler, a Thermo Quest GC 2000 coupled to a Thermo Finnigan Trace MS detector, an OPTIMA-210 (30 m * 0.32 mm, film thickness: 0.25 μ m) Macherey-Nagel column (MN, France, Hoerdt) and He as carrier gas (1.9 mL.min⁻¹).

The injector and the source temperatures were maintained at 250 °C and 230 °C, respectively. The oven temperature program was as follows: held at 50 °C for 2 min, increased from 50 °C to 250 °C at 5 °C.min⁻¹ and held at 250 °C for 5 min.

The samples were analysed by electron ionisation (EI) at 70 eV, in the full scan mode and in selected ion monitoring mode (SIM). In the full scan mode, the scanned mass range was 80-480 Da, and for the SIM mode, three characteristic ions were selected.

3. RESULTS AND DISCUSSION

3.1 Analysis of sugar standards

Fifteen sugars standards were analysed in this study. These compounds were selected for their strong probability to be detected in atmospheric samples.

In contrast to sugar alcohols, anhydrosaccharides, di- and trisaccharides, all of the monosaccharides presented two GC peaks due to their α - and β - configurations. These isomers were regrouped for area calculation.





The fragmentation of sugars derivatives is not characteristic of individual sugars but of group of sugars. The principal fragments (m/z) are for the monosaccharides sugars (204, 217 and 191), for the anhydrosaccharides (204, 217 and 333), for sugars alcohols (217, 319, 307 and 205) and for disaccharides (204, 361, 191 and 417).

The repeatedly of the retention times for all sugar compounds during the different analysis of samples is a very important factor due to similarities in the MS fragmentation patterns observed for the compounds of the same group. Retention time were found to be stable, varying within ± 0.02 and ± 0.05 min according to the compounds, and were summarized in table 1 with the fragments ion selected for sugar derivatives compounds.

Table1. Retention times and selected fragments of the sugars derivatives studied.

Compounds	Retention times	Selected fragments (m/z)
	(min; α-, β-)	
Monosaccharides		
L(+)- Rhammose (LR)	16.74 17.89	204 191
L(+)- Arabinose (LA)	17.32 19.08	217 204 191
D(+)- Xylose (DX)	18.63 19.16	204 217 191
D(+)- Mannose (DMns)	19.59 19.74	204 191 217
D(+)- Glucose (DG)	21.11 23.19	204 191 217
Anhydrosaccharide		
Levoglucosan (L)	21.45	204 217 333
Sugar alcohols		
Erythritol (Er)	13.84	217 204 307
Xylitol (Xy)	17.69	217 307 319
D(+)- Arabitol (DA)	18.07	317 307 319
D(+)- Mannitol (DMnl)	21.85	205 217 319
Inositol (In)	25.45	305 217 318
Disaccharides		
D(+)- Sucrose (DS)	32.24	361 217 437
D(+)- Maltose (DMl)	33.01 33.71	204 361 191
Lactose (Lt)	32.56 34.78	204 361 191
Trisaccharide		
D(+)- Melezitose (DMz)	39.25	361 217 191

Detection limits (LOD), calculated as 3 times the background level, varied between 5 μ g.L⁻¹ and 10 μ g.L⁻¹ for all sugars, with an uncertainty varied from 2.5 % to 8 %. Quantification limits (LOQ) for atmospheric samples varied between 28 pg.m⁻³ and 56 pg.m⁻³ for 540 m³ of air sampled and were determined as follows: LOQ = LOD * 3 (15 μ g in 1 L correspond to 15 ng in 1 m³ and then to 28 pg in 540 m³ of air pumped).

3.2 Analysis of aerosol samples

Among the fifteen sugars measured, only eight were detected in atmospheric samples.

The sampling procedure including four periods by day was used to determine the temporal variations of sugars concentration. However, no significant change was observed between these periods, except a few decrease of sugars concentration for the two periods 0400-1000 and 2200-0400. Accordingly to these results, concentrations of the four samples corresponding to the four periods for the same three days were summed and give a new one sample. These news samples still represent the collection of 540 m³ of air particulate matter. The results for the eight sugars detected were given in Table 2.

Concentrations of total aerosol sugars ranged from 15.50 to 21.83 ng.m⁻³ with maximum concentrations found the week of august sample. Minimum concentrations were observed in the sample collected the week-end of November.

The monosaccharides rhammose and xylose were present in lower concentrations and their interpretation of concentration variation was uncertain. In this way no tendency can be observed.

The concentrations of Levoglucosan were approximately the same for the two seasons. Levoglucosan have previously been identified as major components of organic particulate matter in areas of biomass burning *(Graham et al., 2002).* The highest concentration during the week-end of November could be explained, maybe by some domestic fire activity. During all the campaigns, no special fire was happened and is difficult to understand the constant variation of levoglucosan concentration without a precise indicator of source.

The concentration of disaccharides sucrose and maltose varied as the growing season progressed with some concentrations for these three compounds more important in summer, with a decrease during the week-end.

The monosaccharide glucose was the major compound found in samples (33 % of the total sugars) and the variation of its concentration follows the growing season. However the strong concentration in autumn allows concluding than glucose can be also enriched in the smoke affected sample (*Medeiros et al., 2006*). For the sample during the week- end of autumn, the concentration of levoglucosan increase comparing to the value of the week, but not glucose, so the domestic fire activity was not the consequence or the glucose was less enriched than the levoglucosan.

Compounds	August	(summer)	November	r (Autumn)
	Week $^{(a)}$	Week- end	Week $^{(a)}$	Week- end
Levoglucosan	3.32	3.02	3.15	3.70
D(+)- Glucose	8.12	6.15	4.86	4.50
D(+)- Sucrose	1.92	1.72	1.02	0.96
D(+)- Maltose	0.82	0.62	0.41	0.32
D(+)- Mannose	2.22	2.11	1.98	1.79
L(+)- Rhammose	0.36	0.32	0.24	0.16
Inositol	4.62	4.08	4.23	3.89
D(+)- Xylose	0.45	0.25	0.29	0.18
Total	21.83	18.27	16.18	15.50

Table 2. Concentrations of sugars in ng.m³ during the two seasons.

^(a) average of two samples

The concentrations of monosaccharide mannose were very lightly variable between the two seasons and this tendency can confirmed the enrichment of mannose in the smoke, as for glucose, indicating that wildfires also enhance emissions of uncombusted saccharides (*Medeiros et al.*, 2006).

The sugar alcohol inositol is the second most abundant sugar (23.4 % of the total sugars). The variation of inositol concentration was similar with the variation of levoglucosan concentration and inositol could come from biomass burning. However this hypothesis cannot be confirmed without a sample collected near to a fire source. Moreover, for the sample corresponding to the week end of November, concentration of inositol was less strong than the value corresponding the week. This tendency is not in accordance with levoglucosan and consequently use of inositol as biomarker of biomass burning, complementary of levoglucosan will be maybe imprecise.

4. CONCLUSIONS

A GC-MS method after a derivatization step was developed for the determination of fifteen sugar compounds present in atmospheric aerosols. Only eight sugars were detected in the sample and the concentrations of total aerosol sugars ranged from 15.50 to 21.83 ng.m⁻³. Our results allow to confirm certain conclusions of others studies but did not permits at the present to provide some news information. For this, purpose some new samples will be useful. The sampling campaigns could be performed during three consecutive days on a rural site for a better visualisation of variations and detections. Some campaigns near fires will also be useful especially to confirm the potential role of inositol in biomass burning.

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ANALYSIS OF HEAVY METAL CONTAMINATION IN ROAD DUSTS AT BUSY TRAFFIC

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ABSTRACT

This study analyzed the heavy metal concentrations of the road dusts at 8 locations which have busy traffic density. The concentrations of heavy metals in the road dusts from the rotary areas were lower than those from the highway or circulation areas. The highest concentrations of heavy metals were identified at the downtown rotary, followed by the rotary with a highway and the riverside rotary. The concentrations of heavy metals in the road dusts from a highway road which has high vehicle speed and a circulation road which has a higher proportion of heavy vehicles were higher than those from other roads. The concentrations of heavy metals in the road dusts from a downtown area were lower than those from the highway or circulation roads. These results suggest that the heavy metal contamination of the road dusts in a metropolitan city is greatly affected by vehicle emissions, volume and speeds.

Keywords: heavy metals, road dusts, road side, vehicle emissions, vehicle speed

1. INTRODUCTION

Road dust makes a significant contribution to the pollution in the urban environments. Interest in the levels of contaminants associated with road dust has risen in the recent years. Heavy metals found in road dust are significant for environmental pollution. Many studies throughout the world have identified the sources of heavy metal contamination in road dust as those associated with vehicular traffic, industrial and residential areas, urban constructions, weathered materials, etc. (Ferreira-Baptista et al., 2005; Al-Khashman, 2004; Harrison et al., 2003; Li et al., 2001; Chon et al., 1995). Heavy metals may come from many different sources in urban areas. One of the most important heavy metal sources is vehicle emissions. Road vehicles can produce significant amount of heavy metals in urban areas. Ulsan is a metropolitan city in Korea which has a population of 1.1 million and busy traffic over the whole city areas. Therefore, the environment and human health might be affected by road dust which contains elevated concentrations of heavy metals including Cd, Cu, Pb, Zn and Ni in road dusts obtained from busy traffic areas of the metropolitan city of Ulsan, Korea.

2. METHODOLOGY

In this study, road dust samples were collected at 8 road side locations in the metropolitan city of Ulsan which have busy traffic density and quite different environment as follows: 3 traffic rotaries, 4 highway or expressway areas and 1 downtown area. These road dust samples were taken during early spring (March, 2006). The collected road dust samples by operating a vacuum cleaner were dried at room temperature for 7 days and sieved through a 2 mm stainless steel sieve to remove the road dusts which have a diameter of above 2000 μ m. Then the remained road dusts were separated into four size–fractions by using the laboratory test sieves as follow: 2000 μ m, 850 μ m, 180 μ m and 75 μ m.

In the laboratory, the heavy metals in road dusts samples of 3 grams were extracted with aqua regia solution $(HNO_3 : HCl = 1 : 3 (v/v))$ of 14.4 ml. Then the mixture was boiled for 1 hour at 70 0 C. The extracted solutions were filtered by quantitative filter paper (Advantec 5B with 5 µm in size). After that, the final solutions were made up to 30 ml with deionized water. The concentrations of heavy metals including Cd, Cu, Pb, Zn, and Ni were analyzed by atomic absorption spectrometry (Varian - AA240).

3. RESULTS AND DISCUSSION

The results of the pseudo-total concentrations of Cd, Cu, Pb, Zn and Ni extracted from the road dusts in the different road side areas showed elevated concentrations of the heavy metals.

The average concentrations of the heavy metals in the road dust samples from the traffic rotary areas were much lower than those from highway or circulation road areas. Also, the average concentrations of the heavy metals in the road dusts from the downtown area were lower than those from the highway or circulation roads.

In the rotary areas, the highest pseudo-total concentrations of Cd, Cu, Pb and Zn were identified at the downtown rotary followed by those at the rotary with a highway. The concentrations of heavy metals in the road dusts at the riverside rotary which has advantages for dust dispersion in the atmosphere were lower than those at the downtown rotary and the rotary with a highway end. The higher concentrations of the heavy metals in the road dusts at the rotary areas are due to the increased traffic volume.

The pseudo-total concentrations of the heavy metals in the road dusts from a highway road which has a vehicle speed of 110 km/hr and the industrial circulation road which has a higher proportion of heavy duty vehicles such as industrial trucks were higher than those from other roads. The concentrations of the heavy metals in the road dusts from a high speed road and the city circulation road, which have a higher proportion of gasoline powered small vehicles, were lower than those from other roads. However, the concentrations of the heavy metals in the road dusts from the high speed road, which is passing nearby automobile manufacturing plants and has a vehicle speed of 80-90 km/hr, were higher than those from the city circulation road with a vehicle speed of 70-75 km/hr.

In particular, all the concentrations of the heavy metals in the road dusts increased with decreasing particle sizes of road dusts. This is because of the difference in surface area of different size of road dusts. The road dusts with the smaller particle size have higher available surface area for deposition or coating of the heavy metals released into the atmosphere near road surfaces as compared the larger size ones.



Fig. 1. The concentrations of heavy metals in the road dusts from busy traffic areas



0 + 26883 11 DO0 + 2

Fig. 2. The concentrations of heavy metals in the road dusts from traffic rotaries



Fig. 3. The concentrations of heavy metals in the road dusts from the highway or circulation roads

4. CONCLUSIONS

The analyzed results showed elevated concentrations of the heavy metals in the road dust samples taken from the busy traffic areas. Traffic density and emissions, vehicle speed and type, such as gasoline powered or heavy duty vehicles, and the road environment were important parameters of the contamination levels of heavy metals in the road dusts. The particle size of road dusts was also one of the important parameters of the pollution level by heavy metals.

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CHEMICAL ELEMENTS IN AIRBORNE PARTICULATES OVER ANGRA DO HEROÍSMO, TERCEIRA ISLAND, AND PICO SUMMIT, PICO ISLAND, BOTH AT AZORES (PORTUGAL)

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ABSTRACT

This study deals with aerosol collections from Angra do Heroísmo (sampling height: 74 m), a UNESCO-designated (1983), World Heritage city in Terceira island, Azores. Glass fiber filters with PM10 mass concentrations, sampled by IM from 6 July 2005 to 30 June 2006, were put through instrumental neutron activation analysis for elemental evaluation. Blank contents were taken into account. The urban results from Angra were compared with data obtained near the summit of Pico mountain (sampling height: 2225 m), Pico island, Azores. In Pico, the results show higher medians for most of the chemical element, sodium being an exception (10 times higher in Angra). This may indicate that the atmospheric chemistry of Angra is primarily governed by inputs from marine sources, as expected in such an oceanic environment, while influence of long-range transport of anthropogenic elements cannot be ruled out for the composition of PM10 from the remote, high-altitude site.

1. INTRODUCTION

The first registers of the atmospheric composition performed by the Portuguese Meteorological Observatory "Infante D. Luís" date from middle of the 19th century, however the registers of the amount of suspended particles occurred many years later. In 1974, under recommendation of the World Meteorological Organization (WMO) and the BAPMoN (Background Air Pollution Monitoring Network) program, a few solar radiation measurements were initiated in Lisbon, Coimbra, Porto, Évora, Faro, Bragança and Penhas Douradas. From 1982, the National Institute of Meteorology and Geophysics initiated the sampling of the suspended particles in a regular basis, every 6 days and for 24 h periods, using high volume air samplers with PM10 selective impactors. This occurred in the stations of Bragança, Faro/international airport, Lisbon, Viana do Castelo, Castelo Branco, Angra do Heroísmo (Azores archipelago), and Funchal (Madeira archipelago). Lisbon and Faro stations are not working at the moment, being expected its start in a near future. The PM10 sampling is designated by Global Atmospheric Watch (GAW/ex-BAPMoN). The methodology for determination of the mass concentrations follows the recommended by WMO, keeping the volumetric flow constant during the 24 h sampling and using the gravimetrical method.

Angra do Heroísmo, with a latitude of 38° 40' N, a longitude of 27° 13' W and an altitude of 74 m, started in 1992. From 6 July 2005 to 30 June 2006, mass concentrations between 1.3 μ g m⁻³ (7 April 2006) and 26.8 μ g m⁻³ (10 September 2005) were found, and the sampled volume varied between 656 m⁻³ and 2654 m⁻³. A total of 60 filters were analyzed by neutron activation analysis (NAA) (Freitas et al., 2005).

The PICO-NARE observatory is an experimental site on the summit of the Pico Mountain (38.470° N; 28.404° W; 2225m altitude) in the Azores archipelago (Honrath & Fialho, 2002; Honrath et al., 2004; Fialho et al., 2006; Freitas et al., 2007). This site is in the pathway of air masses traveling from surrounding continents (Africa, Europe and Central and North America). At Pico, the Aethalometer worked for 24 h periods between 6 July 2001 and 15 July 2002. A total of 149 filters were analyzed by NAA.

2. METHODOLOGY

The collected quartz filter spots were identified after removing the tape from the Aethalometer in early July, 2002, and were packed together with unexposed portions of the tape (as blanks) and analyzed for elemental composition. The blanks and the sampled filters were cut from the strips in circular forms with area 0.950 ± 0.086 cm². The exposed side of each spot was covered with piece of similar geometry of the unexposed blank filter, to avoid contamination of the sample; the same procedure was applied to each of the blanks in order to obtain identical geometry. Squares of 1.5 cm x 1.5 cm were removed from each A4 glass fiber sheet, they were rolled

with the sampled part turned to the interior; the same procedure was applied to each of the blanks in order to obtain identical geometry. The samples were weighed in a 0.1 μ g sensitivity balance and packed into aluminum sheets. Each sample or blank was irradiated for 7-11 h with a thermal flux of 1.124×10^{13} cm⁻² s⁻¹ together with one disc (125 μ m thick and 0.5 cm diameter) of a 0.1% Au–Al alloy as comparator. After irradiation, samples decayed for 4 to 6 days and were then measured; after this measurement samples decayed for 2 to 3 weeks more and were measured again. The gamma spectra measurements for each sample were collected on a liquid nitrogencooled hyperpure germanium detector (1.85 keV resolution at 1.33MeV and 30% relative efficiency). The gold alloy disk was also measured in the same detector 7 days after the end of the irradiation. The determination of the elemental composition resulted from the application of the k₀-standardization method (De Corte, 1987).

3. RESULTS AND DISCUSSION

Tables 1 and 2 show the results of the chemical elements obtained by NAA in the filters sampled at Pico summit and Angra do Heroísmo, respectively.

		Geom mean	Median	Arith. Mean	Stdev	Min	Max	Missing
	Count	$(ng m^{-3})$	values (%)					
Total nr.	149							
As	22	1.3	1.4	2.0	1.7	0.11	5.0	127 (85)
Br	108	0.58	0.57	1.1	2.9	0.015	24	41 (28)
Ce	32	0.29	0.37	0.69	0.82	0.0069	3.0	117 (79)
Co	114	0.46	0.54	0.60	0.39	0.015	2.0	35 (23)
Cr	77	0.84	0.85	1.3	1.1	0.093	4.8	72 (48)
Fe	56	147	121	257	350	40	1745	93 (62)
Hf	129	0.085	0.090	0.12	0.14	0.00093	1.4	20 (13)
Κ	72	126	123	338	503	9.0	2504	77 (52)
La	110	0.12	0.10	0.21	0.44	0.029	4.2	39 (26)
Lu	18	0.017	0.018	0.018	0.0069	0.0079	0.032	131 (88)
Mo	99	8.9	9.8	11	6.3	0.15	29	50 (34)
Na	101	63	58	150	437	3.3	4075	48 (32)
Sb	117	15	19	23	26	0.31	257	32 (21)
Sc	92	0.011	0.011	0.037	0.086	0.00037	0.56	57 (38)
Sm	101	0.046	0.046	0.065	0.066	0.0015	0.39	48 (32)
Sr	11	548	655	617	239	109	920	138 (93)
Th	83	0.11	0.12	0.16	0.19	0.010	1.6	66 (44)
U	96	0.20	0.25	0.27	0.16	0.0022	0.80	53 (36)
Zn	118	5.0	5.7	9.9	26	0.059	276	31 (21)

Table 1. Statistical data for the elemental concentrations in PM10, collected in quartz filters at Pico summit.

Quartz filters contain traces of all the chemical elements shown in Table 1 except bromine, chromium, iron, lutetium, strontium, and thorium. The glass fiber filters contain traces of all the chemical elements shown in Table 2, in much higher amount than the ones found in the quartz filters (the ratios range between 0.02 and 3500). In spite of that a larger number of chemical elements could be determined due to the larger volume of air collected, with a ratio to the quartz filters of about 200. Median concentrations in Angra are mostly lower than in Pico, except for sodium. Concentrations for 13 and 23 chemical elements could be obtained in at least 50% of the measurements; at Pico and Angra respectively. Pearson correlation coefficients were determined for such elements and the results are shown in Tables 3 and 4, for Pico and Angra respectively. The main constituents of the soil (Sc, La, Sm, others) showed consistently high correlation (r>0.9) in both sites, and are highly influenced by long range transport of dust from North of Africa (Almeida et al., 2007a; Almeida et al., 2007b). Sodium at Pico and iron at Angra do not correlate with any other element. Zinc and bromine related to traffic (mainly tires and break wear) are well traced as long-transport at Pico summit. The association of molybdenum and uranium may be related to long-transport of nuclear waste processing, as concluded from the air mass trajectories (not shown). Arsenic may have two sources: agriculture in Angra and long-transport from Europe/America at Pico. Further discussion is foreseen in a near future, including assignment of chemical elements to mass trajectories.

		Geom mean	Median	Arith. Mean	Stdev	Min	Max	Missing
	Count	$(ng m^{-3})$	values (%)					
Total nr.	60							
As	12	0.010	0.0076	0.44	1.5	0.00048	5.24	48 (80)
Ba	52	0.34	0.36	0.64	1.0	0.022	5.9	8 (13)
Br	1	n.a.	n.a.	n.a.	n.a.	0.12	0.12	59 (98)
Ca	56	192	262	398	850	3.8	4714	4 (7)
Cd	1	n.a.	n.a.	n.a.	n.a.	1.3	1.3	59 (98)
Ce	58	0.15	0.14	0.35	0.74	0.0016	4.8	2 (3)
Со	47	0.0018	0.0013	0.012	0.060	0.00016	0.41	13 (22)
Cr	54	0.14	0.15	0.22	0.31	0.0086	2.3	6 (10)
Cs	16	0.00056	0.00042	0.0093	0.034	0.000046	0.14	44 (73)
Eu	15	0.00091	0.00084	0.0024	0.0043	0.000052	0.017	45 (75)
Fe	50	2.0	2.3	4.3	6.2	0.018	34	10 (17)
Hf	55	0.083	0.078	0.26	0.81	0.0067	5.1	5 (8)
Hg	34	0.0066	0.0073	0.014	0.020	0.00022	0.096	26 (43)
Κ	1	n.a.	n.a.	n.a.	n.a.	199	199	59 (98)
La	54	0.074	0.064	0.18	0.38	0.0076	2.2	6 (10)
Mo	24	0.020	0.021	0.042	0.098	0.0037	0.49	36 (60)
Na	50	738	610	2298	5924	39	28941	10 (17)
Nd	42	0.050	0.053	0.12	0.33	0.0019	2.2	18 (30)
Rb	50	0.057	0.052	0.27	1.2	0.0026	8.2	10 (17)
Sb	60	0.0091	0.0089	0.018	0.031	0.00023	0.18	0 (0)
Sc	58	0.0032	0.0030	0.0080	0.021	0.00015	0.13	2 (3)
Se	8	0.0018	0.0032	0.0090	0.015	0.000042	0.046	52 (87)
Sm	48	0.011	0.011	0.024	0.043	0.00034	0.25	12 (20)
Та	18	0.00048	0.00040	0.0012	0.0021	0.000061	0.0088	42 (70)
Tb	54	0.0030	0.0036	0.0069	0.017	0.000027	0.10	6 (10)
Th	55	0.018	0.019	0.035	0.080	0.0015	0.54	5 (8)
U	5	0.010	0.023	0.022	0.020	0.00094	0.050	55 (92)
Yb	56	0.018	0.016	0.052	0.15	0.00058	0.87	4 (7)
Zn	58	0.58	0.59	1.4	2.6	0.0086	14	2 (3)
Zr	57	3.2	2.7	17	81	0.10	611	3 (5)

Table 2. Statistical data for the elemental concentrations in PM10, collected in glass fiber filters at Angra do Heroísmo. n.a.: not applicable because n=1.

Table 3. Pearson correlation between the chemical elements at Angra do Pico summit. r>0.50 is in bold.

	Br	Co	Cr	Hf	La	Мо	Na	Sb	Sc	Sm	Th	U
Со	0.03											
Cr	-0.05	0.18										
Hf	0.22	0.27	0.11									
La	0.26	0.26	0.58	-0.02								
Mo	-0.08	0.30	0.40	0.33	0.25							
Na	0.24	-0.06	0.36	-0.01	0.13	0.17						
Sb	-0.02	0.50	0.13	0.77	-0.03	0.43	-0.04					
Sc	0.13	0.28	0.61	0.09	0.97	0.21	0.30	0.09				
Sm	0.07	0.32	0.64	0.17	0.91	0.51	0.31	0.20	0.92			
Th	0.04	0.50	0.22	0.79	0.08	0.38	0.08	0.79	0.34	0.39		
U	0.03	0.27	0.36	0.12	0.33	0.65	-0.07	0.25	0.28	0.41	0.31	
Zn	0.53	0.09	-0.11	0.01	0.16	-0.10	0.09	-0.05	0.18	0.09	0.05	-0.02

	Ba	Ca	Ce	Со	Cr	Fe	Hf	Hg	La	Na	Nd
Ca	0.88										
Ce	0.80	0.88									
Co	0.89	0.93	0.84								
Cr	0.79	0.92	0.93	0.89							
Fe	0.54	0.47	0.34	0.71	0.25						
Hf	0.84	0.96	0.92	0.87	0.92	0.39					
Hg	0.37	0.11	0.68	0.42	0.72	0.08	0.20				
La	0.75	0.87	0.82	0.78	0.81	0.35	0.90	-0.13			
Na	0.66	0.77	0.73	0.69	0.64	0.40	0.79	-0.01	0.70		
Nd	0.94	0.99	0.91	0.88	0.97	0.17	1.00	-0.30	0.87	1.00	
Rb	0.67	0.79	0.94	0.99	0.95	0.30	0.90	0.71	0.80	0.68	0.99
Sb	0.84	0.93	0.86	0.27	0.86	0.49	0.92	0.13	0.82	0.73	0.90
Sc	0.86	0.97	0.92	0.91	0.93	0.47	0.99	0.12	0.90	0.78	0.99
Sm	0.88	0.94	0.94	0.87	0.94	0.43	0.97	0.63	0.87	0.97	0.99

Table 4. Pearson correlation between the chemical elements at Angra do Heroísmo. r>0.50 is in bold.

Table 4 (cont.). Pearson correlation between the chemical elements at Angra do Heroísmo. r>0.50 is in bold.

	Rb	Sb	Sc	Sm	Tb	Th	Yb	Zn
Sb	0.31							
Sc	0.88	0.93						
Sm	0.91	0.93	0.97					
Tb	0.91	0.93	1.00	0.98				
Th	0.94	0.91	0.99	0.98	0.99			
Yb	0.84	0.93	0.99	0.97	0.99	0.97		
Zn	0.55	0.93	0.92	0.93	0.93	0.92	0.92	
Zr	1.00	0.30	0.99	0.98	1.00	0.99	0.98	0.53

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HEAVY METAL CONCENTRATIONS AT THREE FRENCH SITES UNDER INDUSTRIAL AND TRAFFIC INFLUENCES, AND RURAL CONDITIONS PART II: BIOMONITORING BY MOSSES

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ABSTRACT

A whole experiment was undertaken in 2005-2006, that aimed at studying the behaviour of microbial species living in bryophytes and the effects of oxidative stress upon the biochemistry in their cells, when bryophytes are submitted to various kinds of atmospheric pollutions.

This work presents the heavy metal bioaccumulation by mosses transplanted in three French locations selected for the experiment: Montagney, a rural site in East of France, Saclay, a site at the vicinity of a highway of the region of Paris, and Dunkerque, an industrial town located at the North Sea coast, and where the pollution can originate mainly from steel and aluminum productions and petroleum refineries. The PM10 particles composition was characterized at each site. *Scleropodium purum* species were first collected at an initial site located in the Fontainebleau forest, far from pollution sources, then transplanted in 3 stands in each of the 3 sites. Sub-samples were collected every two months at every stand and sites. Average concentrations obtained from 3 stands per site were considered here. The total time of exposition was 8 months. All samples were stored in an oven at 40°C until analysis. The concentrations were determined by neutron activation analysis.

The temporal variability of the whole element average concentrations variations for all elements was studied.

In the rural site of Montagney, only a few element concentrations presented an increasing trend in moss, when compared to the "prior to exposure" composition: Cl, Na, Ca, Cr, Mn, Fe, Co, As, Br, Sr, Cs, Zn, Rb, Sb, Hf and Th denoting a possible enrichment of those concentrations in that site, compared to the initial site. The other element concentrations did not display significant variations.

A clear concentration increase in the sites of Saclay and Dunkerque was observed for elements: Na, Cl, Al, Ca, V, Sc, Cr, Fe, Co, Br, Rb, Sb, Cs, As, Se, Ce, Eu, Sb, Hf and Th. The accumulation velocity in ppm month⁻¹, calculated at both sites can be associated to the pollution source intensities, and also to the bio-accumulation ability of mosses. The ratio of the accumulation velocity between Dunkerque and Montagney, gave the ratio of the source strengths between both sites. Accumulation velocities were compared to the PM10 concentrations also measured at all sites during the same period.

Correlations between concentration differences between two 2-month intervals are studied at the three sites. At the site of Dunkerque, strong correlations between Fe, Co and Zn exist with regression coefficients higher than 0.9 (at α =0.05).

The increase of concentrations during the 8-month period enables to show that the sensitivity of *S. purum* was different for a lot of elements from site to site.

This work enabled to define the major pollutions by heavy metals observed in moss exposed to the traffic or the fumes of an industrial site, as possible parameters acting upon the biochemical behaviour of the accumulators or upon the development of the microbial fauna living on the bryophytes and described elsewhere.

1 INTRODUCTION

Origins of atmospheric aerosols can be natural and anthropogenic, as well. Among natural sources, wind erosion and marine sources are of major importance, but volcanoes activities and forest burnings must also be evoked. Besides the natural origins, anthropogenic sources like mobile sources, industrial and urban pollution bring important contributions, which intensities depend on the distance between the pollution sources and the sampling point. Most of these sources have variable emissions intensities, and their control should need frequent sampling and therefore, expensive analyses. Another alternative is the use of endogenous material at the vicinity of polluting areas, that has the property to accumulate the products of source emissions, after dry and/or wet deposition. Bryophytes were often used. Rühling et al (1994) developed the mapping of the pollution in Nordic countries. A similar mapping of the atmospheric pollution was undertaken in France in 1996-1997 (Ademe,1997), by using several moss species, demonstrating the suitability of this technique in various locations in France.

This work presents biomonitoring data of the atmospheric pollution of heavy metals simultaneously performed at 3 French sites : one in a rural location, a second one near a high density traffic and the a third one in an industrial and urban site. Heavy metal concentrations in mosses are compared to aerosol concentrations data collected at the same sites (Gaudry et al, this conference).

2 SAMPLING, SITES, METHODS

Sampling:

In order to control the timing of the heavy metal deposition, the transplant of a moss species, *Scleropodium Purum* was undertaken. An important amount of *S. Purum* was collected at an initial time

inside the forest of Fontainebleau, 50 km South from Paris, in a place where neither traffic, nor human activities occur. The stock was divided into 3 parts, one for each site, and again into 3 parts for exposition in 3 covered stands, in open air, at 1 meter from the ground, during a total time of approximately 8 months, at each site. One sampling was simultaneously taken every two months at each stand and each station. Due to the existence of a roof above stands, rain did not moisten directly mosses and it was necessary to nebulize water two times water on the surface of mosses twice a week.

Five periods were defined. The initial moss was set up at the time (t_0) , on October 26, 2005, then exposed during approximately 8 months, until June 7, 2006. Sub-samples were taken by intervals of 2 months approximately defing the period 1 (October 26, 2005 to December 19,2005) the period 2 December 19, 2005 to February 15, 2006, the period 3 from February 15 to April 12, 2006 and the period 4 from April 12 to June 7, 2006.

Sites:

The first location, Montagney is a rural site in East of France, 30 km West of Besançon, a town of middle importance, the second one, Saclay is located nearby the N118 highway near Paris, and the third one, Dunkerque is an industrial town located at the North Sea coast, and where the pollution can originate mainly from steel, non ferrous metals productions and petroleum refineries. More details on these sites given by Gaudry et al (this conference).

Methods:

Mosses were kept in an oven at 40°C until the preparation for analysis. All samples were grounded. Three sub-samples were taken. Two of them were pelletized with pure cellulose for instrumental neutron activation analysis (INAA). The third sub-sample of powder was directly digested, then analyzed by inductively coupled plasma mass spectrometry (ICPMS). Details of the analytical conditions are the same as for the analysis of filters and described by Gaudry et al (this conference). The quality control was ascertain by using two reference materials : the SRM lichen 336, and the SRM fucus 140/TM (an alga), both provided by IAEA. Only results obtained by INAA are presented here, pending the final assimilation of ICPMS data.

3 RESULTS

The first important information needed is the characterization of the initial moss content. Nine samples were taken one per stand and per station. The average concentration ($C_{0,i}$) for an element (i) was considered and its standard deviation (σ_i) was used to define on how a signal (A_t) at a moment (t) is significant, by using the criteria $A_t > C_{0,i}+1.645 \sigma_i$ at a confidence level p = 0.05.

The concentrations between stands from a same site differ slightly, because the general environment around these stands was different. For instance, in Montagney, the three stands were contiguous, with no building at the vicinity; in Dunkerque, they were contiguous but a building was very close to one of the stand and it might have disturbed the air turbulence, then the advection of particles; in Saclay, the three stands were separated, had different exposition to the sun, and a building was also present. In this work only data representative of the average concentrations at the three stands were considered and shown in Fig1 a, b and c.



Fig 1a-Time evolution of heavy metal concentrations in scleropodium at



Some trends appear for most of elements. It is interesting to study the correlations at each station of the concentration differences between two consecutive times: $\Delta(C_{t1}-C_{t0}); \Delta(C_{t2}-C_{t1}); \Delta(C_{t3}-C_{t2}); \Delta(C_{t4}-C_{t3})$. In Montagney, strong correlations (at α =0.05 confidence level) with regression coefficients (r) higher than 0.9 are found for the concentration differences of Sc, Cr, Fe, Br, Sb, Eu and Th, between 0.8 and 0.9 for Al, V, Co, Ce and Lu, between 0.7 and 0.8 for Zn, Cs and Sm. These elements may have here a crustal origin, or be characteristic of a same background. In Saclay, several groups of correlations are found. The first one is composed of Sc, Fe, Co, Br, Cs, Ce, Eu, Th with a regression coefficient r > 0.9, of Sb with 0.8 < r < 0.9. Another group is composed of Na, Cl, K, Ca, Cr, Zn, Rb and Sm. Although some elements are recognized by several authors (Zechmeister et al, Harrison et al, Weckwerth, garg et al, De Miguel et al, Dietl et al) to be emitted by traffic, it is not possible to ascertain the anthropogenic or crustal origins from these correlations. A third group of correlation is obtained with Al, La and Cr. In Dunkerque, three main groups of correlation appear. The first group is composed of Sc, Na, Al, Cl, Co, Rb, Sb, Ce, Eu and Hf, with r>0.9 K, V, Cr, Cs, Fe and Ba and Hf with 0.8<r<0.9, and Zn, As, Br with 0.7<r<0.8. In such a case the industrial pollution should be responsible for these groups of correlations, dominated by significant increases of concentrations, much higher than in the other stations. Since Fe is a dominant element produced by the steel production (7 million tons per year) it is observed that its concentrations differences between two periods of time strongly correlates with Co, Zn (r>0.9), for Ca, Sc, Br, Sb, Th (0.8 < r<0.9), and to a certain extent for Na, Rb and Hf $(0.7 \le 0.8)$. Thus, those elements could be associated to that kind of pollution. However, Mn that is another element strongly emitted in Dunkerque strongly correlates only with Al and V. It is worth noting that emissions of Fe and Mn are not linked, as observed from correlations data.

Since aerosol concentrations were also available in PM10 particles (Gaudry et al), it is interesting to compare them with concentrations in *S. Purum*. Aerosol concentrations are linked to source intensities, and therefore to the amount of heavy metal that should be deposited on the mosses and have an effect on the signal observed by the bryophytes. Such a signal was calculated on particular stands at each station, by the ratio of the difference of concentration between t_4 and t_0 , to the concentration of the initial moss and appears on Fig 2.



Fig 2 : Signal/noise defined as $(Ct_4-Ct_0)/C_{t0}$ to for each element in Montagney (stand A), Saclay (stand C) and Dunkerque (stand B).

It can be observed that in Montagney, a clear signal, higher than 2 appears only for a few elements: Na, Cl, As, Br, In Saclay the signal is higher than 2 for the following elements: Na, Cl, Sc, Cr, Fe, Co, As, Br, Sb, Ce and Th. Certain of these elements are supposed to have crustal origins: Sc, Cs, Hf, Th, rare earths, while Fe, Co, Br, Sb were described as elements emitted by the car and trucks traffic. In Dunkerque, the signal is higher than 2 for most elements excepted Mg, K, Rb, Ba, Hf, Au. Industrial sources appear clearly for V, Sc, Cr, Mn, Fe, Co, Br, La, rare earth elements and Th.



Fig 3: Equivalent volume of air (m3) at each site, defined as the ratio between the concentration variation for an element between t4 and t0, to the average PM10 concentration recorded at the same site during the same period

A comparison with PM10 aerosol data was also done. Fig 3 shows the ratio for any element of its concentration variation (average for three stands in a site), between the times t_4 and t_0 (8 months), to the average concentration of the same element in PM10 particles. This figure corresponds to an equivalent volume of air necessary to explain the variation of concentration between t_4 and t_0 . It can be observed that values can be very different for one element, depending on the sites, and therefore on the deposition conditions and the nature of the meteorological conditions and/or the nature of the pollutions. The highest the equivalent volume, the best conditions occur including the efficiency of the moss as a bioaccumulator. For instance best conditions are shown in Dunkerque for Al, Sc, Cr, Fe, La, Ce, Th, while it is for As and Sb in Saclay, for Na, Cl, Mn, Br, Rb in Montagney. Conditions seem particularly bad for V and Zn at every site.

4 CONCLUSION

This biomonitoring experiment with *S. purum* made conspicuous the pollution impact on the floor of the region of Dunkerque, during 8 months of accumulation, by several heavy metals: Al, V, Cr, Mn, Fe, Co, Th. Some other elements not known as toxic are also deposited: Na, Cl, Ca, Br, rare earths and particularly La and Hf. In Saclay, the traffic influence is evident for elements like Sb, Cr, Fe, Co. Mixed origins (anthropogenic and natural) should explain the deposition of Sc, rare earth, Hf and Th, even in Dunkerque, where aerosols contains higher concentrations of those elements. A comparison between biomonitoring data and aerosol concentrations shows that *S. purum* has a weak efficiency for measuring the bioaccumulation of V, Mn, Zn, and As at the 3 sites, but is a good bioaccumulator for the other elements.

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CHARACTERISATION OF TRACE ELEMENTS IN URBAN ATMOSPHERIC DUST AND THEIR SOURCE APPORTIONMENT IN KOLKATA METROPOLIS, INDIA

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ABSTRACT

Objective of study was to find out and characterize the distribution of trace elements including heavy metals in urban particulates deposited on canopy foliage of Kolkata city. Atmospheric dusts deposited on canopy leaves were collected along major streets in winter (2005-2006). Analysis of samples (EDXRF technique) show presence of Ni, Cu, Zn, As, Rb, Sr, Nb, Ag, Cd, Sn, Sb, Ba, Ce, Pb, Ga having differential variation of concentration in particulates deposited on canopy leaves. Statistical analysis showed different groups of classification of elements like natural elements (Sr, Sn, Nb, Ga), urban elements (Ni, Cd, Cu, Pb, As) and mixed origin (Ag, Ce, Ba, Rb). The identified anthropogenic sources are traffic, domestic combustion of fossil fuels and different small-scale industries, responsible for the contamination of atmosphere dusts. This provides the baseline information on elemental contamination in city atmosphere and insists to determine the need for remediation.

1. INTRODUCTION

Pollution through atmospheric particulates specifically from heavy metals and trace element from different anthropogenic sources and subsequent health effects are currently the major problems of the highly urbanized region of the world. Among the trace elements of air borne particulate matter Al, Pb, Zn, As, Cd, Ni, Cr, Cu are commonly known heavy metal, which causes adverse effects on human health and environment due to its toxicity (Deb et al, 2002). They occur naturally in a wide range of minerals but their distribution in environment is due to emission from fossil fuel combustion, industrial activities, and widespread use of pigments, pesticides and other human activities (Tsai et al, 2003; Dara, 1997; O'Neill, 1990). Their concentrations in urban environment vary considerably in roadsides, which is unlikely in case of other natural areas (Chirenje et al, 2001). It is considered that traffic is one of the main reasons for dust pollution (Pandey et al, 1998; Pio et al, 1998; Kleeman and Cass, 1998). Thus traffic, together with other particulate sources from anthropogenic activities contributes to urban pollution, which causes threat to human health. Urban soils are significantly more heterogeneous than non-urban soils, where human activity is playing a dominant role in changing soil structure (Chirenje et al, 2003; Davis et al, 1987 and Craul, 1985). Land use types are also a good basis for classification and characterization of trace elements distribution in urban soils.

Urban particulates can be emitted directly to the atmosphere through combustion processes or through erosion followed by wind transport and subsequently accumulated on surfaces of canopy leaves as well as on street sediments. The amount of dust deposition and the deposition of trace metals severely increases towards the surface in the vicinity of streets and canopy leaves. It is also seen that biological and environmental factors play an important role in the adhesion and subsequent potential accumulation of particulate pollutants. Elements show specific solubility in different dust and street sediments fractions (Tanner and Wang, 2000; Li et al, 2001). Studies on urban atmospheric particulate matter and on street sediments were carried out in some Chinese cities (Shu et al, 2001; Li et al, 2001; Tanner and Wong, 2000; Mao and Chen, 1996; Ning et al, 1996). Four mega cities in India (Delhi, Kolkata, Mumbai and Chennai) are among the top most polluted mega cities in the world. Rapid industrial and population explosion is leading to a fast deterioration in the quality of atmospheric environment and consequently public health. In this regard, little has been done to characterize the composition of trace elements in atmospheric dusts. This highlights the need to investigate the near ground deposition of particulate matter with regard to impact on human and plants. Street canopy leaves are accumulators for urban dust deposition that integrate over the whole assembly of urban pollution sources but will be dominated by traffic pollution. Furthermore, these surfaces themselves are sources of dust due to wind erosion. Therefore atmospheric deposition on leaves was taken along few main roads of Kolkata urban environment and pollution sources other than traffic were studied.

2. METHODOLOGY 2.1 Study area with demographic and meteorological details

However there is a lack of knowledge on the impact of anthropogenic activities on chemical composition of urban particulates of Kolkata city with respect to the concentration of trace elements including heavy metals. Kolkata is a compact city (Lat. $22^{0}25'$ to $22^{0}40'$ N and Long. $88^{0}20'$ to $88^{0}35'$ E), concentrated along the fringes of the river Ganges. The surrounding area is a flat swampy region with a subtropical climate. The major contributor of trace elements in the particulates is mainly vehicular and industrial emission. The number of vehicles on Kolkata's potholed streets has risen from about 300,000 to over 900,000 within a span of 20 years. Among the vehicles some are old and emitting toxin-belchers. The road space is approximately 6 percent of the city's total land area. Kolkata city has a mixed nature of industries of numerous kinds including automobiles, ceramic, chemical, pharmaceuticals, food processing, heavy engineering, and shipbuilding. Besides several small scale industries like rubber, plastic, printing, textile, metallurgical and metal workshops are scattering mainly in north and central part of the city.

Kolkata city has a typical tropical monsoon climate with hot in summer, heavy rains and moderate cold in winter. During the study period temperature varies from 10.6° C to 24.5° C recorded in December 2005 to February, 2006. Rainfall is very trace during the time and relative humidity has been noticed as 72% on average. Moderate wind speed has been observed in the winter season (12 - 25 km/h).

2.3 Sample Collection & Analysis

Atmospheric dust samples deposited on canopy leaves were collected in different major roads of Kolkata city along an east/west and north/south transverse area during winter (December, 2005-February, 2006) to understand the influence of different pollution sources. During sampling leaves were collected from different plants along the roadside at a certain height (about 2.5 m). The deposited dusts were scratched out from the leaf surface and mixed thoroughly. In a particular sampling site 8 to 10 samples were collected and then thoroughly mixed to get the homogeneity. The sample is then brought to the laboratory and sieved through 0.2 mm and finally prepared for XRF analysis.

The trace elements analysis has been carried out by Energy Dispersive X-Ray Fluorescence (EDXRF) technique (SPECTRAEC 5000, BECKER HUGES). The EDXRF capitalizes the particle nature of electromagnetic radiation. The bulk samples were ground to fine powders in an agate mortar to meet the condition of homogeneous dense material and were put in plastic sample cups covered with thin plastic sheets and fix tightly with plastic bands. The covered surfaces had to be very smooth to avoid scattering. Cu, Pd and low N_2 filter were used for different energy excitation ranges of X-Ray. Prior to use of the data, matrix correction was done by normalizing with the Compton peak, to extend the correction to the energy range below the Fe-K absorption edge, a semi-empirical correction has also been carried out.

3. RESULTS AND DISCUSSION

Table 1 presents the results of elemental composition of the dust samples and the statistical analysis of them. The elemental composition of deposited dusts show conspicuously high levels of heavy metals like Ni, Cu, Zn, As, Pb, Cd and other trace elements Rb, Ag, Nb, Sn, Sr, Ce and Ga. Trace elemental pollution in Kolkata city is high taking Cu, Zn, Pb as indicators of pollution in view of their being of anthropogenic origin and toxicity. Kurtosis calculations on the data set have given a negative value for the Rb, Nb, Sn, Ce. This characterizes a flatness of the distribution of the above elements compared with the normal distribution. Positive kurtosis values have been observed for Ni, Cu, Zn, As, Sr, Ag, Cd, Sb, Ba, Pb and Ga that indicates a picked distribution. Skewness calculations in a data set characterize the degree of asymmetry of a distribution around its mean. Positive skewness indicates a distribution with an asymmetric tail extending toward values that are more positive. In data set Rb, Sr and Ce have shown negative skewness which could be the result of probable losses of the element during storage and transit in view of the higher volatility. As far as asymmetry in the data set is concerned this study has shown a wide variability, which is mainly the result of the meteorological effects, and further of the widely changeable diffused vehicular and industrial emission around the city.

Elements	Mean	Median	Standard	Kurtosis	Skewness	Minimum	Maximum
			Deviation				
Ni	59.29	51.81	22.99	2.35	1.82	39.75	112.7
Cu	223.92	210.63	80.22	0.4	1.012	122.46	379.63
Zn	950.25	956.06	239.83	0.18	0.09	538.93	1406.26
As	23.89	23.24	7.62	0.37	0.39	12.51	39.63
Rb	70.93	72.02	5.19	-0.85	-0.34	61.82	78.91
Sr	144.69	145.94	7.56	0.09	-0.12	130.91	158.65
Nb	7.79	7.68	1.50	-0.24	0.59	5.69	10.47
Ag	5.22	4.84	3.06	9.46	2.88	2.1	14.51
Cd	4.54	3.44	2.91	2.47	1.55	1.34	11.72
Sn	25.74	25.27	8.85	-0.26	0.36	11.52	42.21
Sb	11.48	11.77	3.69	1.10	0.70	5.72	19.69
Ba	778.55	742.61	194.74	4.35	1.88	600.28	1298.66
Ce	79.60	79.33	8.06	-1.17	-0.01	67.69	91.61
Pb	565.70	503.70	338.83	4.44	1.99	199.6	1466.74
Ga	23.56	21.68	8.72	2.47	1.34	12.18	45.01

Table 1. Elemental composition $(\mu g/m^3)$ of atmospheric dusts deposited on canopy foliage

Correlation study is a convenient tool for source identification of the elemental composition in the atmospheric dusts deposited on canopy foliage. A correlation matrix has been presented in Table 2. Based on the correlation, different groups of trace elements could be discerned. They are Ni, Cd, Rb, Ag and group; Cu, Zn, As group; Ga, Ba, Sn, Sb, Pb group. Based on the industrial and other anthropogenic sources Ni, Cd, Rb, Ag appears to have been contributed by the diesel exhaust, metallurgical operations and domestic combustions. Another group of Cu, Zn and As is mainly product of smelting operations and coal combustion in industrial and domestic sector. The other group consisting Pb, Sn, Sb, Ga and Ba and their close correlation signifies clearly influence of gasoline emission and industrial emission. The emissions from increasing numbers of vehicles and industries are causing concern to the city to its pollution potential. In general, elemental concentration is significantly higher in particulates deposited on leaves. This is due to prolong deposition of atmospheric dusts on canopy leaves. Some elemental concentrations are noticed higher while in others are low, this clearly demonstrate the variation of anthropogenic input. This has important implications on correlation coefficients of elemental concentration with other natural factors.

Table 2.	Correlation	matrix	of e	elemental	composition
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	Ni	Cu	Zn	As	Rb	Sr	Nb	Ag	Cd	Sn	Sb	Ba	Ce	Pb	Ga
Ni	1.00														
Cu	0.81	1.00													
Zn	0.00	-0.61	1.00												
As	0.31	0.26	0.26	1.00											
Rb	-0.66	-0.76	-0.05	-0.37	1.00										
Sr	-0.63	-0.36	0.03	0.27	0.39	1.00									
Nb	-0.17	0.00	0.44	0.31	0.19	0.67	1.00								
Ag	0.54	0.35	0.14	0.27	-0.38	-0.48	-0.30	1.00							
Cď	0.59	0.11	0.33	0.74	0.03	0.49	0.64	0.25	1.00						
Sn	-0.09	0.32	0.34	0.24	-0.15	0.46	0.65	-0.15	0.48	1.00					
Sb	-0.08	0.20	0.48	0.24	-0.03	0.46	0.76	0.00	0.50	0.91	1.00				
Ba	-0.06	0.22	0.24	0.06	0.05	0.41	0.74	0.03	0.46	0.83	0.90	1.00			
Ce	-0.47	-0.40	0.21	0.06	0.67	0.44	0.40	0.03	0.48	0.29	0.28	0.34	1.00		
Pb	-0.36	0.27	0.15	-0.04	-0.08	0.25	0.58	-0.13	0.07	0.71	0.81	0.85	0.06	1.00	
Ga	0.18	0.43	0.15	0.00	-0.13	0.13	0.56	-0.13	0.08	0.93	0.77	0.78	-0.04	0.93	1.00

4. CONCLUSION

This study aims to find out the elemental composition in urban atmospheric dusts deposited on canopy foliage and their possible source identification. The elemental composition of deposited dusts on canopy leaves is clearly affected by anthropogenic activities especially transport and industrial activities. Cu, Zn, Pb, Ba dominate the trace composition reaching abnormally high levels as high as 223.92 μ g/m³ Cu, 950.25 μ g/m³ Zn, 565.70 μ g/m³ Pb and 778.55 μ g/m³ Ba. Positive kurtosis values of Ni, Cu, Zn, As, Nb, Ag, Cd, Sb, Ba, Pb and Ga indicate deposition from variable emission pattern. However higher skewness values indicate an asymmetric distribution of most of the elements signifying a pronounced effect of the meteorological and source strength effects. The higher amount of elemental composition indicates high pollution level which may affect urban community.

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A COMPARATIVE STUDY OF HEAVY METAL CONCENTRATIONS IN ROAD DUSTS DEPOSITED AT THE INDUSTRIAL AREAS

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ABSTRACT

Industrial activities can significantly contribute to the pollution levels in the environment. This study focused on the investigation of the characteristics of heavy metal contamination in the road dusts deposited at the industrial areas of Ulsan city, Korea. 12 sampling sites in industrial complexes (IC), IC vicinity (residential area), typical residential area (downtown) and background area were selected for this study. The highest concentrations of the heavy metals in the road dusts were observed in the non-ferrous metallic IC areas followed by those in the petrochemical IC areas. The concentrations of heavy metals in the road dusts from the heavy industry zone were lower than those from the non-ferrous metallic IC areas. The concentrations of the heavy metals in the road dusts from the heavy industry zone were lower than those from the non-ferrous metallic IC areas. The concentrations of the heavy metals in the road dusts from the heavy metals in the road dusts from the IC vicinity located in rural environment (residential area) were much higher than those at the typical residential area located in the downtown area.

Keywords: road dusts, heavy metals, industrial complex, residential area, industrial emissions.

1. INTRODUCTION

Ulsan is a representative industrial city which has non-ferrous metallic, petrochemical, automobile and shipbuilding industrial complexes (IC). The rapid industrialization has put great pressure on the local environment. Industrial activities can significantly contribute to the pollution levels in the urban environment. Until recently there have been few attempts to determine the impact of industrial emissions on the quality of the Ulsan area in Korea. Road dust is the material that has been recognized as a significant source of heavy metals in the urban environments, especially in big cities (Charlesworth et al., 2003; Sezgin et al., 2003; Banerjee, 2002; Akhter, 1992). Concentrations of heavy metals in road dust are elevated. In Ulsan city, Korea many of the residential areas are built close to industrial areas, where they are subject to many potential pollution sources. Human health may be badly affected by the emitted heavy metals in the environment. Therefore, contamination by heavy metals associated with road dust is the major concern. However, the levels of heavy metal contaminations from road dust in Ulsan city have not been investigated yet. In this study, a survey was conducted in the metropolitan city of Ulsan, Korea to investigate the current conditions of heavy metal contamination in road dusts. The main objective of this work is to evaluate the variation in the contents of several heavy metals such as Cd, Cu, Pb, Zn and Ni in road dusts caused by the activities of industries.

2. METHODOLOGY

SAMPLE COLLECTION

To investigate the characteristics of heavy metal contamination in road dusts due to industrial activities, road dusts were collected from industrial areas of the metropolitan city of Ulsan, Korea as follows: 3 places in petrochemical IC, 3 places in non ferrous metallic IC, 3 places in heavy industry zone (motors and shipbuilding companies), 1 IC vicinity (residential area), 1 typical residential area and 1 background area. Road dust sampling was carried out in March, 2006. A vacuum cleaner attached VPF – 300 filter inside and run by an electrical generator was used for sampling of road dust. Road dusts were taken along the left and right side of the road. Then these samples were transferred to the plastic bags.

SAMPLE PREPARATION FOR ANALYSIS

In the laboratory, the collected sample was dried at room temperature for seven days. The road dust which has a diameter of above 2000 μ m was removed by using a 2 mm stainless steel sieve. The collected road dusts were divided into four categories of particle size: < 75 μ m, 75 – 180 μ m, 180 – 850 μ m, and 850 – 2000 μ m by sieving through the laboratory test sieves as follows: 850 μ m, 180 μ m, and 75 μ m. After that, the sieved samples were homogenize and stored in desiccator until extraction.

THE ANALYTICAL METHODS

The heavy metals in road dust were extracted by aqua regia extraction method. 3 grams of sample was extracted with 14.4 ml of the mixture of HNO_3 : HCl (1 : 3 v/v), and 15.6 ml of deionized water. Then the solutions were boiled at 70 0 C for 1 hour in the water bath. After filtering the extracted solution by using the Advantec 5B filter paper with 5 μ m in pore size and 110 mm in diameter, the concentrations of Cd, Cu, Pb, Zn, and Ni were analyzed by atomic absorption spectrometry (Varian - AA240).

3. RESULTS AND DISCUSSION

The average values of the pseudo-total concentrations in the road dust samples at non-ferrous metallic IC, petrochemical IC, and heavy industry zone for Cd were 115.30 μ g g⁻¹, 19.76 μ g g⁻¹, 6.19 μ g g⁻¹, respectively; for Cu were 701.77 μ g g⁻¹, 738.49 μ g g⁻¹, 517.41 μ g g⁻¹, respectively; for Pb were 1491.59 μ g g⁻¹, 894.91 μ g g⁻¹, 517.48 μ g g⁻¹, respectively; for Zn were 498.64 μ g g⁻¹, 480.05 μ g g⁻¹, 663.52 μ g g⁻¹, respectively; and for Ni were 241.00 μ g g⁻¹, 304.29 μ g g⁻¹, 196.64 μ g g⁻¹, respectively. The concentrations of heavy metals in the road dusts from three industrial areas were much higher than those from the background area (the pseudo-total concentrations for Cd, Cu, Pb, Zn and Ni were 2.51 μ g g⁻¹, 113.99 μ g g⁻¹, 229.60 μ g g⁻¹, 364.92 μ g g⁻¹, and 56.32 μ g g⁻¹). These values indicate that the analyzed road dusts have elevated concentrations of heavy metals.



Fig 1. Average concentrations of heavy metals with different particle size in road dust at industrial areas

The variation in the concentrations of the heavy metals in collected road dusts from the industrial areas is shown in Figure 1. The highest average concentrations of Cd and Pb in the road dusts were observed in the non-ferrous metallic IC areas followed by those in the petrochemical IC areas. On the contrary, the highest average concentrations of Cu and Ni in the road dusts were identified in the petrochemical IC areas followed by those in the non-ferrous metallic IC areas followed by those in the non-ferrous metallic IC areas. The concentrations of Cd, Cu, Pb and Ni in the road dusts from the heavy industry zone were much lower than those from the non-ferrous metallic IC and petrochemical IC areas. However, the concentration of Zn in the road dust at from the heavy industry zone was highest. The concentration of Zn in the road dust at the non-ferrous metallic IC was higher than that at the petrochemical IC. The difference among the concentrations of heavy metals in the road dusts from three industrial areas was caused by the characteristics of the industrial activities.

Considering the concentrations of heavy metals in four different size-fractions shows that the concentrations of heavy metals increased with the decrease of particle size. The reason is that the smaller size of road dusts have much higher surface areas which are deposited or coated by heavy metals released into the atmosphere than the larger size ones.

The concentrations of the heavy metals in the road dusts from the IC vicinity located in rural environment (residential area) were much higher than those at the typical residential area located in a downtown area. This fact is presented in figure 2. Also, the pseudo-total concentrations of heavy metals in the road dusts collected from the industrial areas were higher than those from the downtown or heavy traffic areas.



Fig 2. Concentrations of heavy metals in the road dusts at the residential areas

4. CONCLUSIONS

The highest levels of the concentrations of Cd, Cu, Pb, Zn and Ni were found in the road dusts at the industrial areas, followed by the IC vicinity area and the residential area in the metropolitan city of Ulsan, Korea. The concentrations of heavy metals increased with decreasing particle size. The emissions of industrial activities greatly contributed to the heavy metal accumulation in the road dusts, in particular, with the smaller size collected from the study areas.

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COMPARISON OF SIZE DISTRIBUTION CHARACTERISTICS OF PARTICULATE MATTER COLLECTED FROM INDUSTRIAL AREAS

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ABSTRACT

This study compared size distribution characteristics of air-borne particulate matter (PM) collected from two industrial sites with different activity types. The samplings sites were located in the central parts of a petrochemical industrial complex (IC) and a non-ferrous metal IC, respectively, in Ulsan, Korea. 10 daily PM samplings from each IC site were conducted using an ambient cascade impactor, which consists of eight steps for particle size separation, during a summer season of 2006. The average concentrations of PMs collected in the petrochemical IC area during the sampling periods were much higher than those in the non-ferrous IC area. The average fraction of $PM_{2.5}$ concentration in the petrochemical IC site was about 68% of PM_{10} concentration. However, the average $PM_{2.5}$ fraction out of PM_{10} concentration in the non-ferrous metal IC site was only about 43%. The difference in fractions of fine particles between two IC sites is caused by a difference in their activity types. The petrochemical IC activities which are mostly oil refining and chemical production can produce more fine particles than the non-ferrous metal IC activities which usually consist of transporting, smelting and processing of non-ferrous metals and their ores.

Keywords: particle size distribution, non-ferrous, petrochemical, industrial complex

1. INTRODUCTION

Human health problems associated with the exposure to particular matter (PM) have been mainly focused on size distribution, concentration, component and toxicity of PM. There are many reports that exposure to fine particulate matter, such as $PM_{2.5}$ or $PM_{1.0}$, is associated with an increase in respiratory disease and mortality rate of cardiovascular diseases (Greenwell et al., 2002; Abbey et al., 1999; Pope et al., 1995; Dockery et al., 1993). The recent US EPA report on air quality criteria for particulate matter has included that $PM_{1.0}$ could be used as the standard cutpoint of fine particles because of a strong relationship between $PM_{2.5}$ and to $PM_{1.0}$ levels (US EPA, 2004).

Ulsan is the largest industrial city which has a population of 1.1 million and the largest industrial complexes (ICs), including petrochemical IC, non-ferrous metal IC and mechanic and shipbuilding IC, in Korea. These many plants and industrial processes located in these industrial areas have produced a lot of PM. Significant amount of particles which have their origins of industrial activities have been transferred to urban areas and thus have deteriorated urban air quality (UAQ) of industrial city. Thus many general people who live in industrial cities have worried about industrial air pollution with industrial origins. In particular, the exposure to fine particles with industrial origins could be more toxic or worse to human health. However, the systematic studies which focus on characteristics of PM or exposure to PM in industrial IC areas have not been conducted yet in Ulsan. This work presents analysis on size distribution and concentration of PM collected from two IC areas, petrochemical and non-ferrous metal IC areas, in Ulsan.

2. METHODOLOGY

This study compared size distribution characteristics of air-borne particulate matter collected from two industrial sites with different activity types. The samplings sites were located in the central parts of a petrochemical IC and a non-ferrous metal IC, respectively, in Ulsan, Korea. Even though traffic density in

unit: ua/m³

the non-ferrous metal IC site was slightly higher than that in the petrochemical IC site, traffic volume of two sites were much lower than that in urban areas. The meteorological conditions at two sampling sites during the sampling periods were similar. 10 daily PM samplings from each IC site were conducted using an ambient cascade impactor, which consists of eight steps for particle size separation, during a summer season (early July to early September) of 2006. PM concentrations of eight factions were analyzed by a gravimetric analysis using an electronic balance which is able to detect a level of 0.01mg. The sampling filters were kept in a desiccator maintained at a conditioned room, with a relative humidity level of 50 ± 5 % and a temperature of 20 ± 2 °C, for 48 hours before measuring their weight before and after PM sampling.

3. RESULTS AND DISCUSSION

Table 1 compares characteristics on size distribution and concentration of PMs collected from the petrochemical IC area and the non-ferrous metal IC area during the summer sampling periods. The average concentrations of PMs in the petrochemical IC site were much higher than those in the non-ferrous IC site. The main industrial activities are oil refinery and petrochemical production in the petrochemical IC, while they are production and ore processing of non-ferrous metals and production of chemicals in the non-ferrous metal IC. Thus the difference in average PM concentrations would be due to the difference in activity types and levels between two IC areas. In addition, the difference in a geological location combined with meteorological conditions could greatly affect the PM concentrations in two sampling sites. Even though two sampling sites are located in the central parts of each IC and the meteorological conditions during the summer sampling periods were north-west and south-east series in the two sampling sites. Two sites are affected by their industrial emissions under the north series of winds. Under the east series of winds the petrochemical IC site is still affected by its industrial emissions, however, the non-ferrous IC site is not affected by its industrial emissions. The sea area is located in the east side of non-ferrous IC site and thus the industrial emissions are easily diluted by eastern series of winds.

								um	ι. μg/m
IC	Petrochemical IC Non-ferrous metal IC								
Size	AM	SD	Max	Min	Size	AM	SD	Max	Min
0~0.4	2.05	1.90	5.31	0.24	0~0.4	1.31	1.02	2.45	0.00
0.4~0.7	11.36	1.43	17.91	6.16	0.4~0.7	6.26	3.01	10.63	1.73
0.7~1.1	11.63	2.40	23.07	3.19	0.7~1.1	7.62	3.15	14.97	4.16
1.1~2.1	9.12	1.44	16.69	3.68	1.1~2.1	7.25	4.28	14.90	1.01
2.1~3.3	6.55	2.20	10.03	2.70	2.1~3.3	7.03	4.47	16.60	1.47
3.3~4.7	5.76	3.82	8.76	3.71	3.3~4.7	6.41	3.61	11.09	0.25
4.7~5.8	5.76	5.41	9.82	2.72	4.7~5.8	7.60	3.73	13.86	2.21
5.8~9	3.87	3.36	7.18	2.21	5.8~9	4.77	2.96	8.76	1.39
9~10	3.87	1.46	6.87	0.98	9~10	4.21	2.98	8.38	0.49
Total	57.92	13.74	76.42	39.34	Total	51.15	13.55	65.32	32.18

Table 1: Size distribution of particular matter collected from the industrial areas.

The highest mass fractions of PM from the petrochemical IC site were observed in the size range of 0.7 - 1.1and $0.4 - 0.7 \ \mu\text{m}$ followed by $1.1 - 2.1 \ \mu\text{m}$. However, the highest mass fraction of PM from the IC site was observed in the size range of 0.7 - 1.0 and $4.7 - 5.8 \ \mu\text{m}$ followed by $1.1 - 2.1 \ \mu\text{m}$. The average fraction of PM_{2.5} concentration in the petrochemical IC site was about 68% of PM₁₀ concentration. However, the average PM_{2.5} fraction out of PM₁₀ concentration in the non-ferrous metal IC site was only about 43% (Table 2). A mean mass (50% of the total mass) is in the range of $1.1 - 2.1 \ \mu\text{m}$ of the PMs in the petrochemical IC, while the mean mass of the PMs in the non-ferrous metal IC was located in the range of $2.1 - 3.3 \ \mu\text{m}$. Oil refinery and petrochemical production produce fine particles such as submicron sized particles or PM_{2.5}. Production and ore processing, such as transport, smelting and treatment, of non-ferrous metals, unloading of non-ferrous metal ore from ships, and production of chemicals in the non-ferrous metal IC produced larger sizes of PM as compared the activities in the petrochemical IC areas. Oil refining, incineration of industrial wastes, etc. were also a part of the metal IC activities. Therefore, the difference in fractions of fine particles between two IC sites is caused by a difference in their activity types.

Fraction	PM _{1.0} / PM ₁₀	PM _{2.5} / PM ₁₀	PM _{1.0} / PM _{2.5}
Petrochemical I.C	0.41 ± 0.05	0.68 ± 0.08	0.61 ± 0.04
Non-ferrous metal I.C	0.28 ± 0.09	0.43 ± 0.11	0.67 ± 0.14

Table 2: Ratios between PM concentrations in the industrial areas.

4. CONCLUSIONS

The average concentrations of PMs in the petrochemical IC site were much higher than those in the nonferrous IC site. This is because of the difference in industrial activity types and geological locations combined with directions of prevailing winds. The petrochemical IC activities, such as oil refining and chemical production, can produce more fine particles than the non-ferrous metal IC activities such as transporting, smelting and processing of non-ferrous metals and their ores.

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INVESTIGATION OF METAL CONCENTRATIONS WITHIN PM₁₀ PARTICLES USING TUNNEL SAMPLING TECHNIQUES

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ABSTRACT

Samples of particulate matter were calculated within a motorway tunnel in the UK during the winter of 2005 and 2006. Sampling periods consisted of 12 hour intervals (AM and PM) using High Volume, Dichotomous Stacked Filter Unit (DSFU) and Partisol samplers stationed at the tunnel entrance and exit. Mean PM_{10} fleet emission factors for both campaigns were calculated to be 36 mg/vkm and 28 mg/vkm using data from High Volume and DSFU samplers respectively. Using DSFU samples, mean $PM_{2.5}$ fleet emission factors for both campaigns was calculated as 14 mg/vkm. These emission factors may be elevated as they include sampling days in which de-icing grit was released within the tunnel. Metal concentrations determined from ICP-AES analysis of the High Volume filters showed good correlation between concentrations of Cu, Fe, Mn, Pb and Sb and traffic volume. Principal component analysis (PCA) of the PM_{10} metal concentration data identified three sources: exhaust, brake wear and road wear/dust.

1. INTRODUCTION

The need to improve our understanding of sources of airborne particulate matter in urban areas has been stimulated by two main factors. Firstly, city authorities are finding it difficult to reduce particulate matter concentrations to meet legislations set out within the 'First Air Quality Daughter Directive (1999/30/EC)'. Secondly, there are still an increasing number of research publications highlighting the link between particulate matter concentrations and human health effects (Pope, 2000). Therefore there is a greater need to understand the sources of these particles. Studies have estimated that over 80% of respirable PM₁₀ present in cities originates from road transport, (Gualtieri et al., 2005). These emissions were thought to be predominantly from the combustion of fuel, but researchers have now calculated that non-exhaust emission such as brake, tyre and road wear, as well as (re)suspension could provide a significant contribution to particulate matter concentrations (Boulter et al., 2005). Using street pollution modelling and emission factor data, Ketzel et al., (2005) calculated that non-exhaust emissions contributed 50-85% of the total PM₁₀ emissions depending on location. Currently there are no EU regulations relating to the control of non-exhaust emissions. This is partly due to the limited amount of information available regarding these sources. This research aims to investigate non-exhaust sources by examining metal concentrations within PM₁₀ collected within a motorway tunnel as part of a wider study involving inorganic and organic source markers.

2. METHODOLOGY

Sampling campaigns were carried out during November-December 2005 and 2006 within the Southbound ('B'Bore) of the Hatfield A1(M) Tunnel in Hatfield, Hertfordshire, UK (48,000 vehicles per weekday). The position of the sampling equipment and tunnel layout is shown in Figure 1. Samples were collected at the tunnel entrance site (38m from the tunnel entrance) and exit site (742m from the tunnel entrance) every 12 hours (7am, 7pm) for 5 weeks at a time.



Figure 1: Diagram illustrating the tunnel layout and sampling location inside the Hatfield Tunnel.

Particulate matter samples were collected using equipment described in Table 1. In total 120 samples were collected by each sampler per campaign. All PM_{10} , $PM_{2.5}$ and coarse concentrations were determined using gravimetric methods. The quartz fibre filter samples collected using high volume samplers were digested using

nitric and hydrofluoric acid and then analysed using ICP-AES (Perkin Elmer Optima 3300RL) to determine a number of metal concentrations within the particle samples collected (Warner et al., 2002). These concentrations were then used within principal component analysis to determine their sources. Samples of NIST standard reference material 1648 and 1633b were also analysed to verify extraction efficiency.

Equipment/ Location	Samples/Data	Final	Resulting Data	Purpose
	Obtained	Analysis		
High Volume	PM ₁₀ Samples	Gravimetric,	PM_{10}	PM ₁₀ used in emission factor
Samplers	(Quartz Fibre	ICP and	concentrations,	calculation. Composition
_	Filters)	GC/MS	particulate metal	data used with receptor
One at Entrance &			and organic	modelling.
Exit Site			concentrations	
DSFU Samplers	Coarse, PM ₁₀ and	Gravimetric	Coarse, PM ₁₀ &	To establish the fraction of
	PM _{2.5}		PM _{2.5}	Coarse, PM ₁₀ and PM _{2.5}
One at Entrance &	(Polycarbonate		concentrations.	concentrations.
Exit Site	Filters)			
Partisol Samplers	PM ₁₀ Samples	Gravimetric	PM_{10}	PM ₁₀ used in emission factor
(Campaign Two	(Zefluor Fibre	and ICP	concentrations,	calculation. Composition
Only)	Filters)		particulate metal	data used with receptor
One at Entrance &			concentrations	modelling.
Exit Site				
NOMAD	Meteorological	Data	Wind Speed and	Wind Speed used in
	Data	Collection	Direction,	emission factor calculation.
Exit Site			Temperature, RH,	
			Pressure	
Marksman 660 Traffic	Traffic Data	Data	Traffic Numbers	Traffic Volumes used to
Counter & Inductive		Collection	and Vehicle	calculate emission factors.
Loops inside the			Classification,	Establishes peak traffic
Tunnel				period times

Table 1: Equipment employed during the sampling campaigns and how the resulting data is used.

 PM_{10} Emission factors were calculated using incremented PM_{10} data (PM_{10} Exit - PM_{10} Entrance Concentrations) using Equation 1 (Weingartner et al., 1997):

$$EF_{PM_{10}} = \frac{(C_{exit} - C_{entrance}) v_{air} t A}{L N}$$
 Equation 1

Where:

 $EF_{PM10} = Emission Factor of PM_{10} (g/vkm)$ t = time duration of sampling (s) $C_{exit} = PM_{10}$ concentration at tunnel exit (g/m^3) $A = tunnel cross section <math>(m^2)$ $C_{entrance} = PM_{10}$ concentration at tunnel entrance (g/m^3) L = tunnel length (m)N = number of vehicles which passed the tunnel in the time interval (t) $v_{air} = velocity of the air (m/s)$

3. RESULTS AND DISCUSSION

During campaign one (winter 2005) there were a number of days when grit was applied to the road surface as part of the national winter maintenance programme. Table 2 shows the fleet emission factors calculated for PM_{10} , $PM_{2.5}$ and coarse size fractions for both campaigns using Equation.1. It can be clearly seen that the emission factors for PM_{10} and coarse fractions are much higher during campaign one. However, when the sampling periods containing gritting are removed, the emission factors decreases by up to 21%. $PM_{2.5}$ emission factors for both campaigns show little difference, as these particles are commonly thought to originate from exhaust emissions. The calculated PM_{10} emission factors correspond well to other mixed fleet emission factors calculated within Europe, which range from 12-209 mg/vkm (Boulter et al., 2005). However, it should be noted that the higher end of this concentration range include locations where studded tyres were used. Proceedings of the 6th International Conference on Urban Air Quality Limassol, Cyprus, 27-29 March 2007

Sampler	Fraction	Mean emission factors Campaign 1	Mean emission factors Campaign 2
High Volume	PM ₁₀	43.5	29.2
DSFU	PM ₁₀	34.9	21.9
	PM _{2.5}	13.6	13.7
	Coarse	21.0	8.4
Partisol	PM ₁₀	-	23.1
High Volume (- Grit Days)	PM ₁₀	37.9	29.2
DSFU (- Grit Days)	PM ₁₀	31.1	21.9
	PM _{2.5}	13.0	13.7
	Coarse	17.6	8.4

Table 2: Mean emission factors for campaign one and two with and without grit days (mg/vkm).

The correlation between the incremented concentrations of Fe (ng/m^3) and traffic volume can be clearly seen in figure 2. The clustering of data, due to the different traffic flow periods in which the samples were collected, is also observed. This cluster effect can also be seen in Figures 3 and 4, which show Cu and Sb incremented concentrations (ng/m^3) plotted against traffic volume respectively.



Figure 2: Fe concentrations against traffic volume



Figure 3: Cu concentrations against traffic volume Figure 4: Sb concentrations against traffic volume

Principal component analysis of metal concentrations within the PM_{10} samples collected during campaign two identified three sources. By examining the metal loadings from each source as shown in Table 3, factor one was determined as an exhaust source based on the high loadings of Mn, Pb, V and Zn, factor two was identified as brake wear owing to the high loadings of Cd, Cu and Sb and factor three was thought to be road wear and road dust combined as a result of the high loadings of Ba, K and Ni as well as moderate loading for elements found in the other two sources (Wåhlin et al., 2006)

4. CONCLUSIONS

This paper describes the results from two tunnel campaigns conducted during the winter of 2005 and 2006. Emission factors were calculated for PM_{10} and $PM_{2.5}$ and particle associated metal concentrations have been used to identify non-exhaust sources. The results show good agreement between the two campaigns, although the impact of de-icing gritting during winter 2005 can be clearly seen in the PM_{10} results. In the case of $PM_{2.5}$, the calculated results from both campaigns compare well with each other, giving mass emission factors for campaigns one and two as 13.6 and 13.7 mg/vkm respectively. This fine size fraction originates mostly from exhaust sources and therefore is barely affected by grit applications. Metal concentrations show good correlation

when plotted against traffic volume, confirming traffic as a source of the metal species. PCA identified three sources of PM_{10} ; exhaust, brake wear and road wear/dust. By analysing Partisol filter samples and carrying out organic analysis of the quartz fibre filters which can provide proven unique tracers for tyre wear and petrol and diesel exhaust, it is hoped that more definitive sources can be established (Table 3). This work is being continued to include organic source markers.

	U	U	
	Exhaust	Brake Wear	Road Wear/ Dust
Fe	.690	.577	.260
Cu	.612	.665	.324
Mn	.766	.506	.320
Cd	062	.788	159
Sb	.459	.714	.212
Pb	.689	.462	.196
Ni	.327	.539	.576
V	.695	.055	.197
Zn	.844	.171	.020
Ti	.767	.231	.192
Zr	.213	.578	.287
Ba	.000	.061	.839
Li	.556	.104	343
K	.162	.134	.883
Cr	.669	.412	.010
Eigenvalue	8.05	1.94	1.23
% of Variance	50.33	12.14	7.70

Table 3: Varimax normalised rotated factor loadings obtained using PCA

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CHEMICAL CHARACTERIZATION AND SEASONAL VARIATION OF THE IONIC COMPOSITION OF PM 1.0 AND PM2.5 AEROSOLS

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ABSTRACT

Although the number of the research studies, is still unclear which of the particulate matter parameter is the key to describe health impacts most adequately.

This work aims to investigate the ionic composition (Na⁺, Mg⁺², K⁺, Ca⁺², NH $_4^+$, NO $_3^-$, SO $_4^{-2}$, Cl⁻) of PM₁ and PM_{2.5}

and its seasonal variation in a suburban area of Athens (Marousi). Measurements were conducted during winter and summer 2005.

Average mass concentrations for both PM fractions reached higher values during wintertime probably due to the intense traffic emissions and the central heating during the specific period.

 SO_4^{-2} were identified as the main components of the two PM fractions during summer period and of PM_{2.5} during winter. Na⁺ was the dominant constitutive element for PM₁ mass during the cold days. The local sources and the prevailing meteorological conditions seemed to be responsible for the (alkaline/neutral/acidic) PM character as well as the formation

of SO $_4^{-2}$ and NO $_3^{-2}$ species.

Keywords: PM1, PM2.5, ionic composition, seasonal variation, meteorology

1. INTRODUCTION

During the last decades an increasing amount of evidence on the association between atmospheric aerosol particles and increased cardiovascular and respiratory morbidity and mortality has been obtained (Pakkanen et al., 2003). World Health Organization (WHO) has estimated that major episodic pollution events can increase the daily mortality rate significantly—as much as 20% for a PM increase of 200 mg/m³ (Choi et al., 2006). According to epidemiological studies, fine particles seem to have considerable impact on human health even at concentrations below the present air quality standards (Gomisceck et al., 2004) as they have an increased probability of deposition deeper in the respiratory tract into the alveolar region of the lungs (Lin et al., 2004).

The concentrations of PM as well as their chemical composition can vary significantly depending on the sources, the season, the meteorological conditions and the topography. The major components of fine particles and more specifically of $PM_{2.5}$ are considered to be sulfate, nitrate, ammonium, organic matter and elemental carbon (Karthikeyan et al., 2006, Lin 2002).

The aim of this study is to present the seasonal variations of the concentrations as well as the chemical composition of the PM_1 and $PM_{2.5}$ fractions. Additionally, the concentrations of both PM fractions are correlated with meteorological parameters (wind speed, temperature and relative humidity).

2. METHODOLOGY

Measurements were conducted at Marousi $(23^{\circ} 47)$ 14" geographical longitude, $38^{\circ} 01$ 51" geographical landitude), an urban area which is located northerly of Athens basin, at the Ministry of Rural Development and Food. This site is situated in close approximately (500m) with highly trafficked and frequently congested avenue of Kifissias and is included in the Air Quality Monitoring Network of Athens, which can provide hourly data for meteorological parameters and concentration of classical air pollutants (NO_X, O₃, SO₂, CO).

Two low-volume (2 Derenda (LVS3.1/PNS3.1-15)) controlled flow rate (2.3 m^3/h) samplers were used for the collection of PM during both seasons. Particles were collected on 47 mm Glass Fiber filters, which were protected in plastic filter holders before and after sampling. The effects of heating and cooling sources such as solar radiation and electrical apparatus were minimized. Daily sampling period lasted 24 h. The samplers were conditioned for at least twenty- four hours before use, in a weighing room with controlled temperature and relative humidity (T=20±1°C and RH=50±5%). The particle mass concentration determination was
conducted gravimetrically using an electronic microbalance with a resolution of $1\mu g$ (MX-5 Mettler Toledo) according to EN12341.

 $SO_4^{2^-}$, NO_3^- and Cl^- anions and Na^+ , K^+ , NH_4^+ , Mg^{2^+} and Ca^{2^+} cations concentrations were estimated, following the Ionic Chromatography Method. In particular, for the cations analysis a Waters system for ionic chromatography was used, while for the corresponding anions the system was a 761 Compact IC of Metrohm. The detection limits for anions and cations were 500 ppb and 100 ppb respectively.

3. RESULTS AND DISCUSSION

The mean concentration levels of $PM_{2.5}$ and PM_1 during both periods (winter and summer) did not exceed 26.3 µg/m³ and 19 µg/m³ respectively. Furthermore, the recorded $PM_{2.5}$ concentrations did not exceed the limit values set by U.S.E.P.A. on a daily basis. According the forthcoming E.U. $PM_{2.5}$ limit (25µg/m³) for adoption, five exceedences were recorded (4 in winter and 1 summer).

Despite the fact that limits have not yet been established for the PM_1 concentrations, the recorded concentrations for the specific PM fractions did not exceed those of other campaigns all over the world (Giugliano et al., 2005, Artinano et al., 2004, Vecchi et al., 2004, Gomiscek et al., 2004, Hauck et al., 2004, Lin et al., 2004, Pakkanen et al., 2003, Viana et al., 2003).

The highest mean concentrations for the two PM fractions occurred during wintertime. Specifically, winter average means of mass concentrations for PM₁ and PM_{2.5} reached 19.0 \pm 10.1 µg/m³ and 26.3 \pm 11.4 µg/m³ respectively, while the corresponding values during summer were 13.9 \pm 5.12 µg/m³ and 17.6 \pm 5.44 µg/m³. This could be attributed to the additional sources acting during winter, such as higher traffic, cold start of engines, density domestic heating (Tsitouridou et al., 2003), as well as to the prevailing meteorological conditions, such as inversion layers, low temperatures, strong winds (Grivas et al., 2004).

 $PM_{2.5}$ proved to be mainly composed of PM_1 during both experimental periods (72% during winter and 78% during summer). Both PM fractions were strongly correlated (R= 94%) during summer, while such a correlation was not observed with any meteorological parameter (wind speed, temperature, relative humidity).

Regarding the whole sampling period, SO_4^{-2} (57.7%) anions and Na⁺ (23.3%) cations prevailed (Table 1).

Table 1: Statistical characteristics of the ion species at PM fractions during both sampling periods

			Na ⁺	NH4 ⁺	\mathbf{K}^{+}	Mg ²⁺	Ca ²⁺	Cl	NO ³⁻	SO ₄ ²⁻
Winter (μg/m³)	$PM_{2.5}$	Avg	3.38				0.95	0.93	1.62	7.78
		Max	4.11				1.13	1.41	2.61	12.8
		Min	2.82				0.78	0.63	0.99	4.33
		St Dev	0.66				0.18	0.42	0.87	4.48
	PM_1	Avg	11.5		0.28	0.20	1.46	0.63	1.01	9.88
		Max	13.1		0.28	0.27	1.51	0.76	1.28	16.0
		Min	9.11		0.28	0.13	1.42	0.51	0.76	5.18
		St Dev	2.14			0.09	0.04	0.12	0.26	5.53
Summer (µg/m³)	$PM_{2.5}$	Avg	1.61	0.61	0.19	0.45	0.70	0.41	1.26	13.9
		Max	3.48	1.38	0.25	0.49	1.02	0.77	1.56	22.4
		Min	0.17	0.19	0.16	0.39	0.43	0.31	0.78	8.66
		St Dev	1.21	0.67	0.05	0.04	0.21	0.18	0.28	5.34
	PM_1	Avg	1.7	0.50	0.21	0.42	0.54	0.27	0.60	12.0
		Max	3.4	1.07	0.25	0.48	0.73	0.31	0.75	20.5
		Min	0.08	0.21	0.19	0.35	0.42	0.23	0.46	7.19
		St Dev	1.65	0.49	0.03	0.05	0.12	0.03	0.11	4.72

Taking into consideration both PM fractions, ions seemed to follow the $SO_4^{-2} > Na^+ > NO_3^{-2} > Ca^{+2} > NH_4^{+} > Cl^{-} > Mg^{+2} > K^+$ distribution.

From Figure 1, the seasonal character of the aerosol species becomes evident. The corresponding sulfates concentration values for cold and hot days reached $8.83\pm4.65 \ \mu\text{g/m}^3$ and $12.9\pm4.90 \ \mu\text{g/m}^3$ respectively. Sodium reached $7.46\pm4.68 \ \mu\text{g/m}^3$ during winter and $1.64\pm1.38 \ \mu\text{g/m}^3$ during summer.



 Na^+ proved to be the most important component of the PM mass concentration during wintertime (42.1%),

Figure 1a

Figure 1b

Figure 1: Ions distribution to the total PM mass during a) winter and b) summer period

while lower concentrations were detected in summer. Similar behaviour was found for Ca^{2+} , NO_3^- , Cl^- and K^+ . Ions NH_4^+ were detected only in summer while during this period SO_4^{-2} ions predominated (70.7%). The seasonal preference of NO_3^- concentration can be explained by the greater partitioning of nitrates in the aerosol phase during cold periods (Hueglin et al., 2005, Hu et al., 2002).

Regarding PM₁ ionic composition, sulfates (12.0±4.72 μ g/m³) and sodium (11.5±2.14 μ g/m³) were the dominant ions during summer and winter period respectively. Additionally, PM_{2.5} proved to be mainly composed of SO₄⁻² ions during both seasons (winter: 7.78±4.48 μ g/m³, summer: 13.9±5.34 μ g/m³).

The contribution of the ions to the two PM fractions varied between the two seasons, indicating different aerosol sources. A uniform distribution was observed for NO_3^- and Cl^- species ($PM_{2.5}$ > PM_1). Moreover, Na^+ , and K^+ presented the same distribution (PM_1 > $PM_{2.5}$) during both experimental periods.

The estimated ion balance, which is represented by the ratio cation/anion, proved the alkaline character of PM only for PM_1 and only during the cold days of sampling. In all other cases, the acidic character of PM predominated.

The equivalent ratio of fine to ultrafine particulate concentrations of NO₃⁻ demonstrated that the formation of fine particulates NO₃⁻ was favoured during both seasons. As far as SO₄⁻² ions are concerned, ultrafine PM

proved to predominate during wintertime. Finally, fine particles were responsible for the SO $_4^{-2}$ formation

during the hot days of the sampling period.

4. CONCLUSIONS

In this study, an attempt was made to assess experimentally the concentration and the chemical characterization of $PM_{2.5}$, PM_1 at an urban area of Athens. It was found that PM concentration as well as their composition presented temporal variations according to local sources and prevailing meteorological conditions. In general, the recorded concentration levels were not high and the traffic emissions seem to be the major contributor. The chemical analysis of PM demonstrated that ions Na⁺ (winter) and SO₄⁻² (summer) were the dominant species. Due to the greater partitioning of nitrates in the aerosol phase during winter, NO₃⁻ reached higher values.

A uniform distribution was observed for NO₃⁻ and Cl⁻ species (PM_{2.5}>PM₁). Moreover, Na⁺ and K⁺ presented the same distribution (PM₁>PM_{2.5}) throughout the whole experimental period. The alkaline character of PM₁ (only during winter) and the acidic character of PM_{2.5} were proved with an ion balance calculation. PM_{2.5}/PM₁ ratio proved that the atmospheric conditions favoured the formation of PM_{2.5} nitrates, during both seasons. As far as PM_{2.5} sulfate is concerned, its formation was favoured during summer. On the other hand, it was shown that winter conditions favoured the PM₁ sulfates formation.

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THE DUST UPTAKE CAPACITY OF *EUONYMUS JAPONICUS* THUNB. LEAF SURFACE AND CAPTURED PARTICLE MORPHOLOGY IN AIR POLLUTED CITY

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ABSTRACT

This investigation measured the amount of dust on the leaves surface of *Euonymus japonicus* Thunb. by sampling beside 4 main roads in Shijiazhuang, the typical air polluted city in northern China, with the result that the average dust uptake capacity of the leaf surface is $0.8614 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, and the maximal accumulative dust uptake capacity of single leaf was 11.6197 g·m⁻², attained in 15 days. The dust captured by the shrub leaves is more than the regional atmospheric dust fall amount by 34.7%, and this excessive part should be derived from the raised road dust and vehicle emission. The SEM images of particles on the leaf surface show that PM₁₀ can be captured efficiently by the plant and the leaf can hold very fine particles even undergone thorough rinsing treatment. This research claims that *Euonymus japonicus* Thunb. is suitable for atmospheric particulate reduction in street environment in the air polluted cities.

1. INTRODUCTION

Atmospheric particulate pollution is serious in China, especially in the northern cities. Relying on some natural processes to eliminate airborne particles may be the most effective environmental protection strategy for the polluted cities under current situations. Among those, dust uptake by plant leaf surface plays an important role (Free-Smith et al., 1997; Beckett et al., 1998; WHO, 2000). Therefore the capacity of dust uptake of different plants should be investigated. Usually, broadleaf plants are thought to possess more dust uptake capacity than ordinary shrub plants and conifer (Wang, et al., 2006). But in the temperate continent zone, defoliation of most kinds of broadleaf occurs every fall and winter – a period when the emission of particulate becomes stronger for the heating, so the evergreen shrub in streets acts as the dust uptake agent. Besides, the average height of the shrub in streets is around 1-1.5m, just near the pedestrian breath range, which also allows the shrub leaf become a good agent to study the relationship of particulate pollution and human healthy. *Euonymus japonicus* Thunb. (EJ for short) is a common evergreen shrub in northern China cities and almost planted along every main traffic road. The dust uptake capacity of this shrub leaves is still unclear. This paper will focus on the measurement of the capacity of dust uptake by the leaves of and discus the morphology of particulate captured on the leaf surface.

2. METHODOLOGY

Shijiazhuang city (38°03 N, 114°26 E) was chosen as the research area for its severe atmospheric particulate matter pollution. Along the 4 main traffic roads growing with EJ in the central part of Shijiazhuang city, leaf sampling sites were set in 3 places of each roadside. In every site, 10 mature leaves on the top of EJ were labeled as samples. All of the sampling was conducted under fine and windless weather after several dry days. First, sprayed the leaf surface by deionized water and dried it with clean tissue paper to make it ready to hold dust. 5 days later, collected the leaves back to lab, washed the leaves surface with deionized water thoroughly, dried and weighted the sullage to calculate the dust amount on the leaf. Meanwhile, the 10 washed leaves' area were measured and parts of the leaves were cut into small pieces of 1×1cm² and got ready for morphological detection on the scan electron microscope of model S-570.

3. RESULTS AND DISCUSSION

The five groups data of the 5-days sampling are shown in Table 1, from which it can be seen that the average dust uptake capacity of the EJ leaf surface in Shijiazhuang city is $0.8614 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ with varying range of $0.4604 - 1.1743 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ under fine and windless weather conditions, and the more vehicle traffic, the more dust captured on the leaves, which was consistent with former research (Prusty, et al., 2005).

Table 1. Dust uptake capacity of Euonymus japonicus Thunb. leaves growing along the street in Shijiazhuang (g·m ⁻²	$^{2} \cdot d^{-1}$
(The sample sites was sorted by the ordinary traffic)	

Somple site	The first	The second	The third	The fourth	The fifth	
Sample site	5-days	5-days	5-days	5-days	5-days	
Yuhua Road	1.1646	0.9872	0.8442	1.1743	0.8026	
Tiyu Avenue	0.9300	1.0074	0.7562	1.0014	0.8001	
Zhongshan Road	0.7497	0.9402	0.7843	1.0602	0.7972	
Yucai street	0.9219	0.8378	0.4604	0.5861	0.6228	
Average	0.9415	0.9431	0.7113	0.9555	0.7557	

There are three ways for particles depositing upon leaf surfaces: by sedimentation under the influence of gravity, by impaction under the influence of eddy currents and by deposition under the influence of precipitation (McCartney and Aylor, 1987), and dry deposit is dominant (Grants, et al., 2003). In this case, wet deposition is out of consideration for the sampling condition limits. Sedimentation by gravity and impaction by eddy currents are two main regimes for dust loading on the leaf surface. The local environment monitoring data demonstrates that regional ambient dust fall amount is 0.6393 g·m⁻²·d⁻¹, and this can be taken as the sediment part on the leaf surface if ignoring the sampling instrument differences. Thus, the excessive part of the dust amount on leaf to the ambient dust fall amount should be derived from vehicle emission by the eddy currents which accounts for 25.8% of the total dust uptake capacity of the leaf.

The continuing measuring of dust uptake capacity of same EJ leaves is shown in Fig. 1, in which the cumulative dust loading capacity column stops increase at the 15^{th} day and decrease a little at the 16^{th} day, demonstrating the maximum dust uptake capacity of single EJ leaf is 11.6197 g·m⁻² lasting no more than 15 days.



Fig. 1 Maximal dust uptake capacity of Euonymus japonicus Thunb. leaf in Shijiazhuang

The single particle morphology shown in Fig. 2(a) illustrates that most of the particle size is under 10 μ m with irregular shape, indicating the strong ability of EJ leaf to capture the suspending particulate matter. After thorough washing, there still remain particles on the leaf surface (Fig.2 b), with particle size less than 5 μ m, mostly less than 1 μ m, and more spheres. These remained fine particles seem destructive to the leaf surface cuticle with a patch of spot beneath them, though the whole organization of the plant works normally. Obviously, dust held by the leaf surface will not come into the atmosphere again but be carried into soil with falling and washing process.



Fig. 2 SEM images of particulates held by *Euonymus Japonicus T*hunb. leaves (a is for the sample just rinsed out once; b is for the sample of thorough rinse)

Compared the two images of Fig.1 (a and b), it can be found that rinse, simulating natural washing process (e.g. rain or snow), may diminish the size and alter the shape of particles held on the leaf surface, but can not eliminate all the particles. Meanwhile, washing process will help part of particle component dissolved, which probably cause the damage of leaf cuticle tissue by chemical reaction from the particle. Mechanical damage to the leaf surface by particle had been reported (Kulshreshtha, et al., 1994), so the particle shape character should arouse much attention. But in this research, no distinct mechanical wound had been found on the leaf surface. The chemical damage must be dominant.

4. CONLCUSION

The results of measurements on the leaf samples in Shijiazhuang city China, claim that the average dust uptake capacity of *Euonymus japonicus* Thunb. leaf surface is $0.8614 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, under temperate, windless weather conditions, 25.8% of the dust held in the leaf surface is derived from vehicle emission; and the maximum dust uptake capacity of single *Euonymus japonicus* Thunb. leaf surface is 11.6197 g·m⁻², attained within 15 days of continuous normal weathers. To keep the dust uptake capacity, the leaf surface are needed to be renewed. Water washing may not be the best method though it's convenient. The SEM images of two leaf surface samples exhibit thoroughly rinse to simulating natural rain wash process actually eliminate most particles of 5-10µm, but there still remain finer particles less than 5µm. What is more, repeat rinse may cause particle dissolved and the chemical reaction accompanying will probably injure the leaf surface cuticle to form a patch of spot beside the particle. Once the dust particle uptaken by the leaf, they are immobile and fall

into soil with the leaf or by rain washing. Though the suitable leaf surface renew methods are under further research, *Euonymus japonicus* Thunb. leaf surface is proved to be a good agent for the atmospheric particulate removal in air polluted cities.

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