AIR QUALITY IN CITIES INCLUDING MEGACITIES SESSIONS

AIR QUALITY AND URBAN CLIMATE INVESTIGATIONS IN THE MEGACITY OF BUENOS AIRES

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ASSESSMENT OF AIR QUALITY IN A DEVELOPING MEGACITY: RESULTS OF DIFFUSION TUBE MEASUREMENTS IN LAGOS, NIGERIA

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THE OXIDATION CAPACITY OF THE CITY AIR OF SANTIAGO, CHILE

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AMBIENT AIR QUALITY MEASUREMENTS IN DAKAR, SENEGAL

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CONCENTRATION RATES AND TRENDS OF ATMOSPHERIC ORGANIC POLLUTANTS IN THE ROME METROPOLITAN AREA

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THE INFLUENCE OF THE CITY OF ATHENS IN THE EVOLUTION OF THE SEA BREEZE FRONT

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AIR QUALITY IN MEGACITIES: RESULTS FROM VOLATILE ORGANIC COMPOUNDS MEASURED IN PARIS, BEIJING AND SANTIAGO DE CHILE

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AIR QUALITY IN AGGLOMERATIONS OF THE CZECH REPUBLIC AND TRENDS OF AIR POLLUTION BETWEEN 1996 AND 2005

Jana Prošková - Czech Hydrometeorological Institute

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AIR QUALITY AND URBAN CLIMATE INVESTIGATIONS IN THE MEGACITY OF BUENOS AIRES

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ABSTRACT

In this paper results of the project BARUCA – **B**uenos **A**ires **R**esearch in **U**rban **C**limate and **A**ir Pollution – will be presented. The project was established to get more knowledge about the air pollution situation in Buenos Aires and the existence of specific local flow systems in the urban atmosphere as well as the interaction of these flow systems on the dispersion of air pollutants, because not much is known up to now in this field. Besides that thermal stress caused by heat waves are subject of the investigations. To achieve the project objectives a combination of continuous measurements / samplings at 10 sites and random measurements on ground at 63 sites and vertical soundings with two tethered balloons are applied as well as modelling simulations. Air pollutants like particulate matter (PM) in the size range of 0.3 to 20 µm, PM_{10} and $PM_{2.5}$, nitrogen dioxide (NO_2), and volatile organic compounds (VOC) such as benzene, toluene etc are measured as well as meteorological parameters.

Keywords: PM_{10}, NO_2, benzene, heat waves

1. INTRODUCTION

1.1 Air pollution situation in Buenos Aires

Buenos Aires, the capital of Argentina, is situated at the delta of the Rio de la Plata. Buenos Aires city is a part of the metropolitan region of Buenos Aires which is the third biggest metropolis in Latin America with an approximate population of 13 million inhabitants and an area of 4,000 km^2. Buenos Aires city has a population of approximately 3 million inhabitants and an area of 203 km^2. Air pollution in Buenos Aires, like in most of the megacities in the world, is of major concern. An effective area covering monitoring of air pollution does not exist there up to now. The rapid increase of the individual traffic, the size of the agglomeration and lack of knowledge about the influence of numerous high buildings on the local circulation reflects a deficit of the implementation of environmental planning.

Buenos Aires city is under the influence of the coastal circulation and the subtropical-sub continental regional climate of the Pampa and also meteorological and topographical conditions which facilitate the dilution of the concentration of gaseous pollutants. The ventilation caused by the land-sea breeze system in the area of the Río de la Plata can crucially reduce unfavourable consequences caused by air pollutants and thermal stress. But the influence of the ventilation on the dispersion of air pollutants is not yet been quantitatively investigated in Buenos Aires. Particularly, information about the range, the vertical extension, and seasonal effect of this wind system is lacking. Within the resulting climatological conditions, the heat waves and the atmospheric pollution are outstanding, and both represent an important harm on the citizens' health, whereas the situation is not as severe as that of other Latin American megacities such as Mexico city, Santiago de Chile, or Sao Paulo [1].

NO_x, particulate matter and volatile organic compounds (VOC) are the main air pollutants in Buenos Aires caused by traffic as main source for air pollutants. The city traffic composes mainly of motorcars and public buses, which generally are not equipped with exhaust catalysts. There are also three power plants located at the side of the Rio de la Plata.

1.2 Objectives

The project BARUCA – **B**uenos **A**ires **R**esearch in **U**rban **C**limate and **A**ir Pollution – was established to get more knowledge about the air pollution situation in Buenos Aires and the existence of specific local flow systems in the urban atmosphere as well as the interaction of these flow systems on the dispersion of air pollutants. The purpose is to form the basis for an effective air pollution prevention management, which should be an important integral part for future city planning (see also Figure 1).

Three German and three Argentinean institutions cooperate in this project to reach the following specific project objectives:

- To get knowledge of the spatial distribution (horizontal and vertical) and temporal variation of air pollutants in Buenos Aires city.

- To understand the local flow systems like land-sea breeze and country wind systems and the influences of these local flow systems on the dispersion of air pollutants.
- To get knowledge of the spatial distribution and temporal variation of the temperature especially during heat waves in order to investigate thermal stress.

2. METHODOLOGY

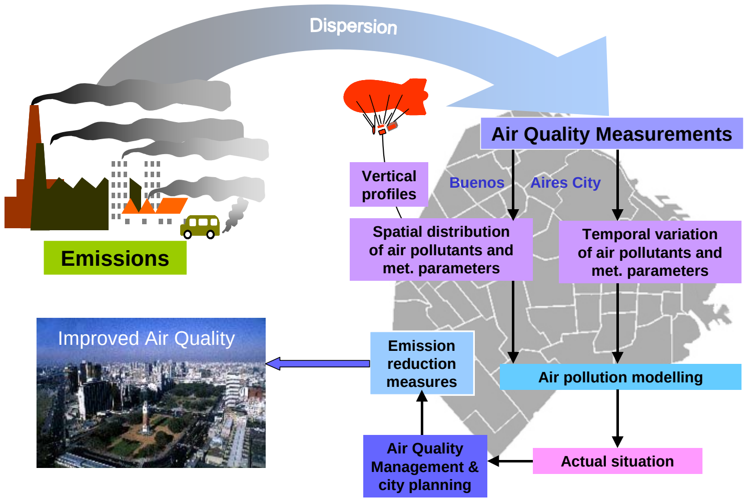


Figure 1: Project strategy applied in BARUCA project to determine the air pollution situation

To achieve the project objectives a combination of continuous measurements / samplings at 10 sites and random measurements on ground at 63 sites and vertical soundings with two tethered balloons are applied. Air pollutants like particulate matter (PM) in the size range of 0.3 to 20 µm, PM_{10} and $PM_{2.5}$, nitrogen dioxide (NO_2), and volatile organic compounds (VOC) such as benzene, toluene etc are measured as well as meteorological parameters. The measurement height of the tethered balloons is 400 to 1000 m above ground. The measurement period is 12 months starting from June 2006.

Finally air pollution modelling will complete the lacking information of the actual air pollution situation in Buenos Aires. This will be the basis for an effective air quality management and city planning for Buenos Aires as well as for emission reduction scenarios and emission reduction management in order to improve the air quality of the city.

3. RESULTS AND DISCUSSION

3.1 Spatial variation of the NO_2 and benzene concentrations

The mean concentration of NO_2 ranges from 31 µg/m^3 to 95 µg/m^3 (Figure 2, left side) in the autumn and winter period from March to September 2006. The lowest concentrations were observed at the rural background station INTA Castelar and at Costanera Sur (site no. G62 in Figure 3), close to the Rio de la Plata. The highest concentration was found at the traffic site Universidad de Flores (site no. G67). As the ranges of the confidence-interval show, the temporal variation is much lower than the spatial variation. In conclusion, the local conditions, especially the traffic but also the ventilation, have more influence on the NO_2 concentration than meteorological conditions.

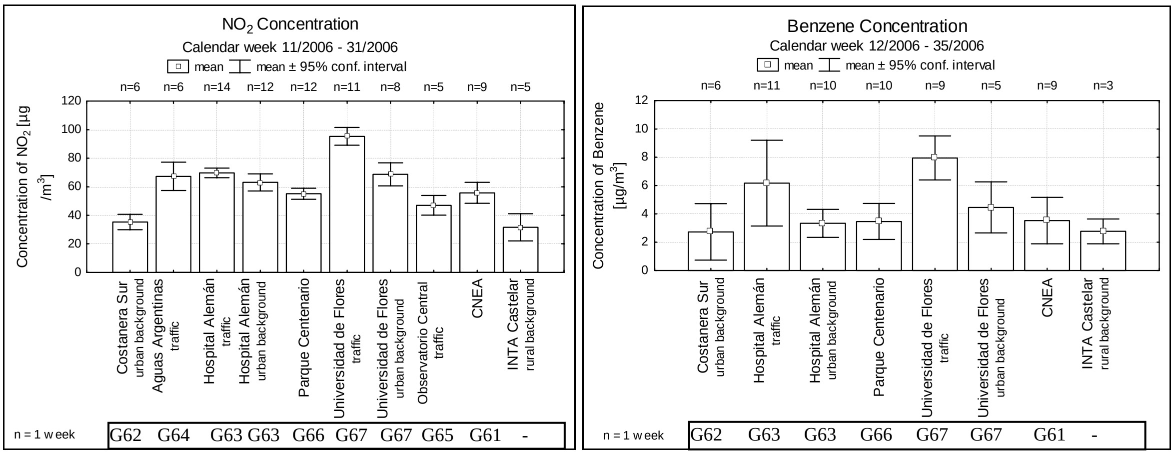


Figure 2: Spatial variation of the NO_2 (left side: 10 sites) and benzene (right side: 8 sites) concentrations in Buenos Aires City in the time period of March to September 2006.

The mean concentration of benzene ranges from 3 µg/m^3 to 8 µg/m^3 (Figure 2, right side). The lowest concentrations were found at the rural background station INTA Castelar and at Costanera Sur (site no. G62). The highest concentration was found at the traffic site Universidad de Flores, like observed for NO_2. Different from NO_2 the spatial variation is lower. However an influence of traffic is distinguishable. The temporal variations, expressed by the ranges of the confidential-interval, is much higher as found for NO_2. So the concentration of benzene seems to be influenced by meteorological conditions as well.

3.2 Spatial variation of the PM_{10} concentrations

Figure 3 show a preliminary (measurements are still performed) evaluation of the results of the grid measurements (according the procedure described in TA Luft 86 [2]) performed during the period from June 2006 to February 2007. The results for each grid area on the map were obtained by calculation of the arithmetical mean value of the measurements of the four corners (grid points) of the area. The concentrations of PM_{10} are in the range between 40 - 100 µg/m^3. The high concentrations were obtained on areas with high traffic incidence. The lowest concentrations were observed in areas with low traffic incidence (mainly residential areas). No conclusions can be made yet concerning if these concentrations are exceeding the national limit value for $PM_{2.5}$ (15 µg/m^3 in 1 year) and PM_{10} (50 µg/m^3 in 1 year) because of ongoing measurements, but most probably the PM concentrations will exceed the national limit values at some measurement sites.

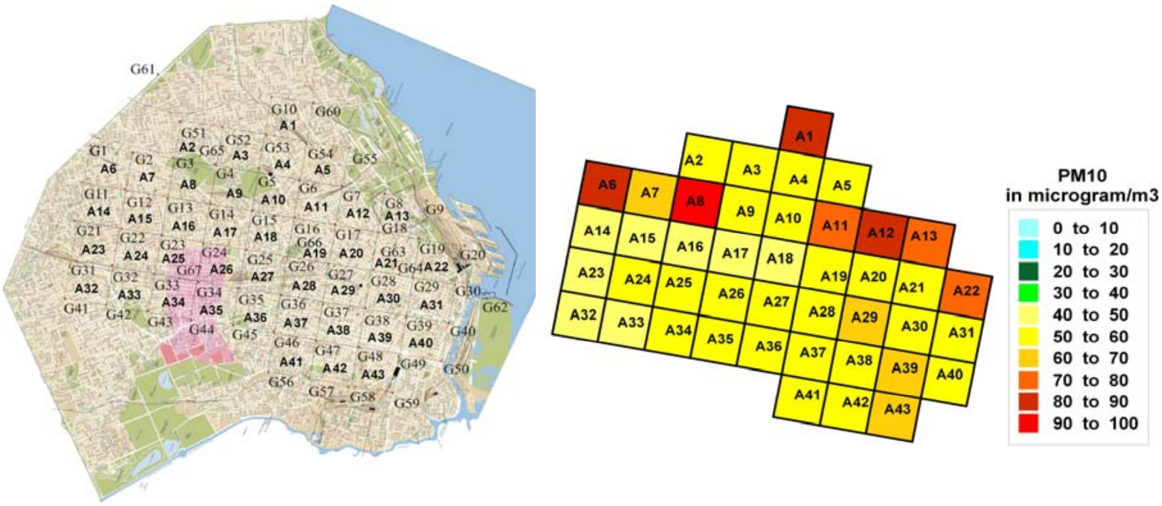
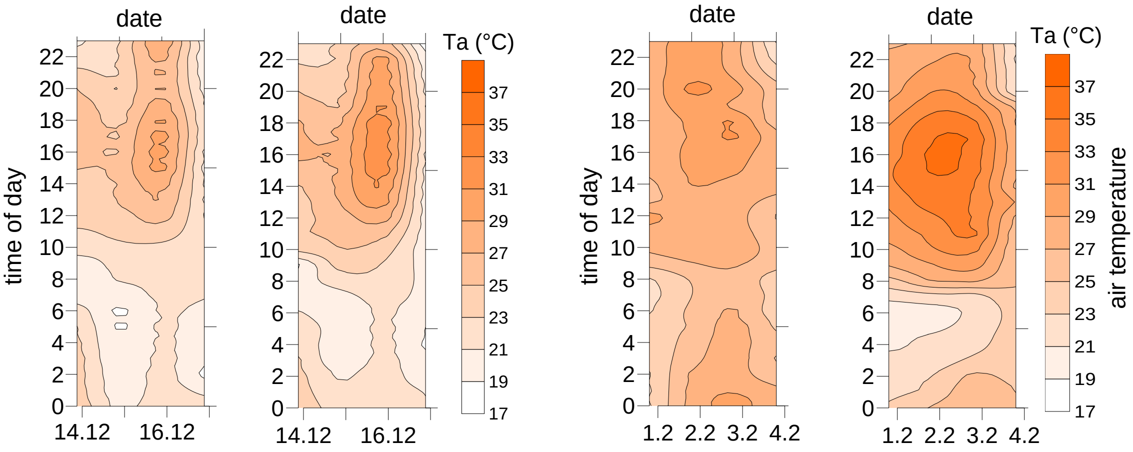


Figure 3: Preliminary results of grid measurements for PM_{10} for the time period from June 2006 to February 2007

3.3 Investigations on thermal stress in Buenos Aires City

Climatic conditions like hot summers with occasional heat waves and high values of relative humidity and solar radiation affect seriously the health and well-being of the population. Two different stations, one situated near the coast of the Rio de la Plata (Costanera Sur, G62), the other in the city centre (Observatorio



Costanera Sur G62 Observatorio Central G65 Costanera Sur G62 Observatorio Central G65

Figure 4: Comparison of air temperatures (Ta) during two heat waves in December 2006 (left side) and February 2007 (right side) at a coastal station (Costanera Sur G62) and a station in the city centre (Observatorio Central G65) in Buenos Aires City.

Central G65), were compared to each other, regarding the air temperatures measured during two periods of heat, in late spring (December 2006) and in summer (February 2007). The results (Figure 4) show clear differences between the two sites. In both periods wind and the water of the Rio de la Plata attenuated the extremes in the coastal area whereas the city itself was affected by much higher temperatures during day- and night-time and over a longer period.

Data of building height, building density as well as vegetation, together with personal and meteorological data was used as model input (model used: RayMan Pro [4]) in order to determine the perception of heat in a residential area with one-family houses of 2-3 floors, narrow streets and some trees situated near the Observatorio Central G65.

The model results are shown in Fig. 5. During both periods very high values of Physiologically Equivalent Temperature (PET), a thermal index, were detected [3]. In December 2006 it lasted only one day (16th) whereas in February 2007 the heat wave persisted during several days. Table 1 shows the relative frequency of modelled hourly values of PET in February 2007, separated in daytime (8 a.m. till 8 p.m.) and night time (9 p.m. till 7 a.m.). The high percentage of hours with strong and extreme heat stress not only affected gravely the health of the population during daytime but disturbed as well the nocturnal recovery.

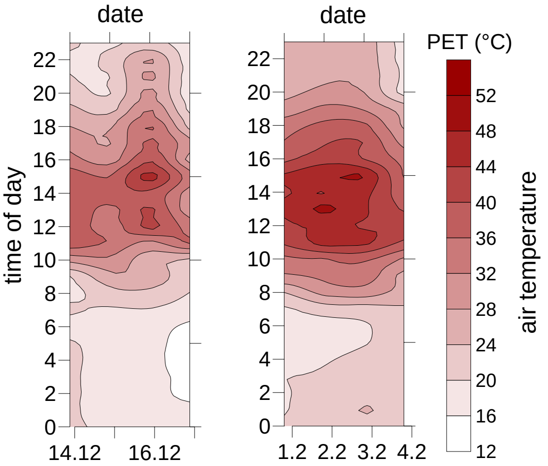


Figure 5: Physiologically Equivalent Temperature (PET) in December 2006 and February 2007 at a residential area in the city of Buenos Aires.

Table 1: Relative frequency of different grades of thermal stress during day- and night-time in February 2007, from 1st till 4th in Buenos Aires City (percentage of hours).

Thermal stress	**rel. frequency February 2007 DAY**	**rel. frequency February 2007 NIGHT**
slight cold	2 %	5 %
no stress	0 %	64 %
slight heat	13 %	32 %
moderate heat	27 %	0 %
strong heat	27 %	0 %
extreme heat	31 %	0 %

Further investigations will concentrate on several, differently structured residential, commercial and recreation areas all over the city in order to detect micro-spatial differences.

4. CONCLUSIONS

First results of the project BARUCA showed varying concentrations within the city. Lower concentrations near the coast of the Rio de la Plata and in the urban background and higher concentrations within the city. The highest concentrations were measured at sites highly influenced by traffic. The mean concentration of NO_2 ranged from 31 µg/m^3 to 95 µg/m^3 within the considered time period. The mean concentration of benzene ranged from 3 µg/m^3 to 8 µg/m^3 and PM_{10} concentrations between 40 and 100 µg/m^3 were determined. A combination of temperature measurements and the application of a simulation model is used to investigate thermal stress. During a heat wave situation in February 2007 thermal stress was determined for a specific residential area in Buenos Aires with a frequency of 98 % during day-time and 32 % during night-time.

5. ACKNOWLEDGEMENTS

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ASSESSMENT OF AIR QUALITY IN A DEVELOPING MEGACITY: RESULTS OF DIFFUSION TUBE MEASUREMENTS IN LAGOS, NIGERIA

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Lagos is of dominant economic importance in Africa, and by 2025, will be the world's third largest megacity with over 25 million inhabitants. In Lagos, air pollution is apparent even without measurements. Perceived poor air quality, health-related effects and the absence of air quality management strategies have necessitated assessment of air quality in Lagos. Diffusion tube samplers impregnated with triethanolamine were deployed at 26 sites in Lagos to measure ambient concentrations of nitrogen dioxide (NO_2) and sulphur dioxide (SO_2). Air mass trajectories over Lagos were obtained with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. High Performance Liquid Chromatography (HPLC) analysis of the diffusion tube samples showed that NO_2 ranged from 3.5 - 40.9 ppbv, SO_2 ranged from 1.6 - 307.0 ppbv, with means of 24 ppbv and 64 ppbv respectively. NO_2 and SO_2 levels exceeded the WHO and EU limits at most sites in Lagos.

1. INTRODUCTION

Lagos has a population of 14 million which is projected to grow to 25 million by 2025, making Lagos the world's third largest megacity with population densities in excess of 15,000 persons per km^2 according to United Nations estimates (United Nations, 2004). However, Lagos suffers many forms of environmental degradation associated with its population explosion. Intense air pollution can be recognised year-round in Lagos even without measurements by strong and widespread turbidity, bad smells and eye irritation. This can be attributed to various factors, but the chief of these is traffic-related emissions caused by the combination of many highly emitting vehicles and frequently congested road traffic. Many heavy duty vehicles are diesel-fuelled and emit plumes of black smoke consisting of soot. Many petrol engine cars emit blue smoke which is caused by un-burnt oil (Baumbach *et al.,* 1995). Moreover, Lagos also has several medium- and large-scale industries sited close to dwellings and large open incineration of waste is common. These lead to emissions of different types of pollutants, sulphur dioxide (SO_2), carbon monoxide (CO), oxides of nitrogen (NOx) and particulates, into the environment with little or no control measures.

In Lagos, health effects of high levels of these air pollutants cannot be overemphasised. Traffic density and congestion are very high, market places and commercial centres are often established around bus stops and many people are exposed to aromatic hydrocarbons, NOx, CO, SO_2, and particulate matter. Assessing the air quality in Lagos and the human health risk is very important as well as apportioning the sources of atmospheric pollution in the wake of integrated sustainable development and environmental concerns. At present, there is no national air quality strategy in Nigeria and no well-defined air quality management action plan for Lagos. Visitors and Lagos inhabitants recognise that the air quality in Lagos is poor, although there has not been any continuous or concerted effort to assess the level of air pollution, its health impact on the public and contributions to global environmental change. This study was aimed at assessing traffic-related air pollution in Lagos..

2. MATERIALS AND METHOD

Diffusion Tube Preparation, NO_2 and SO_2 Sampling

300 diffusion tubes were used in this study as described by Clemitshaw, (2004). The diffusion tubes were impregnated with 20% v/v triethanolamine (TEA) solution in water and deployed at 26 selected sampling sites in Lagos for simultaneous sampling of NO_2 and SO_2. Sampling locations were selected within the Lagos Metropolitan Area and characterised by high population density, high traffic volume and the presence of industries or open incinerators. Sampling points representing the general air quality in Lagos as described by Baumbach *et al.,* (1995) and two background locations were amongst the sites selected. 10 tubes, 8 replicates and 2 blanks, were deployed at each sampling site, affixed to road lampposts and similar structures at approximately 1.5 meters above ground level and as close to the road as possible. A co-locations study of the diffusion tubes was carried out with a chemiluminescence analyser at the Silwood Park Atmospheric Research Station (SPARS), Imperial College, Ascot to measure the performance of the diffusion tube set-up.

Meteorological and Air Mass Trajectory Data Gathering

Back and forward air mass trajectory data for Lagos were obtained using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) transport and dispersion model of the NOAA Air Resources Laboratory (ARL) available at http://www.arl.noaa.gov/ready/hysplit4.html. Air mass trajectory data and corresponding meteorological data were obtained for each day of the sampling period starting and ending at

12:00 UTC for Lagos at Latitude 6.45 and Longitude 3.39 and processed using Esri GIS software. Other meteorological data were obtained in archived form.

Sample Preparation and HPLC Analysis

Diffusion tubes were exposed for 4 weeks and the samples were extracted for analysis by adding 2.0 ml of deionised water and shaking for 10 minutes at 700 motions per minute (mpm) in a KS 125 Basic IKA Labortechnick (Staufen, Germany) shaker. Analyses of 1 ml of the aqueous extract for nitrate and sulphate was performed by High Performance Liquid Chromatography (HPLC) using standard techniques (with a Dionex 500 ion chromatography system, comprising of a GP40 pump, AS3500 autosampler and injection system, with a CD20 conductivity detector, Dionex AS11 analytical column and AG11 guard column. Elution was an isocratic elution using 4 mM NaOH, while analyte detection was by suppressed Ion Conductivity detection using a Dionex ASRS-Ultra suppressor). The elution profile was produced as a computer analysed chromatogram from which concentrations of analytes in μmol/litre were calculated.

Nitrogen dioxide ($NO_{2(g)}$) concentration in ppbv was calculated from the results of the HPLC analysis of nitrite ($NO_2^-{}_{(aq)}$) using the formula:

$$NO_{2(g)} = \frac{7.3099 \text{ x Volume of solution to dissolve TEA (2 ml) x } NO^{-}_{2(aq)} \text{ (ppbm)}}{\text{Time of exposure (in hours)}}$$

Sulphur dioxide ($SO_{2(g)}$) concentration in ppbv was calculated from the results of the HPLC analysis of sulphates ($SO_4^{2-}{}_{(aq)}$) using the formula:

$$SO_{2(g)} = \frac{10.75 \text{ x Volume of solution to dissolve TEA (2 ml) x } SO_4^{2-}{}_{(aq)} \text{ (ppbm)}}{\text{Time of exposure (in hours)}}$$

Quality assurance and quality control methods stated in DEFRA, (2003), and Lewné *et al.,* (2004) were used.

3. RESULTS AND DISCUSSION

Ambient Concentration of NO_2 and SO_2 in Lagos

Diffusion tube samplers have been used in several studies to determine the spatial distribution and mean concentrations of NO_2 and SO_2 in several cities and the technique is found to be suitable (Ferm and Rodhe, 1997, Krochmal and Kalina, 1996 and 1997, Hansen *et al.,* 2001, Plaisance *et al.,* 2002, Hamilton and Heal, 2004). NO_2 concentrations measured in Lagos range from 3.5 to 40.9 ppbv (Table 1) with values at 14 of the 21 sites greater than the World Health Organisation (WHO) and European Union (EU) limits of 21 ppbv (Figure 1). The mean ambient levels of SO_2 are clearly much higher than those of NO_2 for the same sites (Figure 1). The SO_2 concentration ranged from 1.6 to 307.0 ppbv. SO_2 levels at 19 of the 21 remaining study sites were greater than the WHO limit of 19 ppbv and 20 sites had values greater that the EU limit of 8 ppbv. This clearly indicates that SO_2 pollution may be a major concern in Lagos.

As expected, sites with the highest NO_2 and SO_2 levels are those associated with high traffic volume and/or situated close to open incinerators (Table 1). There are over 1,000 industries and open incinerator sites in Lagos. The sites with high NO_2 also have high SO_2 with the ‘hot spots’ (sites 1, 7, 11 and 12) clearly coinciding. This suggests that these sites are downwind of some pollution sources. NO_2 is produced from motor vehicle exhaust and stationary fuel combustion sources like electric utilities and industrial boilers as a by-product of high-temperature combustion (Breysse *et al.,* 2005), while SO_2 results from burning fossil fuels such as oil. Generally, the highest concentration of SO_2 is found near large industrial sources and power plants. Examining the location of these hotspots, open waste incinerators and landfills that are constantly set ablaze are found close by. The Cele bus stop and Ojota landfill are particularly notorious for pollution in Lagos and these sites have some of the highest concentrations of NO_2 and SO_2 measured in this study. Some of the roads with the highest traffic volume such as sites 3, 4 and 5 did not produce the highest pollutant concentration. According to AEA Technology (AEAT, 2003), the road with maximum traffic flow within the area may not produce the highest ambient concentrations if it is situated in an open area such as a dual carriageway. Higher concentrations may be observed at a less busy road with tall buildings on either side (the street canyon effect). This appears to be the case with the NO_2 and SO_2 concentrations at sites 3, 4, 5.

The mean levels of NO_2 and SO_2 in Lagos are calculated to be 24 ppbv and 64 ppbv respectively although measurements from roadside sites will only be representative over a very small area, as NO_2 concentrations close to sources vary considerably, even over short distances (AEAT, 2003). Early studies in London using diffusion tubes showed a sharp decline with distance from the road, with concentrations close to the local background beyond about 20 m from the edge of the road (Laxen and Noordally, 1987; Laxen *et al.,* 1988). However, the Lagos sites over which the concentration is averaged are not widely dispersed and traffic congestion is present over the entire Lagos Metropolitan Area.

Table 1. Mean NO_2 and SO_2 concentrations measured by diffusion tube sample analysis at 26 sites, in Lagos, Nigeria.

Site	Location	Mean NO_2 (ppbv)	Sampling precision (% RSD at 1 SD)	Mean SO_2 (ppbv)	Sampling precision (% RSD at 1 SD)	Estimated average daily traffic at each site
1	Obafemi Awolowo Way, Ikeja	**29.0**	5.3	**84.3**	43.8	27268
2	Allen roundabout, Ikeja	**-**	-			27268*
3	Motorway centre, Ojota	**27.7**	5.1	**79.2**	32.2	68168
4	Dumpsite, Ojota	**20.8**	5.6	**58.2**	34.1	68168
5	Ojota/Mile 12 exchange road	**23.4**	8.3	**45.4**	22.4	68168*
6	Maryland Roundabout	**23.0**	3.3	**41.8**	19.5	27000*
7	Oshodi-Agege motor road.	**22.3**	7.7	**83.9**	49.2	55,007
8	Oshodi-Agege motor road bridge.	**27.5**	4.8	**62.0**	29.1	49,000
9	Oshodi, under bridge.	**37.4**	42.0	**46.6**	42.4	30000*[2]
10	Oshodi bridge (on top)	**21.3**	0.8			50000
11	Oshodi-Mile 2 expressway, Cele	**40.9**	6.9	**307.0**	94.3	50000
12	400m from Cele b/stop opp Scoa	**28.9**	7.1	**91.0**	42.9	50000
13	Mile 2, towards Festac town	**29.1**	-	**38.9**		55000
14	Mile 2, on network bridge	**-**	-			55000
15	CMS-Marina bus stop	**22.6**	4.0	**45.5**	24.0	60,000
16	Ozumba Mbadiwe road, VI	**23.6**	4.3	**75.9**	37.8	30000
17	Ozumba Mbadiwe (law school)	**27.5**	6.3	**49.8**	16.0	30000
18	Alhaji Rewane Road	**20.6**	6.8	**19.7**	8.6	30000
19	3rd Mainland bridge, VI end	**14.3**	6.2	**48.0**	17.0	40000
20	3rd Mainland Emergency point.	**15.8**	4.7	**32.5**	7.5	40000
21	3rd Mainland bridge, behind Unilag	**11.8**	5.8	**29.0**	9.1	40000
22	Down 3rd mainland bridge, O. jnc	**-**	-			40000
23	Iyana Ipaja Garage	**-**	-			-
24	East end, Jakande Estate, Ipaja	**3.5**	0.8	**1.6**	1.1	Nil *[3]
25	33b Olu Akerele street, Ikeja	**15.6**	3.6	**15.6**	14.7	Nil *[4]
26	LASEPA, Alausa, Ikeja	**14.9**	5.7	**19.8**	10.7	12,000*

Mean NO_2 level = 24 ppbv, Mean SO_2 level = 64 ppbv

*(ppbv is parts per billion by volume, * Roundabout, *[2] Bus stop, *[3] Background site,*[4] within home)*

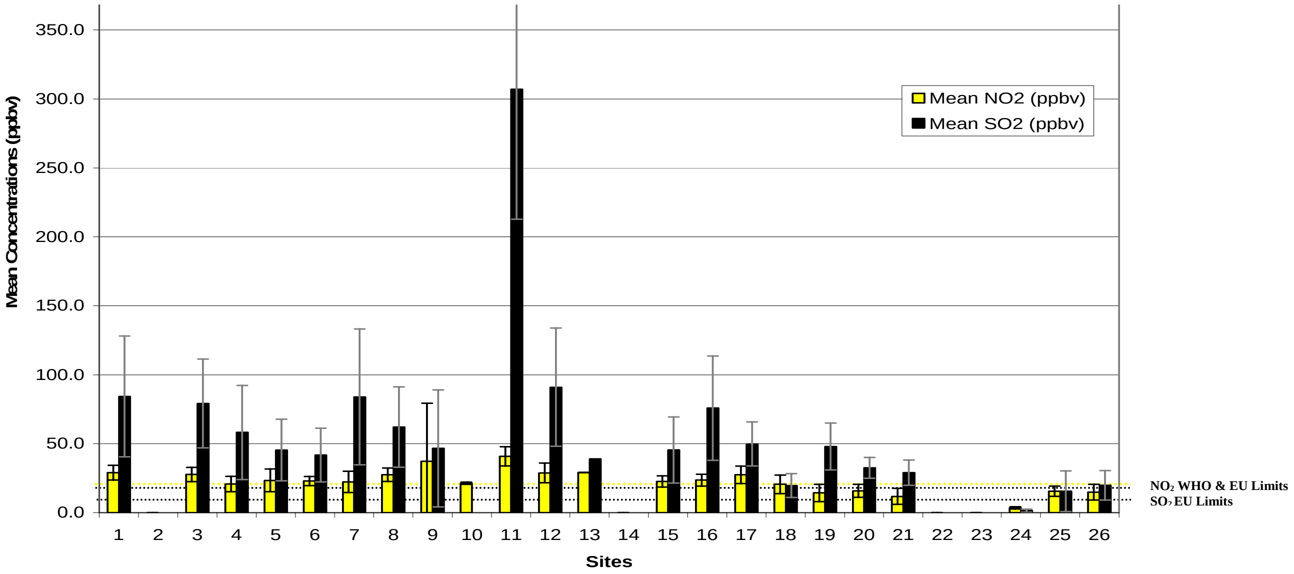

Figure 1. Ambient air concentration of NO_2 and SO_2 at various locations in Lagos compared with international standards.

The significance of the levels of roadside concentrations measured in Lagos is that many people spend considerably long hours around bus stops and along roadsides in Lagos as local markets and residences are indiscriminately situated very close to roadsides or bus stops (Baumbach *et al.*, 1995). Lagos has a poorly maintained vehicle fleet, and less stringent emission standards and the use of catalytic converters are not enforced. With less control over emissions from vehicles, pollution from motor vehicles is a significant threat to human health in Lagos. It is interesting to note that the mean concentration of NO_2 within the confines of a typical Lagos residence is the same as that of SO_2 (15.6 ppbv). Although, the standard deviation and errors associated with each measurement differs, it suggests that Lagos residents may be subjected to unhealthily high concentrations of air pollutants, especially SO_2. This is not surprising as industries and open incinerators are common all over the city. The burning of fossil fuel and wood to produce energy is also common place and most buildings are fenced. This can result in a build-up of pollutants within residences.

In a separate study, diffusion tube measurements were compared with a chemiluminescent monitor at SPARS and absolute bias of the diffusion tubes was found to be 2.7 ppbv while the accuracy (relative bias) was 24%.

4. CONCLUSION

Elevated levels of NO_2 and SO_2 pollution are of major concern in the megacity of Lagos and the urgent need for an air quality management strategy in Lagos is demonstrated in this study.

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THE OXIDATION CAPACITY OF THE CITY AIR OF SANTIAGO, CHILE

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ABSTRACT

Two field campaigns were performed in Santiago, Chile in order to study the oxidation capacity of a very polluted urban area. One focus was the hydroxyl (OH) radical budget, which has been evaluated during the late summer campaign from March 8-20, 2005. A simple quasi-stationary-state model has been used and constrained with simultaneously measured HONO, HCHO, O_3, CO, NO, NO_2, J_{O^1D}, J_{NO_2}, 20 alkenes and meteorological parameters. For the main OH radical precursors, namely HONO, HCHO and O_3, mixing ratios were found to be in the range 0.8-7 ppbV (HONO), 0.9-11 ppbV (HCHO) and 0-125 ppbV (O_3). HONO photolysis was shown to be the most important primary OH radical source comprising alone more than 50 % of the total production rate followed by alkenes ozonolysis (22 %) and photolysis of HCHO (17 %) and O_3 (9 %). Based on the experimental results a daytime source of HONO is proposed.

Keywords: *oxidation capacity, mega cities, nitrous acid, HONO, internal alkenes.*

INTRODUCTION

The hydroxyl radical (OH) is the primary oxidant in the atmosphere, responsible for the oxidation and removal of most natural and anthropogenic trace gases. In addition, the chemistry of the OH radical leads to the formation of harmful photooxidants, such as ozone and PAN. Thus, the identification and quantification of the different OH radical sources is of paramount importance.

During the last years it has been demonstrated that the contribution of nitrous acid (HONO) to the primary production of OH radicals:

$$\mathrm{HONO} + h\nu\ (\lambda < 400\mathrm{nm}) \rightarrow \mathrm{OH} + \mathrm{NO} \qquad (1),$$

has been underestimated (Ren et al., 2003, Kleffmann et al., 2005, Acker et al., 2006). High measured daytime concentrations point to an additional strong HONO source, for which several photochemical reactions have recently been proposed from laboratory studies (Zhou et al., 2003; George et al., 2005; Bejan et al., 2006; Stemmler et al., 2006). According to the high reported contribution of HONO to the OH radical budget, measurements of nitrous acid are of paramount importance to quantify the oxidation capacity of the atmosphere. Apart from a previous study (Rappenglück et al., 2000), which did not include the main OH radical source HONO, the work reported here is the first evaluation in the city of Santiago, Chile that take into account all main OH radical sources, namely the photolysis of HONO, formaldehyde (HCHO) and ozone (O_3) as well as the reaction of ozone with alkenes.

METHODOLOGY

The measurements were performed in the city of Santiago, Chile, which is located at -33.45° latitude and 70.67° longitude about 550 meters above sea level and surrounded by two mountain ranges, the Andes Mountains and the Cordillera de la Costa, respectively. The main measurement site was located in the third floor of the Physics Department of the University of Santiago, Chile (USACH).

The main measured parameters included HONO (using the high sensitive LOPAP technique, Kleffmann et al., 2006), HCHO (Hantzsch reaction based instrument), NO (chemiluminescence analyzer), NO_2 (DOAS-OPSIS optical system), photolysis frequencies J_{NO_2} and J_{O^1D} measured by filter radiometers. In addition, hydrocarbons (sampled on adsorption tubes and analyzed off-line by GC-FID), PAN (GC-ECD), O_3 (short-path UV absorption at $\lambda = 254$ nm), CO (IR absorption based monitor) were monitored. Meteorological data were obtained from P O'Higgins station, 1.8 km southeast the USACH measurement site.

Simple Quasi-Stationary State Model

For the purpose of the data evaluation, all the data were averaged over 10 min time intervals. The simultaneous data have been used in the model calculations using measured parameters and the latest recommended rate constants. The photolysis frequencies of HCHO and HONO were calculated by the measured J_{NO_2} and J_{O^1D} data (Holland et al., 2003). For the calculation of the net OH production by HONO photolysis (1) and the reverse reaction:

$$OH + NO + M \quad \rightarrow \quad HONO + M \qquad (2),$$

the OH radical concentration has to be known. However, since this quantity was not measured directly, OH was calculated by a steady-state assumption using the measured total OH-production rates and the OH-loss rates by reactions of OH with NO and NO_2, only. For the prevailing high NO_x conditions in present study ($VOC/NO_x \approx 5$) the net loss rate of the OH radical is mainly caused by reactions with NO_x (Ren et al., 2006).

OH-Production rate (P_{OH}):

$$P_{OH} = J_{HONO}\times[HONO] - k_2\times[NO]\times[OH] + 2\times J_{HCHO(rad)}\times[HCHO] + J_{O_3}\times[O_3]\times\Phi_{O+H_2O} + \Sigma(k_{O_3+Alkenes}\times[Alkene]\times\Phi_{OH})$$

Loss Rates (L_{OH}):

$$L_{OH} = k_{NO_2+OH}\times[NO_2]\times[OH] + k_{OH+NO}\times[NO]\times[OH]$$

OH Photo stationary state:

$$P_{OH} = L_{OH}$$

RESULTS AND DISCUSSIONS

The average day diurnal variations of the main trace gases are shown Fig 1. The average HONO concentration reaches a maximum of 3.7 ppbv at around 08:00 h during rush hour and a minimum of 1.5 ppbv around 17:00 h. A similar rush hour peak was also be observed for averaged NO data with a maximum of 180 ppbv, while the NO_2 maximum was shifted to later time caused by small direct emissions and formation by the reaction of NO with ozone, which is obviously only formed by photochemical reactions. From the rush hour peaks of HONO and NO_x a mean $HONO/NO_x$ ratio of 0.008 was estimated, which is in excellent agreement with direct tunnel measurements (Kurtenbach et al., 2001). HCHO and O_3 show typical diurnal variations with daytime maxima of 7 ppbv and 65 ppbv, respectively, demonstrating their photochemical formation. However, from the fast increase of HCHO in the early morning, when the O_x ($NO_2 + O_3$) increase was still small, a significant contribution from direct emissions was also identified.

The daytime HONO concentrations are significantly higher than in other polluted urban areas as New York or Milan, where the minimum mean daytime concentrations were 0.3-0.6 ppbv (Ren et al., 2003; Kleffmann et al, 2006). The high values for Santiago point to a very strong daytime source of HONO in the atmosphere. This additional source, for which different photochemical reactions have been proposed from laboratory studies, becomes obvious from the diurnal variation of the $HONO/NO_x$ ratio (see Fig. 2). While the nighttime behaviour, with a linear increase from 2-5 %, is very typical for urban conditions and can be explained by known heterogeneous conversion of NO_2 on ground surfaces (Kleffmann et al., 2005), the second daytime maximum, reaching almost 8 %, has never been observed in our previous urban studies in such a pronounced manner. This can be only explained by a very strong additional HONO source during daytime.

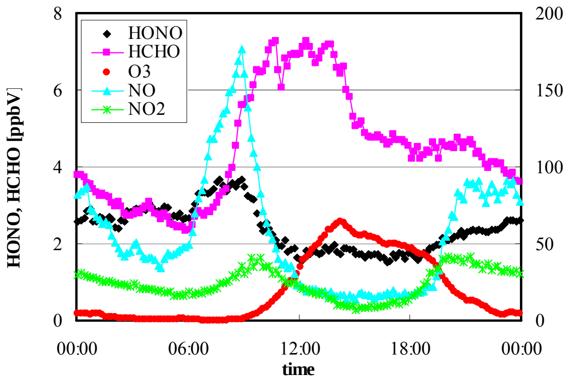


Fig. 1: Average of the diurnal variations.

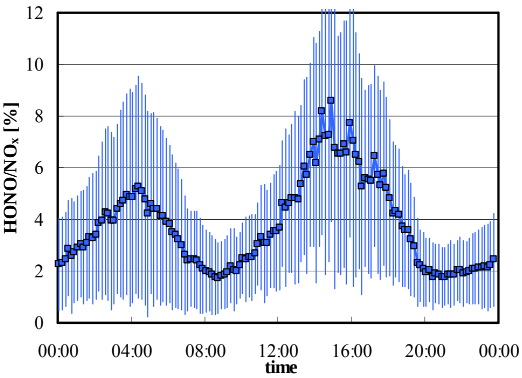


Fig. 2: Mean diurnal variation of the $HONO/NO_x$ ratio.

Production rates of OH radicals:

The averaged relative contributions of the main OH radical sources are shown in Fig. 3, while the averaged absolute diurnal contributions are shown in Fig. 4. HONO photolysis had by far the highest contribution of 52 % followed by alkene ozonolysis (22 %), HCHO photolysis (17 %) and ozone photolysis (9 %). The high relative contribution of HONO is in excellent agreement with other recent studies (Ren et al., 2003, Kleffmann et al, 2005, Acker et al., 2006), in which an integrated contribution of up to 56 % was reported. For the average day, mean and maximum OH production rates by HONO photolysis of 1.8 ppbv/h and 3.3 ppb/h have been determined, which are the highest absolute values ever reported and which demonstrate the unique situation in Santiago. While during almost all daytime the HONO contribution was higher than any other source, in the early evening the contribution by alkene ozonolysis exceeded the one by HONO. This is caused by the decreasing light intensity (reaction (1)), but remaining high ozone concentrations. In addition, during the night, alkene ozonolysis was the dominant OH radical source.

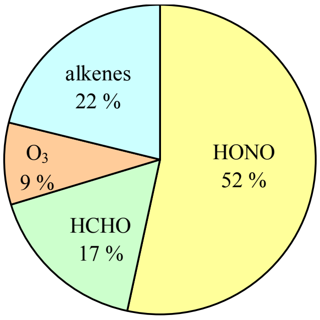


Fig. 3: Average OH production rates.

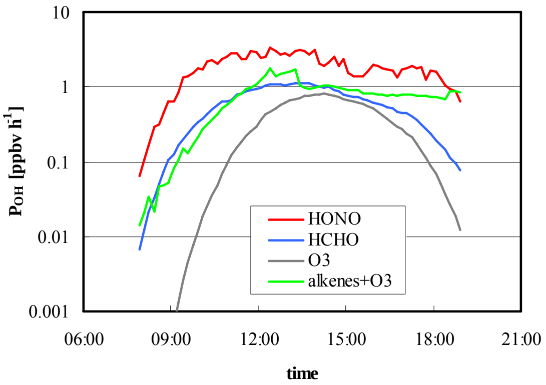


Fig. 4: Absolute average daytime OH-production rates.

HONO daytime source

Based on previous field and laboratory studies photochemical formation of HONO has been proposed to explain high measured daytime concentrations of HONO. Three mechanisms were identified recently, two of them are well correlated to J_{HONO} or J_{NO_2} (George et al., 2005; Bejan et al., 2006; Stemmler et al., 2006), while the photolysis of nitric acid (Zhou et al., 2003) would be better correlated to J_{O^1D}. This was tested from the experimental data by plotting the net production rate of OH radicals by HONO photolysis (reactions (1) and (2)) against J_{HONO} and J_{O^1D}. Both plots show that the daytime source is correlated with the light intensity, confirming former assumptions. However, since a better correlation was obtained when J_{HONO} was used, the photolysis of nitrate can be most probably excluded for the urban conditions of Santiago, whereas heterogeneous conversion of NO_2 on photosensitized organics and gas phase photolysis of nitro aromatic compounds may be of higher importance.

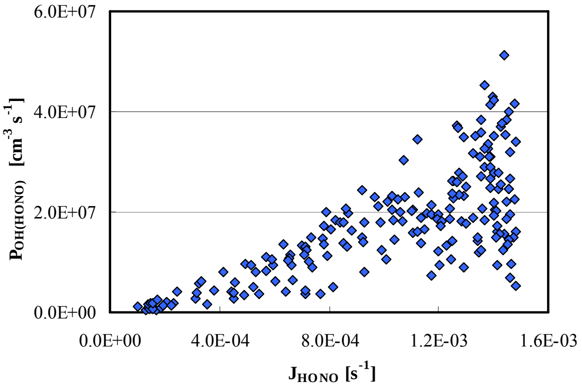


Fig. 5: Correlation of $P_{OH(HONO)}$ with J_{HONO}.

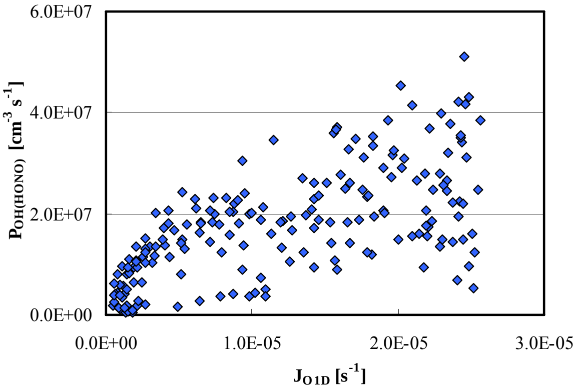


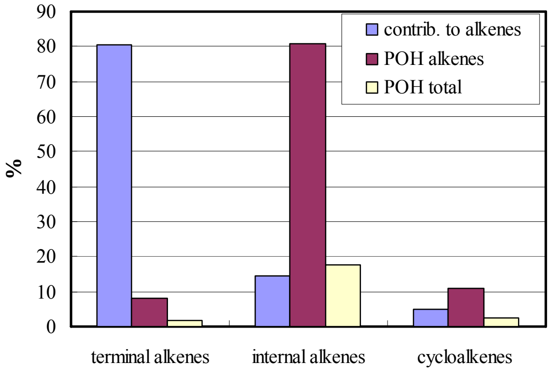
Fig. 6: Correlation of $P_{OH(HONO)}$ with J_{O^1D}.

Alkenes contributions:

The ozonolysis of alkenes was found to be the second most important OH radical source. Although their total concentrations are only 14 % of the total alkenes, internal alkenes contribute to the total OH radical production of alkenes by more than 80 % (Fig. 7). The order of alkenes OH production is:

***internal alkenes* > *cycloalkenes* > *terminal alkenes*.**

Among the internal alkenes, 2-methyl-2-butene and 2,3-dimethyl-2-butene had the highest contribution to the OH radical production of 35.7 % and 29.8 %, respectively (Fig. 8).



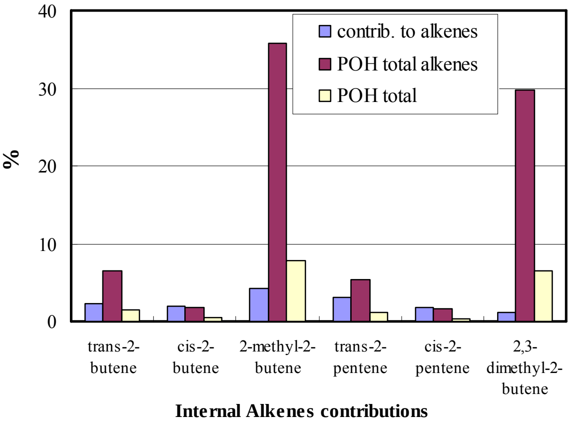


Fig.7: Contribution of the different alkenes

Fig.8: Contributions of the internal alkenes

CONCLUSION

The OH radical sources have been calculated for a late summer campaign in Santiago, Chile. HONO photolysis was found to be the most important OH radical source comprising alone more than 50 % of the total production rates. Based on the experimental data photochemical production of HONO was proposed, in agreement with recent laboratory studies.

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AMBIENT AIR QUALITY MEASUREMENTS IN DAKAR, SENEGAL

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ABSTRACT

In order to design an air quality monitoring programme for Dakar, a screening study to determine the present air quality in Dakar has been conducted. Passive samplers of NO_2, SO_2, VOC and O_3 were placed at about 50 selected sites. Moreover PM_{10}, $PM_{2,5}$ and CO were monitored in one heavily crowded street. This screening study shows that the major air pollution source in Dakar is traffic, although industry is also an important source in some areas. Generally the air quality in heavy trafficated areas and industrial areas is poor, even though the meteorological conditions are overall favourable for dispersion of air pollutants. For example, the measured daily averages of PM_{10} concentration were 2 to 7 times higher than the EU limit values, and the daily averages of $PM_{2,5}$ were also high. A large fraction of the $PM_{2.5}$ originates from combustion sources, while a large part of the PM_{10} coarse fraction is soil dust and sea salts.

1. INTRODUCTION

The Norwegian Institute for Air Research (NILU) is assisting the Senegalese authorities in establishing an Air Quality Management Centre with an air quality monitoring network for Dakar. As part of the present project it was necessary to gain knowledge of the present air quality situation in Dakar. Thus comprehensive measurements of air pollution were conducted between October 2005 and January 2006 in order to collect background information for designing a permanent air quality monitoring programme for Dakar. This screening study represents the first comprehensive investigation of the air quality in Dakar. The measurements data has been analysed and the main results are presented in this paper.

2. METHODOLOGY

2.1 Design of screening study

In order to design this screening study the areas where the pollution were assumed to have the highest impact were identified, based on simple modelling in conjunction with the location of the main emission sources and existing meteorological data (Guerreiro et al., 2005). Based on this knowledge, the measurement sites and compounds to be measured were selected in order to cover different microenvironments (e.g. road side, urban background, industrial area, regional background) and emissions.

The samplers for the selected compounds were located downwind from the emission sources in areas where impacts were expected. The screening study has been designed along five traverses, perpendicular to the prevailing wind direction: north and north-northeast. Passive samplers were located at 50 different locations in the city and in the surrounding suburban areas (Figure 1). SO_2 and NO_2 were measured at all sites, O_3 at 10 sites and VOC at 8 sites. To map the O_3 levels in Dakar the O_3 sites were selected based on three main criteria: 1) to measure the regional background concentration levels; 2) to identify the O_3 contribution to NO_2 generation in the city and 3) to evaluate the generation of O_3 in the urban area (Sivertsen et al., 2006).

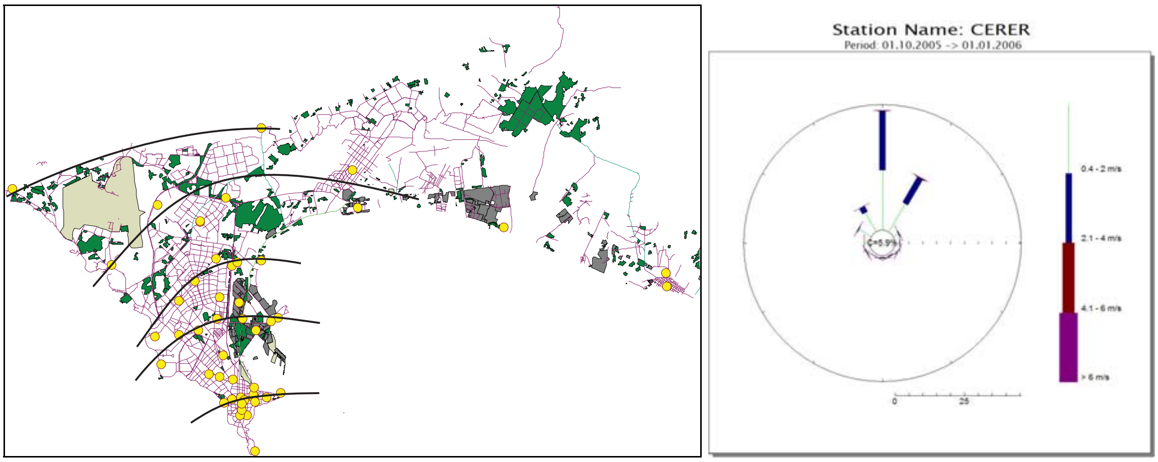

Figure 1: Geographical distribution of the sampling sites (yellow dots) along five traverses in urban and suburban area of Dakar (left) and calculated wind frequency distribution for 01.10.2005 to 01.01.2006, based on hourly wind measurements from the meteorological station at CERER, Dakar (right).

2.2 Instruments and samplers

Sensitive diffusion samplers for SO_2, NO_2 and O_3 in ambient air have been used (IVL, 2006). The sampling technique is based on the property of molecular diffusion of gases; the gas molecules diffuse into the sampler where they are quantitatively collected on an impregnated filter or an absorbent material with a solution specific to each pollutant measured. Thus a time-integrated concentration is achieved. The chemical analysis of the SO_2 and NO_2 samples were undertaken at NILU's laboratory applying ion chromatography and spectrophotometry, respectively. The ozone samples were analysed at the Swedish Environmental Research Institute (IVL).

The VOC samples are taken on standardised Perkin Elmer adsorption tubes, filled with Chromosorb or Tenax TA, and analysed at NILU using thermo desorption followed by GC-MS analysis.

The instrument used for daily monitoring PM_{10} and $PM_{2.5}$ was a sequential gravimetric sampler, of type SEQ47/50. The filters are weighed before and after exposure and the concentrations of PM_{10} and $PM_{2.5}$ were determined by NILU. A TSI Q-track has been used to measure hourly CO concentrations.

3. RESULTS AND DISCUSSION

The measurements were carried out in the period from October 2005 to January 2006. The passive sampling of SO_2 and NO_2 was performed during October, while the sampling of O_3 was performed in January. The samplers were exposed for 4 weeks. Passive samplers of VOC were exposed over 3 to 7 days in the beginning of October. The measurements of particulate matter (PM_{10} and $PM_{2.5}$) and CO in a busy street in the city centre were carried out from 5 October 2005 to 2 January 2006.

The daily concentrations of PM_{10} exceed the daily EU limit value (EC, 1999) every day of the sampling period (Figure 2). The PM_{10} values range from 52 to 338 μg/m^{3,} with an average value of 133 μg/m^3.

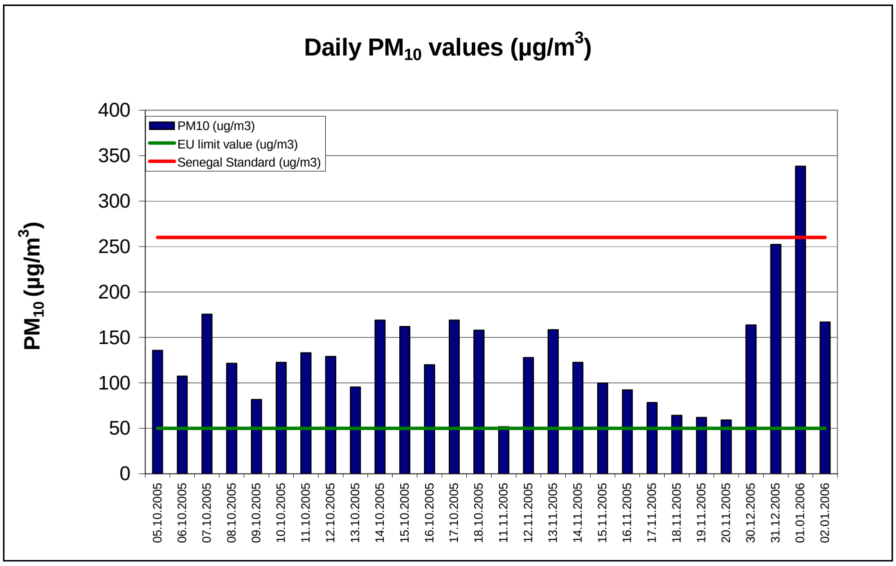

Figure 2: Daily concentrations of PM_{10} measured by sequential samplers at Rue Carnot from October 2005 to January 2006.

The $PM_{2.5}$ levels in Dakar were also high compared to concentration levels observed in other urban areas in the world (WHO, 2005); the average $PM_{2.5}$ concentration in the 4 weeks sampling period was 38 μg/m^3.

Some samples of PM_{10} and $PM_{2.5}$ were analysed further to provide knowledge on the chemical composition of the particulate matter in Dakar. The following compounds were analysed: 1) Trace elements such as lead (Pb), cadmium (Cd), vanadium (V) and arsenic (As), Copper (Cu), Zink (Zn), Chromium (Cr), Nickel (Ni), Cobalt (Co), Aluminium (Al); 2) Analysis of elemental carbon (EC) and organic carbon (OC); 3) Water-soluble components like sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), nitrate (NO_3), sulphate (SO_4), ammonium (NH_4) and chloride (Cl).

The analysis of trace elements identified no exceedances of EU limit and target values and WHO guideline values for any of the elements tested. The average content of the 10 trace elements analysed was 4 % and 2 % of the PM_{10} and $PM_{2.5}$ weight, respectively. Aluminium (Al) was the dominating element, which is an important component of mineral dust.

The elemental carbon/total carbon (EC/TC) ratios were on the average 0.36 for PM_{10} and 0.30 for $PM_{2.5}$ for the samplers analysed. As pointed out by Seinfeld and Pandis (1998), an EC/TC ratio ranging from 0.28 to 0.38 can be expected in areas where a mixture of emission from gasoline cars and diesel cars is the dominant source. Thus the fine particles in Dakar originate mainly from combustion sources, whose size and composition will lead to a greater impact on human health (Kaiser, 2000).

Sea salt and other water-soluble components were also expected to contribute to the PM concentrations in Dakar due to the proximity to the Atlantic Ocean and anthropogenic sources. The average percentage of water-soluble components was 18% for PM_{10} and 15% for $PM_{2.5}$. On the average, the contribution from NO_3, SO_4 and NH_4, which originate mainly from anthropogenic sources, is 4.7% for PM_{10} weight, while 12.9 % of PM_{10} are Na, K, Mg, Ca and Cl, which originate mainly from natural sources. For $PM_{2.5}$, on the other hand, the contribution from the anthropogenic and natural sources are both 7.3%. This result indicates that water-soluble components from natural sources contribute more to PM_{10} than anthropogenic sources. For water-soluble components in $PM_{2.5}$, however, the anthropogenic sources contribute as much as the natural sources.

The maximum NO_2 concentration measured with passive samplers in October 2005 was 56 µg/m^3 and the average concentration at all sampling sites was 27 µg/m^3 (Figure 3). Based on the assumption that the monthly averages are representative as long-term averages, exceedances of the annual NO_2 WHO guideline of 40 µg/m^3 (WHO, 2000) would occur at 7 traffic sites.

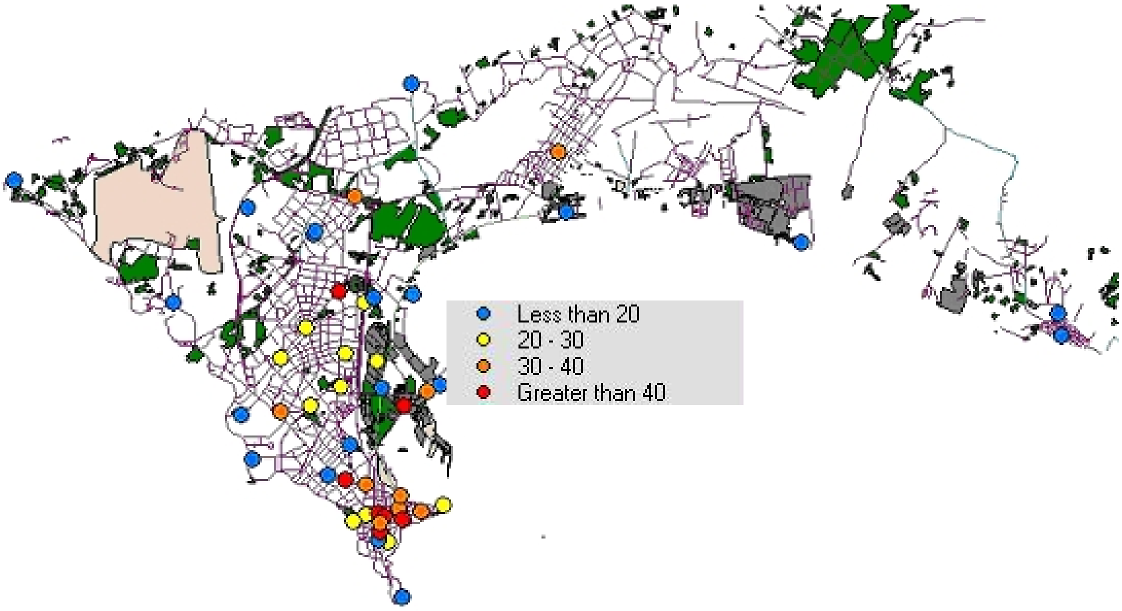

Figure 3: Geographical distribution of NO_2 concentrations (µg/m^3).

The highest measured O_3 concentrations (two weeks average) are above 60 µg/m^3 and were measured at the regional background sites. These concentrations are high and likely to exceed the 8 hours running average WHO guideline of 120 µg/m^3 (WHO, 2000). The lowest O_3 concentrations are measured in heavy traffic areas, close to the highway and in the city centre. The ratio between the measured concentration of O_3 at the regional site and the heavy traffic areas is 3.8, which indicates that the local NO emissions in the city centre consume a significant part of the regional O_3 in order to generate NO_2.

The maximum measured SO_2 concentration was 46 µg/m^3 (industrial area), which did not exceed the WHO guideline of 50 µg/m^3 (WHO, 2000). The average SO_2 concentration at all sampling sites was 13 µg/m^3.

The hourly values of CO (measured in a street canyon at about 5 meters above ground) indicate no exceedances of limit values. However, CO concentrations closer to the ground and the traffic are higher.

Short-term measurements of CO in traffic (at about 1 meter above ground) showed high concentrations during traffic jams, while cars are idling with high CO emission rates.
The Total Volatile Organic Component (TVOC) concentrations measured ranged from 31 µg/m^3 to 359 µg/m^3. The highest concentrations are measured at two industrial sites; near a refinery and near a road inside an industrial area. Benzene average concentrations over the sampling period were above 5 µg/m^3 at 3 of the 8 measurements sites, with the highest value of 20 µg/m^3 measured at the industrial site near the refinery. The annual EU limit value for benzene is 5 µg/m^3 (EC, 2000).

4. CONCLUSIONS

Measurements of air pollutants in Dakar, Senegal, have been presented. These measurements represent the first comprehensive investigation of the air quality in Dakar. This investigation shows that the major air pollution source in Dakar is traffic, although industry is also an important source in some areas. Generally the air quality in heavily trafficated areas and industrial areas is poor, even though the meteorological conditions are overall favourable for dispersion of air pollutants. The following results were obtained:

1) The measured daily averages of PM_{10} concentration were 2 to 7 times higher than the EU limit values (EC, 1999), and the daily averages of $PM_{2,5}$ were also high;
2) A large fraction of the $PM_{2.5}$ originates from combustion sources, while a large part of the PM_{10} coarse fraction is soil dust and sea salts;
3) The monthly average SO_2 concentrations did not exceed the annual WHO guideline (WHO, 2000);
4) The annual WHO guideline for NO_2 (WHO, 2000) would be exceeded at 7 traffic sites;
5) O_3 concentrations measured at the regional background sites are high and likely to exceed the 8 hours running average WHO guideline of 120 µg/m^3 (WHO, 2000).
6) Measured concentrations of benzene were higher that the annual EU limit value for benzene of 5 µg/m^3 (EC, 2000) at 3 of the 8 sites investigated.

5. ACKNOWLEDGEMENTS

This research is part of the project “Improvement of Air Quality in Dakar” (QADAK), financed by the Nordic development Fund, in which NILU is assisting the Conseil Exécutif des Transports Urbains de Dakar.

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GAS/PARTICLE PARTITIONING OF HALOACETIC ACIDS (HAAs) IN THE ATMOSPHERE OF ATHENS

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ABSTRACT

In this study the gas/particle partitioning of haloacetic acids (HAAs) in an urban area is studied. Six haloacetic acids (mono-, di- and tri- chloro- and bromo- acetic acid) were determined in 26 samples in both gas and particle phase. The total suspended particles (TSP) were collected using a high volume sampler and the gas phase samples were collected using a lab made denuder. The determination of HAAs was carried out using gas chromatography coupled with an ECD detector. Concentrations of the six haloacetic acids in particle phase ranged from 3.76 to 10.1 pg m^{-3}, whereas in the gas phase concentrations of the six HAAs ranged from 350 to 640 pg m^{-3}, where tribromoacetate (TBA) was more abundant. The concentration of the six haloacetic acids in the particle phase is increased during October and November, whereas in the gas phase it is increased during April, May and July. The influence of temperature, wind direction and relative humidity on the gas/particle partitioning constant, K_P, was also investigated.

1. INTRODUCTION

Haloacetic acids may arise from both anthropogenic and natural sources (Frank *et al*., 1995; Bakeas *et al*., 2003). They have become of great concern due to their widespread occurrence in the environment and the related ecotoxicological effects in drinking water and plants (Frank *et al*., 1995; Bakeas *et al*., 2003). The major sources of haloacetates that are currently under debate are (a) formation in the atmosphere by photochemical degradation of chlorinated solvents, (b) formation in the hydrosphere by reaction of active chlorine with dissolved organic matter (e.g. chlorination of drinking water), and (c) formation in soil by processes involving haloperoxidases. However, the relative importance of these sources is not known, and the proposed mechanisms of formation are not fully proven.

Since the p*K*a values of the acids are low, airborne haloacetates are expected to be associated with atmospheric condensed liquid water. An important input pathway of HAAs into the biosphere is washout by hydrometeors, and HAAs have been found in rainwater, snow, and cloud water (Frank *et al*., 1995; Bakeas *et al*., 2003). Furthermore, they are also present in surface waters of rivers and lakes, in seawater and in drinking and wastewaters treated with free chlorine for disinfection. Although there is much work on HAAs levels in a variety of media, there are surprisingly few data on HAAs in air (Frank *et al*., 1995; Bakeas *et al*., 2003; Martin *et al*., 2003).

This work investigates six HAAs in air both the gas and particle phase: mono- (MCA), di- (DCA) and tri-chloro (TCA) and mono- (MBA), di- (DBA) and tri-bromo acetic acid (TBA). To the best of our knowledge, this is the first report on HAAs gas/particle partitioning. Our aim was to investigate the gas/particle partitioning of those compounds and the factors affecting their gas/particle partitioning constant K_P.

2. METHODOLOGY

2.1 Sampling

The sampling site was on the roof of the building of the Ministry of the Environment (25 m height) at Patission Street, located near the center of Athens. Patission Street has a heavy traffic load with about 60,000 vehicles passing per day. The traffic consists mainly of light-duty gasoline engine motor vehicles. Particle phase sampling was carried out with a high-volume sampler (General Metal Works, USA) equipped with a holder for glass-fiber filters (25 cm x 20 cm, Whatman, UK). Sampling volume was 1008 m^3, collected within 24 h (0.7 m^3 min^{-1}). After sampling, glass-fiber filters were stored in glass containers at -40 °C until analysis, for no more than a week. Gas phase sampling was carried out using lab made glass denuders (500 mm x 8 mm). Three denuders were connected in series and were coated with a Na_2CO_3 solution in glycerol diluted with water (85:15). A low volume sampler was used to pump 2.5 L min^{-1} for 2 d. The sampling volume was 7.2 m^3. To account for contamination effects, field blanks were handled identically.

2.2 Sample Preparation

Before extraction, the filter samples were allowed to warm to room temperature (20 °C). The filters were cut in half, and each of the halves was further cut into small pieces (nearly 0.5 cm x 0.5 cm). The pieces of each half were extracted with 15 mL of deionised water in a sonicator bath for 2 h, a time selected according to recovery experiments with extraction times of 0.5, 1, and 2 h. The extracts were combined and derivatized to the relevant methyl esters. The denuders were extracted with 25 mL deionised water and the extract was derivatized to the relevant methyl esters (EPA, 2003).

2.3 GC Determination

GC analyses were performed on a gas chromatograph (model 3300, Varian Instruments, U.S.A.) equipped with an on-column injector and ECD (Model 02-1792-01); helium was used as carrier gas. Aliquots of 5 µL of the derivatized samples in MTBE were injected onto a deactivated fused-silica retention gap (8.0 m x 0.32 mm). Gas chromatographic separation was carried out on a fused-silica column coated with cyano(7%)-phenyl (7%)-methylsilicone (007-1701, 50 m x 0.32 mm, film thickness 1.0 µm; Quadrex, UK). The initial oven temperature was 45 °C (6 min) followed by a temperature program of 3 °C min^{-1} to 116 °C, 20 °C min^{-1} to 200°C, 2 min isothermal. Calibration was performed by spiking deionised water with a solution of HAAs, leading to calibration concentrations ranging from 0.5 to 1000 ng mL^{-1}, followed by sample preparation and GC/ECD analysis as described before**. Figure 1** shows a typical chromatograph for the determination of six haloacetic acids in gas phase.

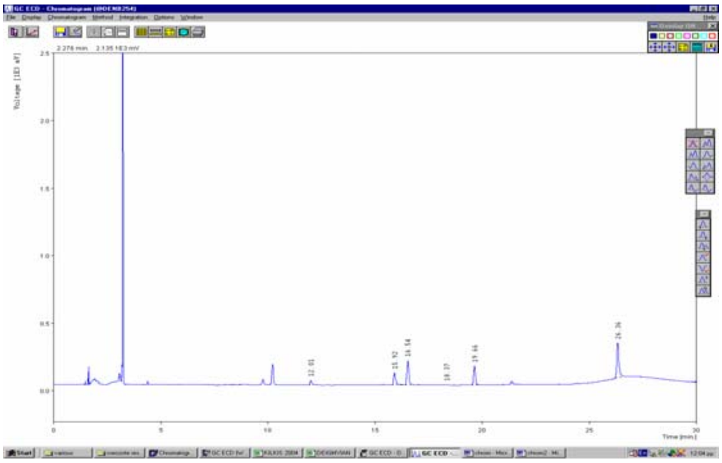

Figure 1. Typical chromatograph of gas phase sample for 6 Haloacetic Acids. Peak 1:MCA , 2:MBA , 3:DCA , 4:DBA, 5:TCA , 6:TBA

3. RESULTS AND DISCUSSION

3.1 Variations of HAAs concentrations

The arithmetic mean values of the studied compounds for the particle phase ranged from 3.76 to 10.1 pg m^{-3} and in the gas phase they ranged from 350 to 640 pg m^{-3}. In general, the gas phase concentration was higher than the particle phase showing a seasonal trend. In **Figures 2A** and **2B** the concentration variation for particle and gas phase is shown.

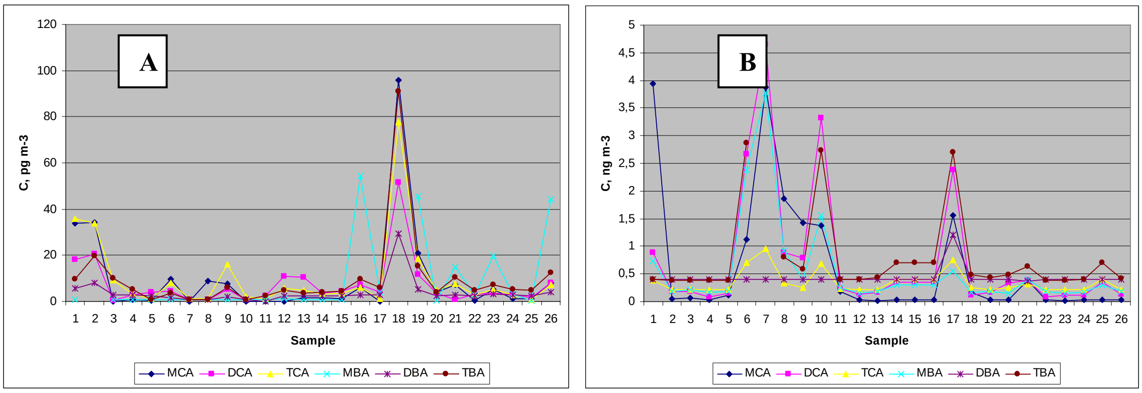

Figure 2. Variation of HAAs concentration in particle (A) and gas phase (B) during the period April-November 2005 (n=26)

From Figure 2A it is obvious that the HAAs concentration in the particle phase is increased during the winter and in the gas phase during the spring and summer. Calculating the parameter φ (Martin et al., 2003) it was shown that it was ranged from 0.009 to 0.080 depending on the acid. In some cases the φ value was up to 0.4 (MCA) showing that this acid was nearly equal distributed between the two phases.

3.2 Correlations of HAAs with other pollutants and metereological parameters

The correlation of the studied HAAs with the criteria pollutants showed, as previously mentioned (Bakeas *et al*., 2003), that the MCA is correlated with CO in particle phase.

During the study it was observed that some meteorological parameters affect the concentration of HAAs in both phases. Temperature was not correlated with HAAs concentration levels. Correlation with relative humidity was found to be significant, except with DBA probably due to the fact that the determined concentration levels of DBA were near to the LOQ of the method. It is very interesting that chloroacetic acids (CAAs) were significantly correlated with the relative humidity in particle phase (r^2 = 0.65-0.87, n = 26) depending on the pKa value of the acid. It is well known (Martin et al., 2003) that due to their pKa values HAAs tend to be in the water phase and this has also been shown for the air, indicating that HAAs are either washed out by wet deposition or are adsorbed in the particle phase through the water vapours.

In the particle phase the concentration of MCA, DCA, TCA, DBA and TBA was increased in the case of winds coming from the industry sector of the region. In the gas phase a different situation was observed. With the exception of TCA, MBA and DBA the concentration was increased with winds coming from the sea area. In both phases, only MBA exhibits a significant increase in concentration when the wind is coming from the sea area.

3.3 Study of partitioning constant K_P

In order to study the gas/particle partitioning of those compounds and the factors affecting their gas/particle partitioning constant $K_{P,}$ the following equation was used (Sitaras et al., 2004):

$$\log k_p = f(T^{-1}) \qquad (1)$$

where k_p= $C_p/(C_g \times TSP)$, C_p= concentration in particle phase, C_g= concentration in gas phase, TSP=concentration of total suspended particulates and T= air temperature (K).
Table 1 shows the partitioning of 6 haloacetic acids, Kp=Cg/Cp in the range of 13.44-21.87 ^{O}C.

Table 1. Partitioning of 6 Haloacetic Acids, Kp=Cg/Cp in the range of 13.44-21.87 ^{O}C

No	MCA	MBA	DCA	DBA	TCA	TBA
1	74.0	743	18.3	91.6	87.1	75.1
2	27.8	337	6.17	88.6	76.9	60.0
3	71.5	445	16.6	201	178	142
4	67.7	167	10.2	101	98.1	96.3
5	70.8	134	73.7	101	95.4	94.8
6	187	315	860	201	270	487
7	353	161	3485	101	155	334
8	80.0	86.6	63.2	97.2	92.33	90.9
9	259	154	99.5	202	186.5	197
10	141	84.6	823	99.8	127	189
MEAN	133	263	546	128	137	177
MIN	27.8	84.6	6.17	88.6	76.9	60.0
MAX	353	743	3485	202	270	487

From the correlation the following were concluded:

- the distribution depends on each acid and is not uniform for all HAAs
- relative humidity is not a statistically significant factor which affects the distribution
- wind direction significantly affects the gas/particle distribution of HAAs.

4. CONCLUSIONS

The concentration levels of HAAs in particle and gas phase clearly show a seasonal variation between warm and cold period. In both phases the concentration is mainly affected by the relative humidity and the wind direction. The gas/particle correlation coefficient is mainly affected by the wind direction coming either from the industry or from the sea area and to a less degree by air temperature. On the contrary, it was found that the relative humidity does not affect significantly the distribution.

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CONCENTRATION RATES AND TRENDS OF ATMOSPHERIC ORGANIC POLLUTANTS IN THE ROME METROPOLITAN AREA

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Abstract: The concentration levels and trends of organic compounds associated to airborne particulates were investigated at Montelibretti (semi-rural area 30 km NE of Rome, Italy) and in downtown Rome (inside the Villa Ada city garden) to draw information about the ambient quality (presence of toxicants) and nature of sources (anthopogenic/natural, direct/secondary).

1. Introduction:

It is well known that organic aerosols play a key role about the global effects induced by pollution onto human health and ambient air quality. Indeed, although accounting for a minor portion of particulate material, the organic fraction give rise to most of long-term toxicity, owning to association of several potent carcinogens and mutagens to nano- and micro-particles. In addition, the knowledge of particulate composition provides suitable information about both the nature and relative impact of the contamination sources, as well as of the incidence of reactions producing secondary pollutants.

2. Experimental:

In that perspective, an extensive study is conducted at Montelibretti (RM, Central Italy) started in July 2005, and parallel measurements are carried out in downtown Rome since June 2006. The former location is semi-rural, around 30 km NE of Rome centre, while the second sampling site is the city garden of Villa Ada, assumed by the Civic Network as representative of background pollution in Rome. Groups and compounds of different polarity/acidity properties are investigated, in particular: C_{17}~C_{37} *n*-alkanes, PAH with MW ranging from 202 (fluoranthene) to 302 (dibenzopyrenes), C_{12}~C_{30} fatty acid, NPAH (restricted to nitrofluoranthene and nitropyrene isomers) and two polar species, i.e. nicotine and caffeine.

Collection of suspended particulates (PM_{10} and $PM_{2.5}$ size fractions) is conducted by means of a sequential sampler equipped with two independent gas lines. Daily samples are grouped by looking two main indexes, i.e. the year month and the $PM_{2.5}/PM_{10}$ mass ratio (which seems strictly related to dominating meteo-climatic situation, then the organic burden is extracted with soxhlet and fractionated into three classes of polarity. For this purpose, the extract is transferred to a neutral alumina column and eluted with isooctane, isooctane/dichloromethane and dichloromethane/acetone, in sequence. The neutral non-polar (*n*-alkanes), low-polar (PAH/NPAH) and highly-polar (nicotine/caffeine) fractions are collected in this way. Concurrently, a short minor aliquot of the crude extract, lead to react with BF_3./propanol, allows to evaluate organic acids. All concluding analyses are made through HRGC-MSD.

3. Results:

Table 1 shows an example of pooling of airborne particles accordingly to $PM_{2.5}/PM_{10}$ ratio [R]. The case shown refers to August and September 2005, when four and five series were discriminated, respectively. R, expressed as % $PM_{2.5}$ vs. PM_{10}, ranged from 0.30 to over 0.90.

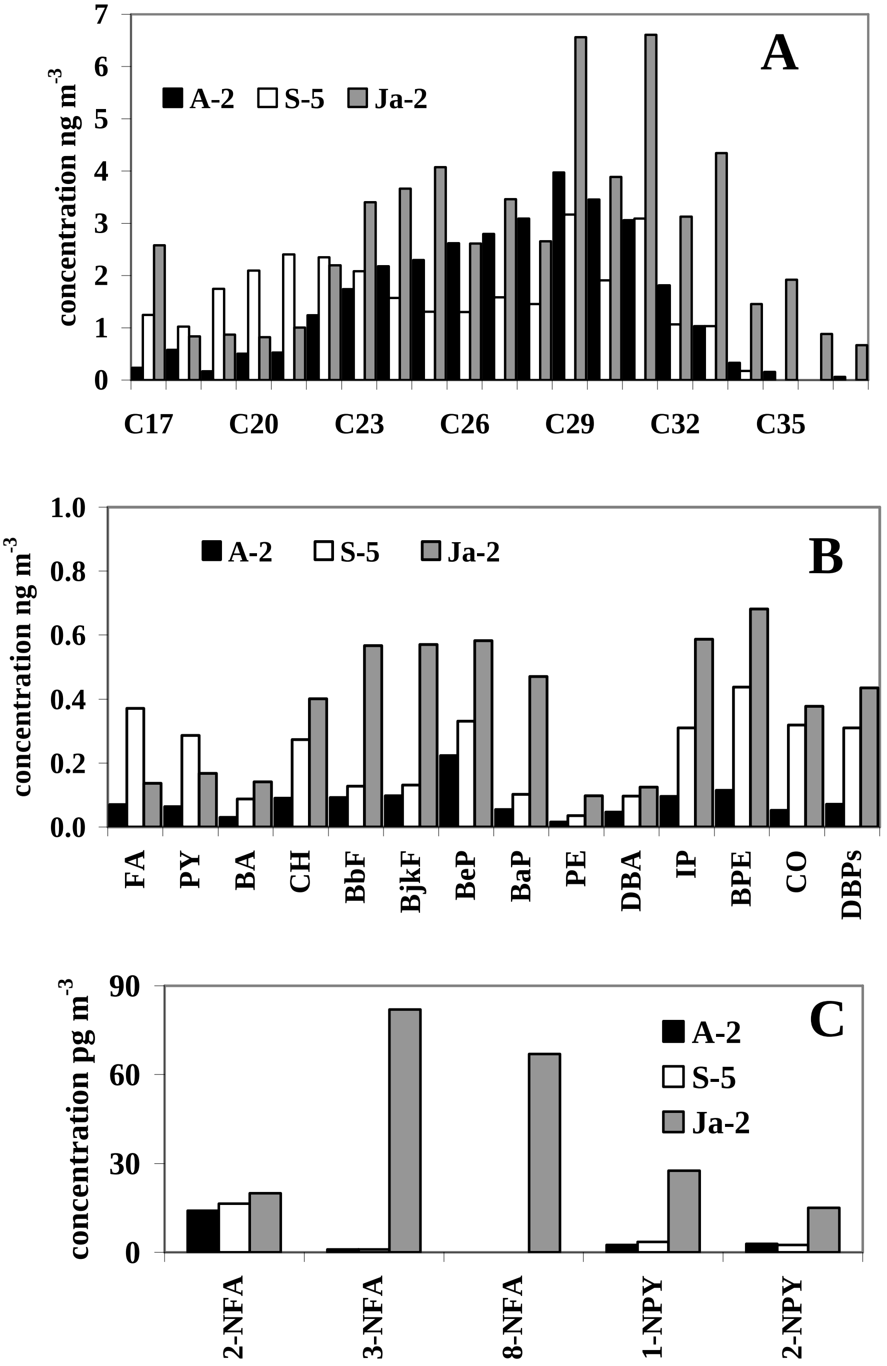
The average concentrations of *n*-alkanes, PAH and Nitro-PAH during three different periods of the year (in August, September and January) are reported in Figures 1A/C, respectively.

Besides the wide ranges of variability observed for aerial concentrations of all the groups investigated, marked differences were found by comparing the distribution profiles of individual compounds within the respective groups. For instance, in summer the semi-volatile n-alkanes were low when compared to high-boiling homologues (Figure 1A), and a similar behaviour was associated to PAH. Nitro-PAH presented large differences with year time; in particular, 2-nitrofluoranthene was predominant in summer and autumn (suggesting the secondary origin of the class through gas-phase reactions), while 3- and 8-nitrofluoranthene as well as 1-nitropyrene, typically associated to vehicle exhaust or to gas/particle reactions, were found solely in winter (Figure 1C).

Table 1. Sample pooling based upon $PM_{2.5}/PM_{10}$ ratio [R]. Montelibretti, August 01 - September 30, 2005. Concentrations of $PM_{2.5}$ and PM_{10} are in µg m^{-3} units. R is expressed as percentage.

date	PM_{10}	$PM_{2.5}$	R	*set*	date	PM_{10}	$PM_{2.5}$	R	*set*
Aug-01	45.0	22.2	49.3	*A-1*	**Sep-01**	40.8	27.7	67.8	*S-3*
Aug-02	46.1	26.5	57.6	*A-2*	**Sep-02**	45.7	38.8	85.0	*S-3*
Aug-03	30.0	15.3	51.2	*A-1*	**Sep-03**	41.6	32.2	77.4	*S-3*
Aug-04	16.0	12.7	79.4	*A-3*	**Sep-04**	26.0	18.5	71.4	*S-2*
Aug-05	17.3	14.6	84.5	*A-3*	**Sep-05**	27.7	18.9	68.3	*S-2*
Aug-06	24.6	22.7	92.3	*A-3*	**Sep-06**	26.9	19.7	73.4	*S-2*
Aug-07	35.1	14.6	41.6	*A-1*	**Sep-07**	28.9	17.5	60.5	*S-2*
Aug-08	34.0	16.6	49.0	*A-2*	**Sep-08**	50.6	18.5	36.6	*S-4*
Aug-09	25.4	16.6	65.5	*A-2*	**Sep-09**	38.6	14.2	36.8	*S-4*
Aug-10	31.1	19.3	62.2	*A-2*	**Sep-10**	18.6	9.9	53.2	*S-1*
Aug-11	43.1	20.2	46.9	*A-1*	**Sep-11**	25.5	12.6	49.4	*S-1*
Aug-12	50.7	18.9	37.3	*A-4*	**Sep-12**	24.4	15.3	62.5	*S-2*
Aug-13	36.4	17.9	49.0	*A-1*	**Sep-13**	26.3	16.0	61.0	*S-2*
Aug-14	32.9	16.8	51.2	*A-1*	**Sep-14**	25.9	16.2	62.7	*S-2*
Aug-15	28.8	11.4	39.4	*A-4*	**Sep-15**	21.9	14.9	67.9	*S-2*
Aug-16	35.8	10.5	29.4	*A-4*	**Sep-16**	30.1	18.4	61.2	*S-2*
Aug-17	14.7	7.6	51.7	*A-1*	**Sep-17**	29.9	18.3	61.3	*S-2*
Aug-18	21.1	16.0	75.9	*A-2*	**Sep-18**	29.3	10.8	36.8	*S-1*
Aug-19	22.8	17.4	76.0	*A-2*	**Sep-19**	16.7	8.7	52.3	*S-1*
Aug-20	31.2	16.3	52.4	*A-1*	**Sep-20**	15.2	8.4	55.5	*S-1*
Aug-21	18.6	10.5	56.6	*A-2*	**Sep-21**	14.1	7.5	53.5	*S-1*
Aug-22	14.3	7.0	48.6	*A-1*	**Sep-22**	17.2	9.8	57.1	*S-2*
Aug-23	30.4	15.2	50.2	*A-1*	**Sep-23**	16.5	13.5	82.2	*S-5*
Aug-24	23.0	16.9	73.7	*A-2*	**Sep-24**	20.8	18.8	90.1	*S-5*
Aug-25	23.1	13.4	58.1	*A-2*	**Sep-25**	25.8	21.9	85.2	*S-5*
Aug-26	23.9	15.7	65.6	*A-2*	**Sep-26**	29.9	21.6	72.2	*S-2*
Aug-27	23.6	14.2	60.3	*A-2*	**Sep-27**	35.0	25.8	73.8	*S-2*
Aug-28	23.6	16.9	71.6	*A-2*	**Sep-28**	35.4	24.8	70.1	*S-2*
Aug-29	25.0	19.2	76.9	*A-2*	**Sep-29**	29.8	21.1	70.6	*S-2*
Aug-30	27.4	21.1	77.0	*A-2*	**Sep-30**	20.3	13.9	68.3	*S-2*
Aug-31	31.6	20.0	63.1	*A-2*					

Figure 1. Aerial concentrations of particulate *n*-alkanes (A), PAH (B) and Nitro-PAH (C) at Montelibretti in three typical summer (August, A-2), autumn (September, S-5) and winter (January, Ja-2) periods of the year. The three distribution profiles of *n*-alkanes correspond to CPI_{25} rates equal to 1.1, 1.4 and 1.7, respectively.



4. Acknowledgments:

We are indebted with our colleague Dr. Antonio Febo and his scientific team, who not only provided the data about PM_{10} and $PM_{2.5}$ ratios but also shared with us the fruitful discussion leading to particulate sample grouping.

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TETHERED BALLOON SOUNDINGS OF AIR POLLUTANTS ABOVE THE CITIES OF NICOSIA AND LIMASSOL IN CYPRUS

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ABSTRACT

Tethered balloon soundings were carried out in winter and summer 2003 in Nicosia and in Limassol. The vertical profiles of the meteorological parameters wind direction, wind speed, temperature, humidity and of the air pollutant concentrations of NO_2 and O_3 were determined within four campaigns (two at the edge of Nicosia, two in the centre of Limassol) over four to six days each. When the wind speed was not too high around every three hours vertical profiles were measured from ground level up to 800 m above ground. On the poster typical vertical profiles of all parameters are presented. The vertical extension of inversion layers and the pollutants accumulation within these layers are illustrated in isoplete diagramms over a whole campaign (six days). In Nicosia the mountain-valley winds and in the coastal city of Limassol the land-sea breezes and their cleaning effects for the cities could be determined and depicted. Conclusions of the measurement results are given.

1. INTRODUCTION

Within a project “Preliminary Assessment of Air Quality in Cyprus " two tethered balloon campaigns were arranged in Cyprus in February / March and two in May/ June, 2003. The purpose of these campaigns was to investigate the vertical air pollution profiles over the cities of Nicosia and Limassol up to the height of 1000 m above ground. During these campaigns, the vertical concentrations distribution of Ozone and NO_2 were measured above the two cities. Besides that, different meteorological parameters (Temperature, wind speed and wind direction) were also recorded. The main target of these soundings was to find out the effects of inversion layers on the atmospheric air pollutants concentrations in the cities, their influence on the dispersion conditions in the atmosphere and the correlation with the weather classes. In addition the effect of Mountain-Valley breeze on the pollutant concentrations in the city of Nicosia and of Land-Sea breeze on the pollutant concentrations in the city of Limassol should be investigated.

2. METHODOLOGY

Firstly, the different weather types in Cyprus were studied and investigated by evaluating data provided by the Meteorological Service of Cyprus. The classification of weather types was necessary to assess the representativity of the weather conditions during the tethered balloon soundings.

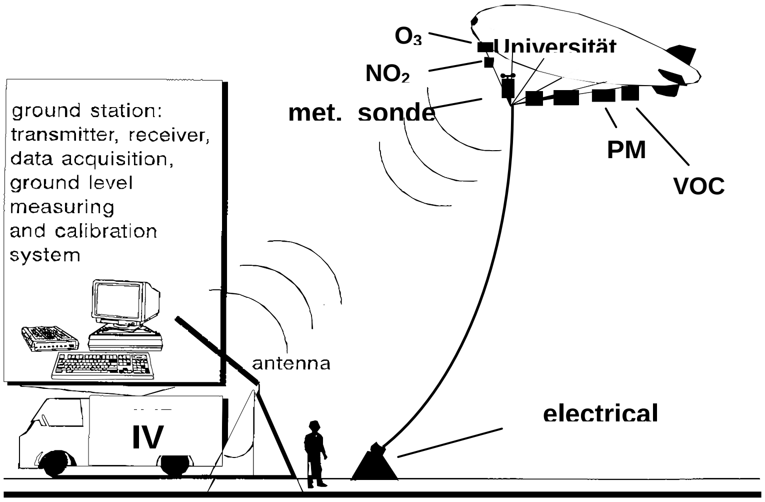


Figure 1. Tethered balloon measurement system

The used tethered balloon is filled with 50 m^3 of helium and connected via a stable rope with an electrical winch at the ground. The sensors for $NO_{2,}$ O_3 and meteorological parameters are fixed below the balloon. The data are electrically recorded and every 10 seconds they are transmitted to the ground station. The balloon system is described in detail by Baumbach and Vogt (1995). The main principle is shown in Figure 1.

In Nicosia the sounding place was located on the measurement site of the Meteorological Service in Athalassa, at the south-east edge of Nicosia. In Limassol the sounding place was located on the playground of a school nearly in the centre of Limassol.

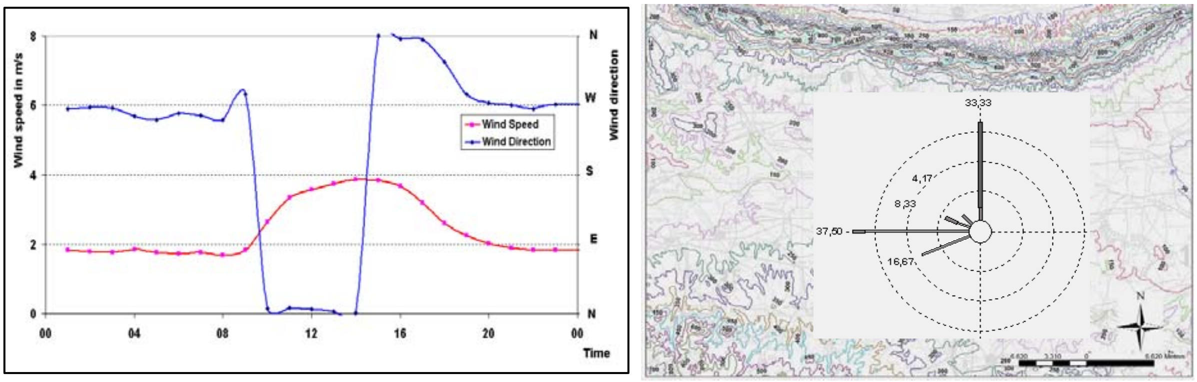
When the weather conditions were appropriate (wind speed not too high, no rain or thunderstorm) every two or three hours vertical soundings were carried out during day and night. Each campaign covered a period of some days. The duration was dependent on the stability of weather conditions.

3. RESULTS AND DISCUSSION

3.1 Winds in Nicosia and Limassol

In Nicosia the wind direction during day shows northerly winds. During night time the winds are coming from southwest and west which indicates the mountain wind coming from the Troodos mountains located west to southwest from Nicosia. In Limassol the land-sea breeze can be observed: During day the winds are coming from south (seaside). During night are coming from east to north east (land breeze). In summer in Limassol the wind system is determined by the overall weather conditions which are prevailing (Baumbach, Pfeiffer 2004).

a) Nicosia



b) Limassol

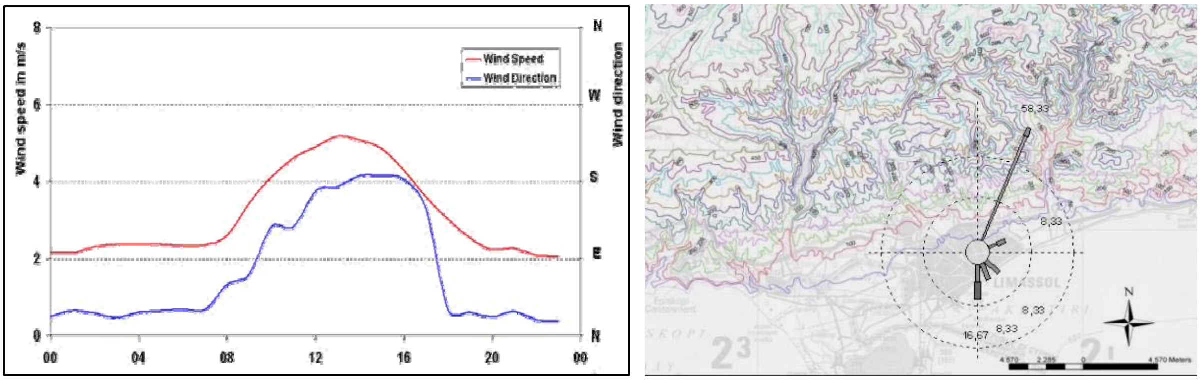


Figure 2. Mean diurnal profile of wind speed and direction frequency distribution for winter months a) in Nicosia b) in Limassol

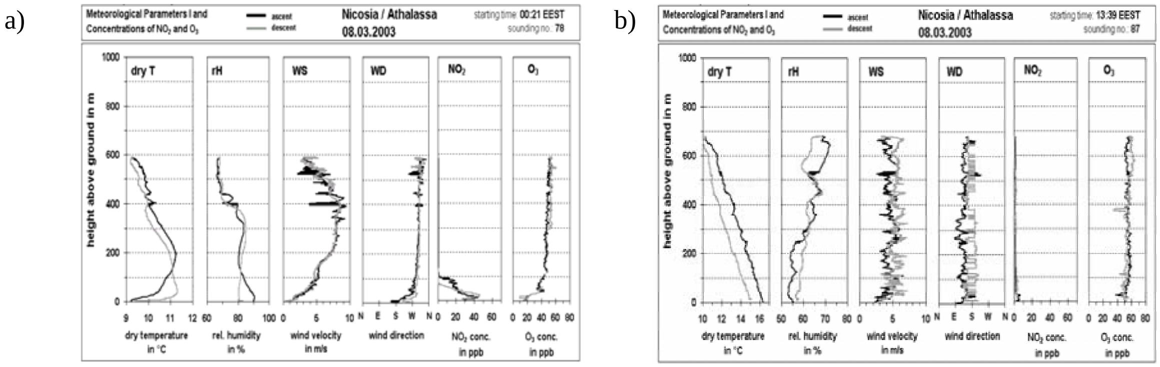


Figure 3. Vertical sounding profiles in Nicosia during winter a) night time, b) day time

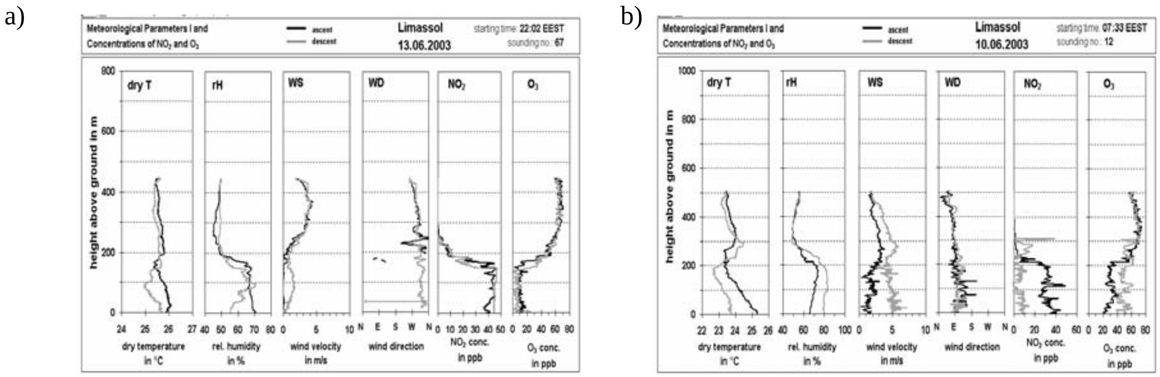


Figure 4. Vertical sounding profiles in Limassol during summer a) night time, b) morning time

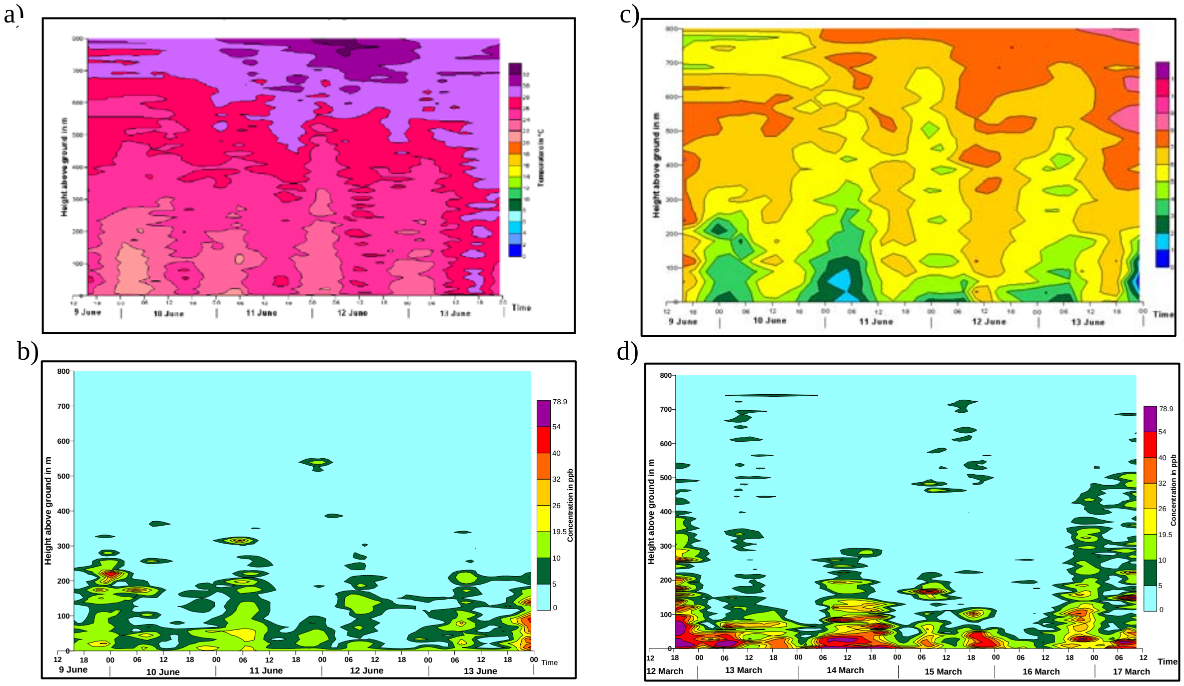


Figure 5. Vertical distributions over 5 days in Limassol for a. potential temperature, b. NO_2 (summer) c. O_3 (summer) and d. NO_2 (winter)

In Figures 3 and 4 typical vertical sounding profiles are shown. On the y-axis the vertical height above ground is depicted. In the diagrams the profiles of the dry temperature, the relative humidity, the wind velocity and direction and the vertical profiles of NO_2 and ozone concentrations are shown. Always the profiles from ascent and from decent are plotted. In Figure 3 two profiles from the winter campaign in Nicosia are presented. The left diagrams (a) reflect the conditions during night time, the right (b) during day time. It can be seen that during night a temperature inversion is existing (temperature increase with height) up to 200m above ground. Below the inversion the NO_2 concentration is increased and the ozone accordingly decreased. Above the inversion the NO_2 concentration shows very little values but high ozone concentrations. We are here in the so called “ozone reservoir” above the city. The barrier character of such an inversion is obvious. In 400m height a small second inversion can be recognized. But this inversion layer has only effect on the humidity, not on the pollutant gases because the NO2 concentration is still very low in this height. During day all inversions over the sounding height are dissolved the air is well mixed over the height (“mixing height”). According to this NO_2 and O_3 show very even profiles, NO_2 with very low concentration, O_3 at higher level.

The summer profiles are selected from the Limassol campaign, see Figure 4. The midnight profiles (left, b)) show a very strong surface inversion layer with very high NO_2 concentrations below. This layer acts as a very effective barrier layer against the distribution of pollutants in the upper layers. In the morning hours the surface inversions are elevated (see Fig. 4 b)). In the meantime between the ascent and the decent of the balloon the wind speed increased in the lower level and the elevated inversion had shifted a little bit. These two effects caused a better mixing and thus lower NO_2 concentrations below the elevated inversion. It can be clearly seen that this mixing leads to an input of ozone. During the day all inversions are dissolved and ozone shows even profiles over the whole sounding height, same as in winter, but on higher level.

From sounding sequences over several days isopleth diagrams could be drawn by interpolating the values of the adjacent profiles. In Figure 5 such isopleth digrams are shown for the sounding campaigns in Limassol. In a) the potential temperature during the summer campaign is depicted. Always during night the formation of cold air can be recognized up to elevations of 300m. In the morning hours the cold air inversions are dissolved and the mixed air can be recognized by an even temperature distribution during day time. In Fig. 5 b) the NO_2 enrichment within these cold air inversions can clearly be seen. Since in winter the inversions are more potent (higher) the NO2 enrichment is stronger within these layers (see Fig. 5d)). Within the NO2 enriched cold air layers the ozone depletion takes place during night. This becomes evident considering the ozone isopleth diagram (Fig. 5 c)).

4. CONCLUSIONS

The critical pollution situations occur during night time when surface inversions are blocking the vertical air exchange. To maintain an acceptable air quality during night in the cities the possibility of low flow ventilation should be not blocked by closed building lines.

5. ACKNOWLEDGEMENTS

The study project “Preliminary Assessment of Ambient Air Quality in Cyprus” was carried out by the Institute of Process Engineering and Power Plant Technology, Department of Air Quality Control of the Universitaet Stuttgart in co-operation with the Greek Cypriot Community and the Turkish Cypriot Community. The project was supported by US Agency for International Development (USAID) and the United Nations Development Programme (UNDP) under coordination of the United Nations Office for Project Services (UNOPS). The authors wish to thank all the staff members of Universitaet Stuttgart, Medisell Co Ltd and all GCC and TCC participants who were incorporated in this project.

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THE INFLUENCE OF THE CITY OF ATHENS IN THE EVOLUTION OF THE SEA BREEZE FRONT

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Abstract

In the present study, an attempt is made to examine the dynamics of a sea breeze front interacting with the heavily urbanized city of Athens. The effect of the urban heat island is also examined in combination with the spatial distribution of the wind flow, during a sea breeze day in the greater Athens area. The simulations were performed by the PSU/NCAR Mesoscale Model (MM5), by applying the non-local MRF (Hong and Pan, 1996) PBL parameterisation scheme, plus the MRF-urban scheme (Dandou et al., 2005), whereby urban features are considered. An unrealistic run was also performed by the MRF scheme, where Athens was replaced by dry cropland and pasture surface, as in the surrounding area. The model results were compared with routine meteorological data. A slowing in the sea breeze front was found and a reasonable frictional retard concerning its penetration, as the air moved over the city of Athens.

1. INRODUCTION

Land and sea breezes are mostly observed mesoscale phenomena, which play an important role in coastal areas where industries are located and a large population resides. The interaction of sea breezes with heavily urbanized areas is discussed by several authors – both in terms of the enhanced surface drag and the interaction with the urban heat island (Gedzelman et al., 2003). For example, synoptic and sea breeze frontal passages can be frictionally retarded by 50% as they approach New York city (Loose and Bornstein 1977; Bornstein and Thompson 1981; Thompson et al., 2006), while in the city of Säo Paulo, the presence of the urban region increases the sea-breeze front propagation mean speed by about 0.32 m/s when compared with the situation of no city (Freitas et al., 2007). Nevertheless, even in this case, it stalls over the city for about 2 hours and then it propagates beyond at a decelerated rate when the heat island dissipates. Thus, there is no complete agreement concerning the impact of the urban heat island on the propagation speed of the sea-breeze front in urban areas. In the present study, an attempt is made to examine the dynamics of a sea breeze front interacting with the heavily urbanized city of Athens. The effect of the urban heat island is also examined in combination with the spatial distribution of the wind flow, during a sea breeze day in the complex terrain of the greater Athens area.

2. METHODOLOGY

The numerical simulations were performed by the PSU/NCAR Mesoscale Model (MM5) (Grell et al., 1994), version V3-6-1. The high resolution non-local MRF (Hong and Pan, 1996) PBL parameterisation scheme was applied based on the Troen and Mahrt's (1986) representation for counter-gradients and K-profiles in the well-mixed convective boundary layer. In addition, the MRF-urban PBL scheme (Dandou et al., 2005), a modified version of the MRF scheme whereby recent advances in the urban boundary layer are considered, was also applied. In this urbanised version, additional updated fields for different parameters, such as the roughness length, albedo, thermal inertia, emissivity and moisture availability were also considered. This was achieved by applying an aggregation method in combination with detailed information derived from satellite image analysis (Landsat 5 Thematic Mapper image), with high spatial resolution (30 m). In order to examine topographic influences on air motions in the city, an unrealistic 'no-city' run was also performed by the MRF PBL scheme, where the city of Athens was replaced by dry cropland and pasture surface, as in the surrounding area.

The MM5 numerical simulations were performed by applying two-way nesting. The coarse domain covers the extended area of Greece, with spatial resolution 6 x 6 km, and the second domain is centred on the Attiki peninsula, with spatial resolution 2 x 2 km. The 25-category USGS land-use classification scheme was adopted to provide land-cover data for the model domains. The initial and lateral boundary conditions for the outermost domain were provided by the European Center for Medium range Weather Forecast (ECMWF) numerical prediction model. The model results were compared with routine meteorological data and measurements from the MEDiterranean CAmpaign of PHOtochemical Evolution (MEDCAPHOT-TRACE) experimental campaign (Ziomas, 1998).

3. RESULTS AND DISCUSSION

The numerical simulations were performed for 15 September 1994, a selected day from the MEDCAPHOT-TRACE experimental campaign. For this day, apart from the surface measurements, tethered balloon soundings were also available, up to a height of 600 m at the NOA and Marousi stations (Batchvarova and Gryning, 1998). On that day, the surface synoptic circulation over the greater Athens area was characterized by the ridge from an extended anticyclone centered over northern Africa, and the synoptic wind was weak from the northern sector. Due to the weak opposing background flow, the developed sea-breeze circulation was characterized by an intense front, penetrating inland with strong winds, covering the whole Athens basin. The sea breeze with a south/south-westerly direction reached NOA at 1000 LST and a maximum wind speed of 4–5 m/s was measured between 1200 LST and 1800 LST (Batchvarova and Gryning, 1998). Therefore, these conditions favoured the development of a more confined internal boundary layer.

During the day, wind simulations, performed by the MRF-urban scheme, showed a slowing in the sea breeze front and a reasonable frictional retard concerning its penetration, as the air moved over the city of Athens, compared with both the MRF scheme (not presented) and the unrealistic ‘no-city’ MRF run. In Figure 1, the spatial distribution of the horizontal wind speed differences between the MRF-urban scheme and the unrealistic ‘no-city’ MRF run, at 1400 LST, are presented. A slowing of the wind speed up to 1.5 m/s in the Athens centre is apparent, which is mainly attributed to the higher roughness of the urban canopy, compared to the surrounding area. It also appears that urban heating plays a role in distorting near-surface temperatures as the sea breeze fronts passes (not presented).

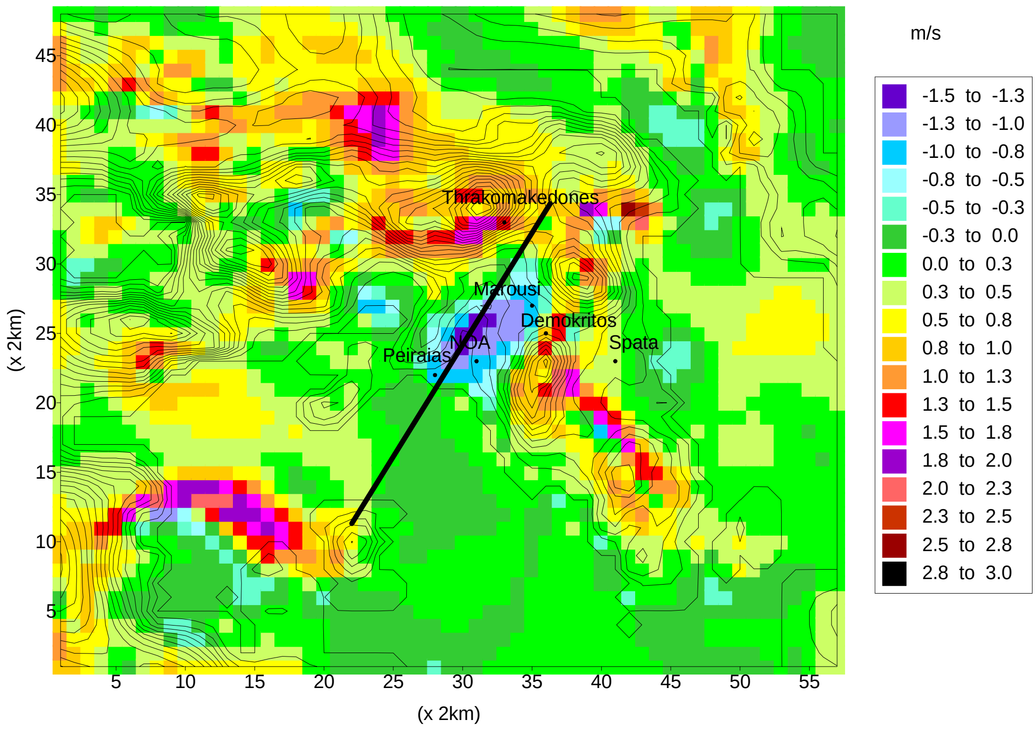
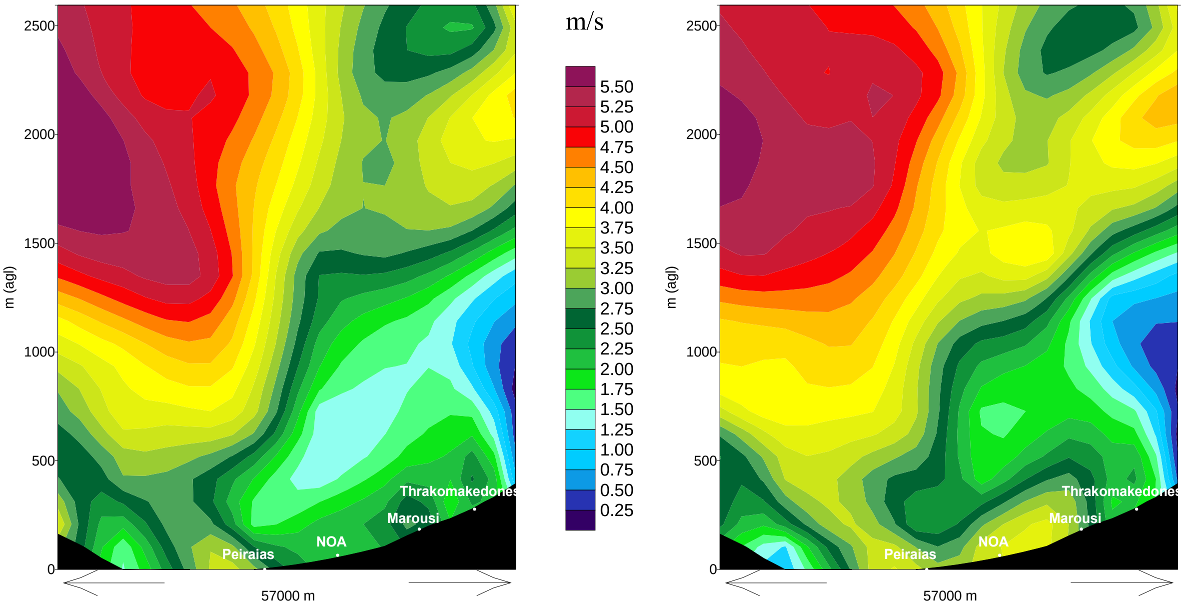


Figure 1: The spatial distribution of the horizontal wind speed differences (at 10 m agl) between the MRF-urban PBL scheme and the unrealistic ‘no-city’ MRF run, on 15 September 1994, at 1400 LST. The position of six measurement stations (Peiraias, NOA, Marousi, Demokritos, Thrakomakedones and Spata) is presented, as well as the sea breeze axis (black line).

In Figure 2, the vertical cross section of the horizontal wind speed along the sea breeze axis is presented for the MRF-urban scheme and the unrealistic ‘no-city’ MRF run, at 1400 LST. The sea breeze front is slowed down near the surface and is vertically limited e.g. up to ~450 m at NOA station, compared to ~650 m with the ‘no-city’ MRF run. It should also be mentioned that the sea breeze development was delayed by 1-2 hours compared to the unrealistic ‘no-city’ MRF run (not presented).



a **b**

Figure 2: The vertical cross section of the horizontal wind speed along the sea breeze axis, on 15 September 1994, at 1400 LST, as calculated by a) the MRF-urban PBL scheme and b) the unrealistic 'no-city' MRF PBL scheme. The projection of the position of four stations (Peiraias, NOA, Marousi and Thrakomakedones) along the sea-breeze axis is also presented.

During nighttime, vertical profiles of simulated temperature (not presented) and wind speed showed a maximum over the lower atmosphere in the city centre. In Figure 3, the simulated vertical wind speed and direction profiles are presented at the NOA station, at 0300 LST. The maximum wind speed values, calculated by the MRF-urban scheme in the lower atmosphere, could be directly related to the influence of the urban heat island, which is more intense during the night due to the heat storage and the anthropogenic heat that are both released into he urban canopy (Oke, 1987). It should also be mentioned that during the night, the MRF-urban scheme calculates a continuation of the sea breeze (S-SW) due to the urban heat island. However, the wind speed is very low (less than 1 m/s) near the surface, so any comparison with wind direction measurements is meaningless.

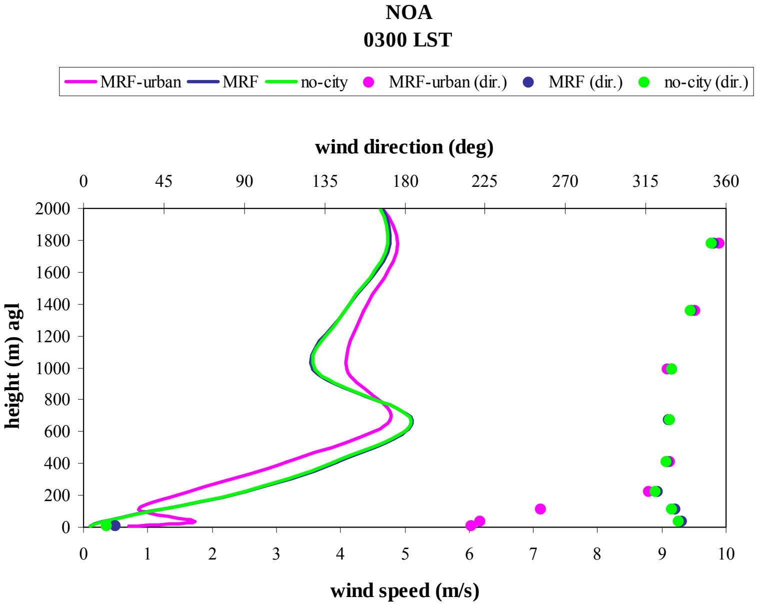


Figure 3: The vertical wind speed and direction profiles at NOA station, on 15 September 1994, at 0300 LST, as calculated by the MRF-urban, MRF and 'no-city' MRF schemes.

4. CONCLUSIONS

The MRF-urban scheme calculated a slowing of the sea breeze front and a reasonable frictional retard concerning its penetration, as the air moved over the city of Athens, during the day. This can mainly be attributed to the higher roughness of the urban canopy compared to the surrounding area. It also appears that urban heating plays a role in distorting near-surface temperatures as the sea breeze fronts passes.

During nighttime, vertical profiles of simulated temperature and wind speed showed a maximum over the lower atmosphere in the city centre. These maximum wind speed values, calculated by the MRF-urban scheme, could be directly related to the influence of the urban heat island, which is more intense during the night due to the heat storage and the anthropogenic heat which are both released into he urban canopy.

Finally, the unrealistic 'no-city' MRF run revealed the existence of other important mechanisms (e.g. sea-breeze) which coexist with urban influences, when an urban area is surrounded by complex topography.

5. ACKNOWLEDGMENTS

We are grateful to the COST Action 728 'Meteorological parameterization/applications' activities which actually inspired this study.

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AIR QUALITY IN MEGACITIES: RESULTS FROM VOLATILE ORGANIC COMPOUNDS MEASURED IN PARIS, BEIJING AND SANTIAGO DE CHILE

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ABSTRACT

Atmospheric samples have been collected in Paris, Beijing and Santiago de Chile in order to characterize ambient VOC mixing ratios, to determine their speciation, and to assess their diel variations. VOCs were either measured in-situ (Paris, May 2005), measured from canisters samples (Beijing, August 2004) or collected in cartridges (Santiago, January 2006) and subsequently analysed in the laboratory by GC-MS (gas chromatography – mass spectrometry).The results presented here concern VOC compounds including alkanes, acetylene, aromatic compounds and halogenated species. Mixing ratios of those compounds are compared for the three cities and show significant differences (eg. benzene ranges from 0.01 to 2.7 ppbv in Paris and from 0.3 to 10 ppbv in Beijing). Observed mixing ratios of VOCs are discussed in terms of admissible levels of pollution for health impact, and ozone formation potential. Observed diel variations show elevated values of the VOCs in the morning and in the late afternoon, due to the combined influence of pollution (mainly due to traffic) and local meteorology. Especially noteworthy is the diel cycle observed at Beijing which shows also a peak during the night. This event is discussed in terms of source influences based on correlation with other parameters such as carbon monoxide and black carbon.

1. INTRODUCTION

The rapid development of megacities in the world is a major environmental problem for the next decades. In 1950, New-York and Tokyo were the only two urban complex with a population of more than ten millions, at present, this number reaches twenty and by 2015, it is expected than four billion people will live in urban areas, with 40% in area of more than one million inhabitants and 12% in megacities. Megacities are consequently large point sources of air pollution and in some cases, megacity emissions are even greater in magnitude than those of the entire country. Studies of their impact on atmospheric composition becomes of primary importance since air pollution in megacities is not only relevant to local to regional scale air quality but also to global change.

Volatile organic compounds (VOC), are key constituent for the lower atmosphere in terms of chemistry and health impact, they include many different species with various origins and source magnitude. Major sources of VOC in the atmosphere are emissions from motor vehicles, emissions from industrial activities and solvent use. Some of these compounds influence directly human health due to their toxicity (carcinogenic and mutagenic effects). VOC are also important precursors of photochemically induced secondary pollutants, such as ozone and carbonyl compounds. Since the individual VOC has specific reaction rate with oxidants and degradation mechanisms, they also differ in their contribution to photochemical ozone formation.

In this work, VOC measurements have been done in Paris, Beijing and Santiago de Chile in order to characterize ambient VOC mixing ratios, to determine their speciation and to assess their diel variations. Results presented here concern VOC compounds including acetylene, aromatic compounds and halogenated species. Their mixing ratios are compared for the three cities and are discussed in terms of admissible levels of pollution for health impact, and ozone formation potential.

2. EXPERIMENTAL

During the campaign in Beijing (39°48N, 116°28E), 15 air samples were taken on 18 and 19 August 2004. The samples were collected at atmospheric pressure on stainless steel canisters and subsequently analysed in the laboratory by GC-FID (gas chromatography/flame ionisation detection) for NMHC and by GC-MS (gas chromatography /mass spectrometry) for halocarbons species.

The campaign in Paris (48°44N, 2°24E) took place at the Town Hall square in Paris, from May 9th to 29th. NMHC's mixing ratios were monitored with two automated GC's, for C_2-C_6 and C_5-C_{12} species, and performing every 30 minutes ‘in situ’ measurements over 10 minutes averages with detection limits of about 50 pptvs.

The Bicycl’Air project (bicyclair.free.fr), was conducted from December 2005 to March 2006; 30 air samples were taken from 19 to 22 January 2006 in Santiago de Chile (33°27S, 70°39W). Samples were collected on cartridges and later analysed in the laboratory by GC-MS. The GC-system was calibrated twice daily using a gas standard containing alkanes, alkenes and aromatic compounds at concentration of 1 ppmv.

3. RESULTS AND DISCUSSION

3.1. Observed levels

The mixing ratios expressed in pptv of the main VOC are given in Table 1 with their average value, standard deviation, and minimum and maximum values.

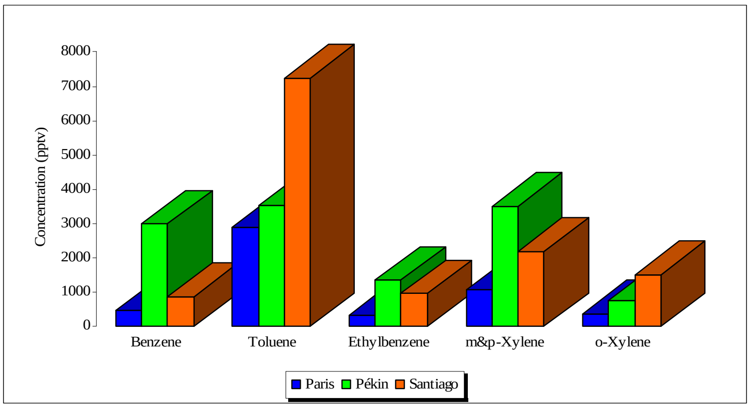
Table 1: Emission of VOC in pptv measured in the different campaigns

	Paris				**Beijing**				**Santiago de Chile**			
Compound	**Mean**	**σ**	**Min**	**Max**	**Mean**	**σ**	**Min**	**Max**	**Mean**	**σ**	**Min**	**Max**
Acetylene	1090	836	102	7075	4783	2724	1854	10542	n.m.	n.m.	n.m.	n.m.
Benzene	446	459	14	2712	2985	1580	311	6641	858	717	156	2342
Toluene	2904	2591	135	20173	3511	1894	554	8290	7234	11506	988	54734
Ethylbenzene	333	445	12	7307	1342	873	299	4005	951	858	76	3002
m&p-Xylene	1062	909	58	6339	3504	1725	928	6884	2187	1722	375	5260
o-Xylene	364	334	17	2280	763	338	239	1257	1506	1182	239	3733
1,3,5-TMB	n.m.	n.m.	n.m.	n.m.	68	42	32	201	325	280	46	1299
1,2,4-TMB	n.m.	n.m.	n.m.	n.m.	273	150	97	684	1065	744	262	2604
1,2,3-TMB	n.m.	n.m.	n.m.	n.m.	42	20	20	96	305	206	80	765
Trichloroethene	n.m.	n.m.	n.m.	n.m.	69	27	27	110	n.m.	n.m.	n.m.	n.m.

For these three campaigns, toluene, acetylene and m&p-xylenes are the main compounds observed. In Paris, VOC measured mixing ratios are lower than those measured in Santiago de Chile. VOC concentrations measured in Santiago de Chile are also generally lower than VOC concentrations measured in Beijing except for toluene and trimethylbenzenes. For these two compounds, their concentrations are higher in Santiago de Chile.

3.2. VOC-composition and diurnal cycle

Figure 1: Composition in aromatics in pptv



The composition in aromatics is displayed in Figure 1. They are comparable in Paris and in Santiago de Chile, with toluene as a major compound. The composition in Beijing appears very different, with similar contributions of benzene, toluene and xylenes.

This observation suggests that Paris and Santiago de Chile are dominated by similar source (transportation) whereas Beijing seems characterized by a more complex source mixture.

Diurnal cycles of benzene, toluene and m&p-xylenes are given in figure 2, 3 and 4. The figure 5 shows these three diurnal cycles in May 2005 for Friday 20 and Saturday 21.

Figure 3: Diurnal cycles of VOC in Santiago de Chile

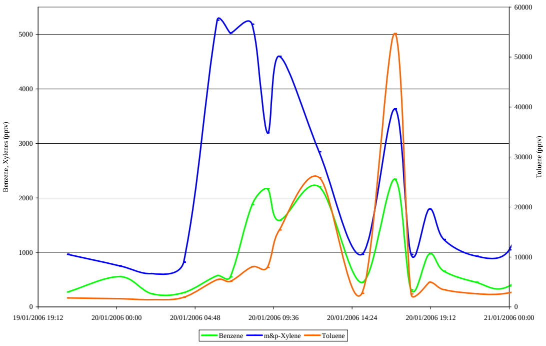


Figure 4: Diurnal cycles of VOC in Paris

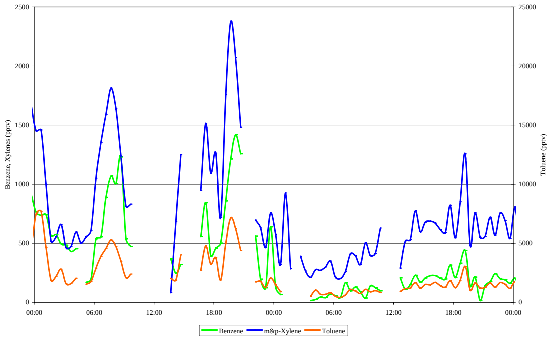


Figure 5: Diurnal cycles of VOC in Beijing

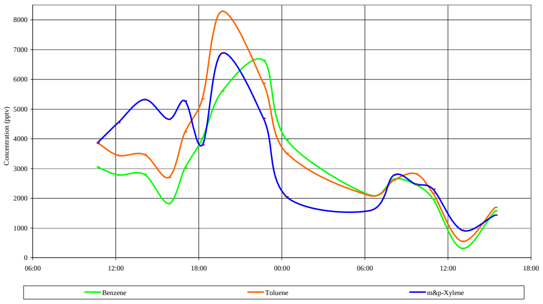
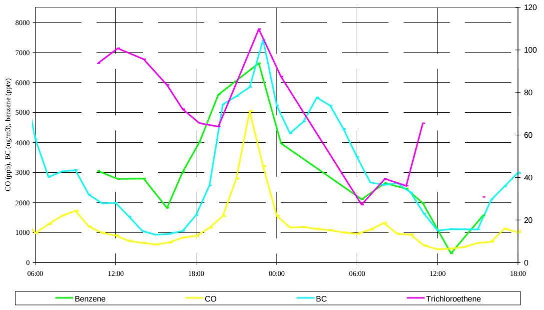


Figure 6: Diurnal cycles of CO, BC and trichloroethene in Beijing



Observed diel variations show elevated values of VOC in the morning and in the late afternoon. These elevated values of VOC in the morning (between 8 and 9 a.m. for Paris and between 6 and 9 a.m. for Santiago de Chile) and in the late afternoon (between 5 and 7 p.m.) are mainly due to anthropogenic emissions linked to traffic activity.

For Paris (Figure 5), diurnal cycles of benzene, toluene and m&p-xylenes show a very high variability from day to day. This variability of aromatic compounds shows that the pollution in Paris is mainly linked to traffic and not to industrial activities. Especially noteworthy is the diel cycle observed at Beijing which shows also a significant maximum during the night. During this campaign, others parameters such as carbon monoxide (CO), black carbon (BC) (combustion tracers) and trichloroethene (used as industrial emissions tracer) have been measured.

Observed diel variations of these compounds (Figure 6) show two peaks for BC. The first one occurs at 7:40 p.m. and the second peak occurs at 10:40 p.m. The first one can be related to toluene and xylenes peaks, which are the main fraction of VOC found in the automotive exhaust emissions. The second one can be connected to benzene and trichlororethene production. This shows influence of the diesel source (trucks circulation allowed in the city only during the night) and of industrial sources.

3.3. Benzene emissions

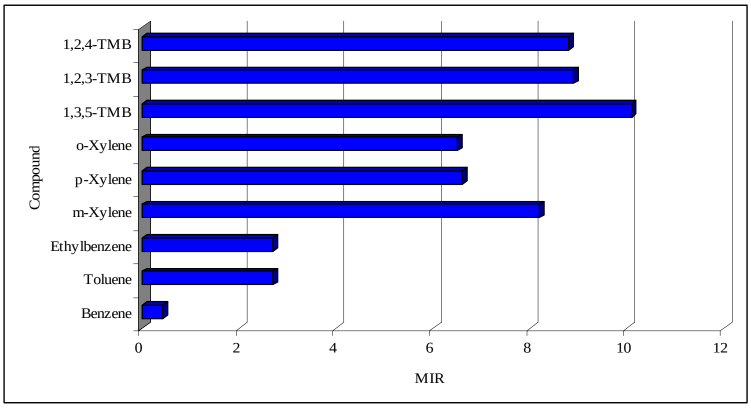
Some of VOC (benzene, toluene) include a risk of human health. Thus, air quality regulations for maximum admissible levels have been established for some species. The European regulation for benzene corresponds to a limit of 5µg/m^3. During the measuring campaign in Paris, benzene concentrations are comprised between 14 pptv and 2712 pptv, with an average of 446 pptv or 1.42µg/m^3. Thus, the European norm has been observed during this campaign. For the campaign in Beijing, benzene concentrations are included between 311 pptv and 6641 pptv, with an average of 2985 pptv or 9.52µg/m^3, indicating that the benzene mixing ratio reaches about twice the maximum level established in Europe.

3.4. Ozone formation potential

The ozone reactivity scale for VOC, MIR (Maximum Incremental Reactivity) scale, by Carter (1994), allows to assess the measured VOC emissions concerning the photochemical ozone production. The

MIR-factor corresponds to amount in grams of ozone formed per gram of each VOC emitted. Then the ozone formation potential varies accordingly to the MIR factor. The highest ozone formation potential is observed for trimethylbenzene and for xylenes. However, aromatic compounds are not species with the highest MIR-factor since species showing the highest MIR-factor are usually alkenes.

Figure 7: Maximum Incremental Reactivity of some VOC



4. CONCLUSIONS

These preliminary results show contrasted source influences on VOC measured in Paris and in Beijing which need to be further investigated through more complete measurements.

In the framework of the AEROCOV project (financed by the French agency ANR), intensive field campaigns with in-situ measurements of VOC (GC-FID and GC-MS) will be performed in Beijing (August 2007) and in Paris (June 2007). Aerosol chemistry will be measured as well on-line allowing a better understanding of VOC and aerosols interactions.

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AIR QUALITY IN AGGLOMERATIONS OF THE CZECH REPUBLIC AND TRENDS OF AIR POLLUTION BETWEEN 1996 AND 2005

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ABSTRACT

This contribution assesses air quality in agglomerations and trends of pollutant concentrations between 1996 and 2005 in the Czech Republic. Mann-Kendel test and Sen's method were used for testing the presence of statistically significant trend. Statistically significant decrease is evident at some sites (not all tested) in PM_{10}, CO, benzene, Cd, Pb, Ni in Prague, Pb in Brno, benzene, arsenic, lead in the Moravian-Silesian Region and NO_2 and lead in the Ústí nad Labem Region. There was found out only one statistically significant increase (ozone, at 4 sites in the Ústí nad Labem Region). The lead is the only one pollutant, which decreased in all tested areas.

1. INTRODUCTION

Current air quality and trends of air pollution between 1996 and 2005 are assessed in Prague, Brno, in the Moravian-Silesian Region and in the Ústí nad Labem Region. Prague and Brno are 2 biggest cities in the Czech Republic with high population density. The main air pollution source is heavy traffic. The Moravian-Silesian Region and the Ústí nad Labem Region are areas with high density population and intensive industry.

Figure 1. The Czech Republic with assessed agglomerations

Aglomeration	Area (km²)	Population	Density of population (inh/km²)
Prague	496	1169106	2357
Brno	230	376172	1636
The Moravian-Silesian Region	5554	1269467	229
The Ústí nad Labem Region	5335	820219	154

Table 1. Overview of area (km^2), population and density of population (inh/km^2)

2. METHODOLOGY

We used nonparametric Mann-Kendel test for testing the presence of mononotic increasing or decreasing trend and the nonparametric Sen's method for estimating the slope of a linear trend. The Mann-Kendel test requires at least 4 values, we used time series with at least 5 values, including year 2005. Limit values (LV) from EU directives are used for assessment.

3. RESULTS

PRAGUE

Both 24-hour PM10 LV (at 12 sites) and annual LV (at 1 site) were exceeded in 2005. In the beginning of the assessed period concentrations had decreased, minimum was reached between 1998 and 1999; afterwards no noticeable trend was detected. Only at one site, Prague 5–Mlynářka, statistically significant decrease was found out between 1996 and 2006.

Both hour and annual **NO_2** LV were exceeded in 2005 in Prague (at 1 station also LV + margin of tolerance was exceeded). Hour LV was exceeded at traffic hot spot (Prague 2-Legerova) both in 2004 and 2005. No statistically significant trend was found out any at 8 assessed sites.

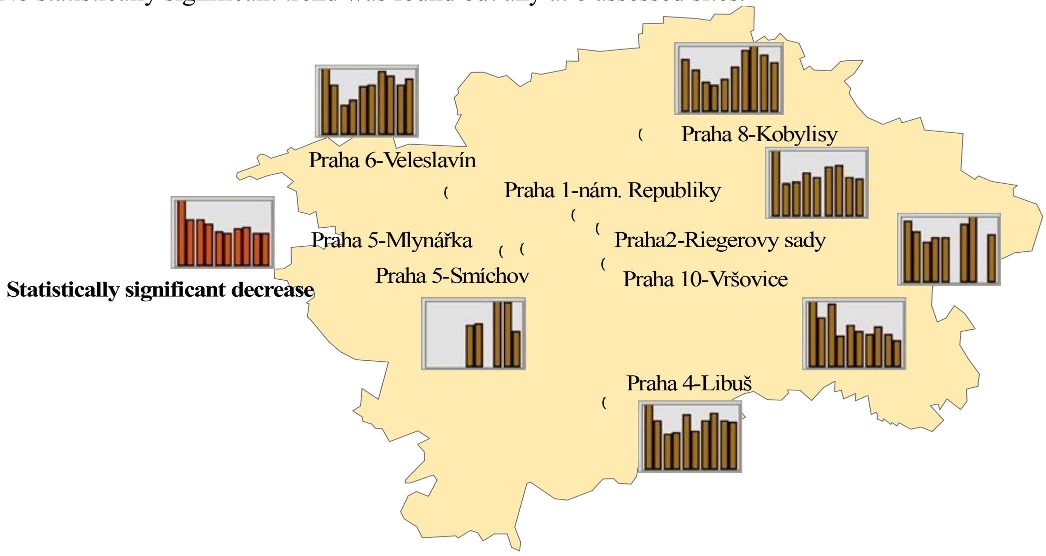

Figure 2. Annual average concentrations of PM_{10} in 1996-2005 in Prague.

The **benzo(a)pyrene** concentrations exceeded target LV at all (3) sites, which measured it in 2005. Statistically significant trend was not found out.

Ozone target LV was also exceeded (at 6 of 9 sites). A number of exceedances of 8-hour running mean (above 120 $\mu g*m^{-3}$) averaged for 3 years was tested. No statistically significant trend was found out at 6 assessed sites.

The LV for **CO** was not exceeded. In spite of this fact, maximum 8-hour running average per year and 98th percentile of 8-hour running means per year were tested. Statistically significant decreases were found out at 3 of 8 sites (Prague 1-nám. Republiky, Prague 5-Svornosti, Prague 9-Vysočany) and in case of 98th percentile at 2 sites (Prague 5-Mlynářka, Prague 5-Svornosti).

Similarly, **benzene** LV was not exceeded in Prague. Statistically significant decrease was found out at site Prague 4-Libuš.

Lead concentrations were also below LV. Extensive decrease occurred after 2001, when obligatory use of unleaded petrol was established. Significant decrease was found at 5 of 7 assessed sites. **Arsenic** LV has not been exceeded since 1997 in Prague. No statistically significant trend was found out at any of 7 tested sites. **Nickel** LV has not been exceeded since 1999. Statistical test found out significant decrease at 1 site (Prague 5-Svornosti).

BRNO

Brno with population of 376172 is the second biggest city in the Czech Republic.

Both 24-hour **PM_{10}** LV (3 sites: Brno-střed, Brno-Tuřany, Brno-Kroftova) and annual LV (1 site: Brno-střed) were exceeded in 2005. Statistically significant trend was not found out.

NO_2 annual LV was exceeded at both sites, which was measuring it in 2005 (Brno-střed, Brno-Kroftova). None of these sites showed any significant trend of concentration.

Benzo(a)pyrene LV was also exceeded at both sites in Brno, which measured it in 2005 (Brno-Kroftova, Brno-Húskova). Only site Brno-Húskova has been measuring during longer period, slightly increase is not statistically significant.

Ozone target LV was exceeded at 1 of 2 sites, which measured it (Brno-Tuřany). Number of exceedances of 8-hour running mean averaged for 3 years was tested. Statistically significant trend was not found out at 1 assessed site.

CO limit value has not been exceeded in the long term. The trend of CO concentration was not evaluated, because there is no site with longer time series in Brno.

Benzene LV was not exceeded in 2005; there was no site with longer time series for statistical testing.

Lead, arsenic and nickel LVs were not exceeded in 2005. The lead concentrations showed statistically significantly decrease at both 2 sites (Brno-Dobrovského, Brno-Krasová). No significant trend of arsenic concentrations was found out at 2 tested sites. The trend of nickel concentration was not evaluated, because there is no site with longer time series in Brno.

THE MORAVIAN-SILESIAN REGION

There is high population and industry density mainly in cities Ostrava, Karviná, Havířov, Český Těšín a Třinec.

Both 24-hour **PM_{10}** LV (19 sites) and annual LV (17 sites) were exceeded in 2005. None of 14 tested sites showed any significant concentration trend.

Annual **NO_2** LV was exceeded at traffic hot-spot (Ostrava-Českobratrská). No significant trend was found at 15 tested sites.

This area has the highest **benzo(a)pyrene** loads in the Czech Republic. The concentrations above LV were measured at all sites in this area (Ostrava-Přívoz ZÚ, Český Těšín, Ostrava-Poruba/ČHMÚ, Karviná ZÚ). They did not show any significant trend.

Ozone target LV was exceeded at several sites, mainly with lower traffic loads. Number of exceedances of 8-hour running mean (above 120 $\mu g*m^{-3}$) averaged for 3 years was tested. No statistically significant trend was found out at 7 assessed sites.

CO limit value has not been exceeded in the long term. No significant trend was found out.

Another problem is caused by the high **benzene** concentrations which exceeded LV at 2 sites with the highest industrial loads, i.e. Ostrava-Přívoz (ZÚ and CHMI). There was also exceeded LV + margin of tolerance at the first of these stations. It was confirmed that higher concentrations are connected with industrial activities (coke production). The exceedances have been since 2000 (respectively 2001), when sites started measuring. There was a long-term decrease which was not statistically significant.

The annual **arsenic** average in the site Ostrava-Přívoz ZÚ with highest industry loads amounted relatively close below target LV (5.8 $ng.m^3$). The target LV was exceeded in 2002 and 2003. Statistically significant decrease of arsenic concentrations was found out at 1 of 3 tested sites (Ostrava-Poruba IV).

Lead and nickel LVs were not exceeded in 2005. The lead concentrations showed statistical significantly decrease at 3 from 4 sites. No trend of nickel concentration was found out.

THE ÚSTÍ NAD LABEM REGION

This is the area with high population density, where many of pollutant concentrations are above LVs.

Both 24-hour **PM_{10}** LV (14 sites) and annual LV (4 sites) were exceeded in 2005.

No statistically significant trend was found out at any of 13 tested sites.

In 2005, annual **NO_2** LV plus margin of tolerance was exceeded at the site Děčín-ZÚ with high traffic loads. Statistically significant decrease was found out at 3 of 14 sites (Krupka, Tušimice, Ústí n.Labem-Kočkov).

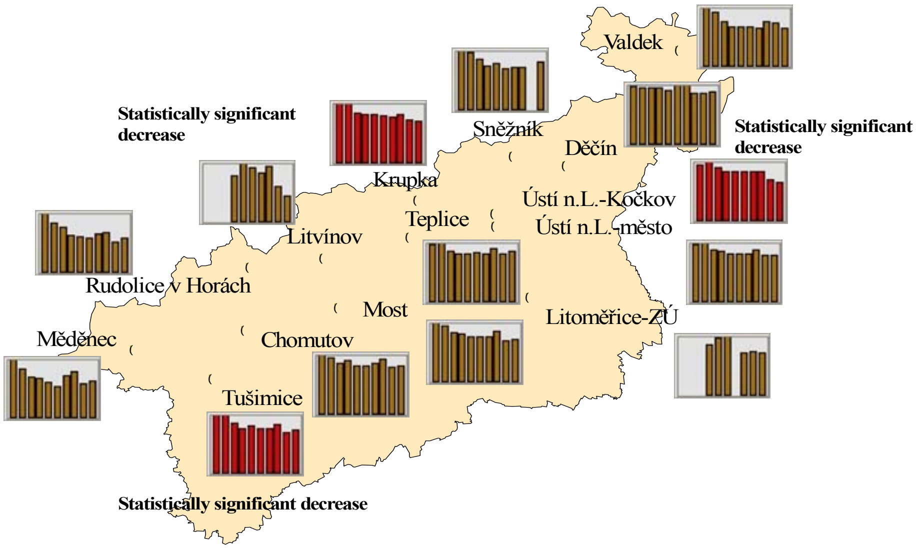

Figure 3. Annual mean concentrations of NO_2 in 1996-2005 in the Ústí nad Labem Region.

Benzo(a)pyrene LV was exceeded in Ústí nad Labem, Teplice and Most. Statistically significant trend was not found out at one tested site with longer time series.

Ozone target LV was markedly exceeded similarly as in other part of the Czech Republic and mainly at the sites with lower traffic loads. Number of exceedances 8-hour running mean (above 120 µg*m^{-3}) averaged for 3 years was tested. Statistically significant increase was found out at 4 of 7 tested sites (Rudolice v Horách, Teplice, Ústí n.L.-město, Litoměřice-ZÚ).

CO limit value has not been exceeded in the long term. No statistically significant trend was found.

Benzene LV was not exceeded in 2005. No statistically significant trend was found out.

Lead, arsenic and nickel LVs were not exceeded in 2005. Statistically significant decrease of lead concentration was found out at 1 of 4 assessed sites (Ústí nad Labem-Kočkov). The arsenic and nickel concentrations did not show any significant trend.

4. CONCLUSIONS

Statistically significant trends were not found for any pollutants at all assessed sites except lead, which decreased because of obligatory use of unleaded petrol after 2001. The overview of the established trends is presented in the following table.

	PM_{10}*	***NO_2***	***CO^{**}***	***CO*****	***B(a)P***	***C_6H_6***	***As***	***Cd***	***Pb***	***Ni***	***O_3^{****}***
Prague	**↓1(8)**	0(7)	**↓3(8)**	**↓2(8)**	0(1)	**↓1(1)**	0(7)	**↓2(7)**	**↓5(7)**	**↓1(4)**	0(6)
Brno	0(2)	0(2)	0(0)	0(0)	0(1)	0(0)	0(2)	0(2)	**↓2(2)**	0(0)	0(1)
The Moravian-Silesian Region	0(14)	0(15)	0(1)	0(1)	0(2)	0(1)	↓ **1(3)**	0(4)	↓ **3(4)**	0(1)	0(7)
The Ústí nad Labem Region	0(13)	↓ **3(14)**	0(6)	0(6)	0(1)	0(2)	0(6)	0(5)	↓ **1(4)**	0(5)	↑ **4(7)**

Table 2. ↓(↑)x(y) decreasing (increasing) trend at x sites (y-total number of assessed sites). Assessed site means site with at least 5 annual data between 1996 and 2005 (concentration or number of exceedances including 2005).
No statistically significant trend was found at the rest of assessed sites.
* annual average
** maximum 8-hour running average
*** 98th percentile of 8-hour running average
**** number of exceedances of 8-hour running means (above 120 µg*m^{-3}) averaged over 3 years