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EUROPEAN LEGISLATION ON AIR-QUALITY AND HEALTH; ISSUES RELATED WITH THE CITY OF ISTANBUL BASED ON AN INVENTORY OF EMISSIONS

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ABSTRACT

For atmospheric pollution, dose-response relationships are not easily established due to the limited number of effects which are usually well within the error margins of statistical analysis. With this work we are trying to forecast the health effects at the greater metropolitan area of Istanbul based on emissions and concentrations reported in scientific literature. This area has the second highest population in Europe and is one of the highest developing infrastructures where emissions are expected to change significantly during the coming years. The European legislation is also reviewed for air-quality, emission and health standards with which will be set the standards for future compliance.

Key Words: Urban Air-Quality, Emission Health, European Legislation, Istanbul.

1. RELEVANT LEGISLATION

Environmental policies for sustainable development in urban and rural areas are formulated so they meet environmental and economic objectives. These objectives can be expressed in various ways as applied to different time periods mostly with data following the temporal evolution of emissions. Ideally, the policies should cover reasonably long time periods since some of the effects (for example, on human health) may be partially cumulative in nature, and therefore air-quality and emissions in several consecutive years are of importance.

The European Commission with the Environment and Health Strategy in 2003 (COM (2003) 338 final) and the European Environment and Health Action Plan in 2004 (COM (2004) 416 final) has set the objectives to reduce among others the human exposure by environmental factors in the EU and to identify and prevent new health threats caused by the environment. In order to strengthen the capacity for policy making in this area researchers are called upon to recognize the novel potential of integrated assessments for monitoring atmospheric pollution and in deployment of new technological tools which attribute the pollutant concentrations to emission sources.

Relevant EU legislation with regards to emissions and air-quality are shown at Table 1 (http://europa.eu.int/comm/environment/legis_en.htm). There is shown an early emphasis on mobile-source regulation, other than heating and stationary source

regulations. Then “optional harmonization” process was introduced which was then followed by examination of the ozone-forming VOCs and NO_x. These were thought to be primarily mobile-source problems whereas acidifying sulphur dioxide emissions were thought to be primarily stationary-source problems.

Table 1. Extract of environmental legislation at EU.

Directives	Year	Main Provisions
90/313	1990	Established requirements for the public’s freedom of access to environmental information.
91/441	1991	Extended small-car standards of 89/458 to all size classes.
91/542	1991	Tightened heavy-duty diesel vehicle CO, HC, NOx standards. Established heavy duty diesel PM standards
92/72	1992	Requires O_3 monitoring. Sets health and vegetation-based O_3 concentration standards.
94/12	1994	Introduces more stringent limit values for all ambient pollutant concentrations. Reflects Auto/Oil study recommendations to evaluate all transportation-related policies according to cost/effectiveness guidelines.
96/61	1996	Integrated Pollution Prevention and Control Directive created multi-media permitting system.
96/62	1996	Air-Quality Framework Directive. Defines and sets objectives for ambient air quality. Requires assessment of ambient air quality and the availability of this data to the public, including alert notices when threshold values are exceeded. Requires maintenance of good air quality.
96/63	1996	Controls VOC emissions from petrol storage and distribution.

The objectives of the present work are to increase the current understanding of the situation at Istanbul, before commitments are taken for decreases in total emissions (or for assessing the effects of reduced trans-boundary fluxes). Based on a comparison of local emissions and air-quality in urban domains with similar population density a forecast is made about health effects at the metropolitan area of Istanbul. This area, with the second largest population in Europe, is one of the highest developing infrastructures where emissions are expected to change significantly during the coming years. Hence, it should be possible to demonstrate “dose-response” relationships at numbers which are outside the error margins of statistical analysis as is frequent the case in all other European domains. The add-value of this work is also the direct comparisons of emission inventories based on the technologies established during the AutoOil programmes.

2. HEALTH IMPLICATIONS

For the domain of Istanbul it is difficult to carry out full scale epidemiological studies for assessing the importance of atmospheric pollution to the population health. Monitoring data for ozone and particulate matter are only emerging in the scientific literature now so for the purposes of this study we will utilise ambient air NO_2. This is in large part derived from the oxidation of NO, the major source of which is combustion emissions, mainly from vehicles. NO_2 is therefore a clear

indicator for road traffic. NO_2 is also subject to extensive further atmospheric transformations that lead to the formation of O_3 and other strong oxidants that participate in converting NO_2 to nitric acid and SO_2 to sulphuric acid and subsequent conversions to their ammonium neutralization salts.

The current WHO guideline values for NO_2 1-hour level are 200µg/m3 and for the annual average 40 µg/m3. Since the previous review, only a small number of additional human exposure studies have been carried out. Health risks from nitrogen oxides may potentially result from NO_2 itself or its reaction products including O_3 and secondary particles. Oxides of nitrogen destroy organic matter such as human tissue. Animals exposed to NO_x are less able to ward off bacterial infections and die more often. Their susceptibility to viral infection increases, exposure to high levels of NO_x for weeks causes emphysema-like changes in the lungs of animals. Children aged 12 and younger who are exposed to NO_x have more respiratory illness (Harrington et al., 1985). Those exposed to high levels of NO_x outdoors had more colds that settled in their chests, chronic wheezing and cough, bronchitis, chest cough with phlegm, and episodes of respiratory illness (Hasselblad et al., 1992).

Epidemiological studies of NO_2 exposures from outdoor air are limited in being able to separate direct and indirect risks to human health. Evidence of the health effects of NO_2 by itself thus comes largely from toxicological studies and from observational studies on NO_2 exposure indoors. The studies of outdoor NO_2 may be most useful under the following circumstances:

- Evidence for NO_2 effects assessed at fixed levels of exposure to other pollutants
- Evidence for modification of PM effects by NO_2, possibly indicating potential consequences of HNO_3 vapour and/or PM nitrate.

Indeed, some additional emphasis might be given to NO_2 as a marker for traffic and industrial-related air pollution and an important source of a range of more toxic pollutants that probably act in combination to produce adverse health effects.

3. THE URBAN INFRASTRUCTURE

For the identification of health effects due to environmental factors it is necessary to look in domains with high population concentrations. In Europe apart for the Greater metropolitan area of Moscow the three largest areas are the metropolitan areas of Istanbul, Paris and London (Bliss, 2000). Among those areas, Istanbul has a warmer climate closer to Mediterranean for this reason for realistic emission comparisons we also include at this study the domain of Athens. The populations at these domains are summarised at Table 2 (www.factbites.com/topics/):

Figure1 also shows the population density at the Istanbul, Paris and London which are the second, third and forth most populous urban areas in Europe. The population density is homogeneously processed from the census data of early 2000s with a locally developed algorithm with a spatial resolution of 1x1 km2. As seen from Tables 2 and 3 and from Figure1, the Greater Metropolitan area around Istanbul is expected to have increases in urbanisation rate due to continuing immigration. In

addition the increased rates of industrialization are expected to increase the rate of unwanted urban pollution in the atmosphere.

Table 2: Population Comparisons

Domain	Population (million inhabitants)	Max Population Density (inhabitants/km^2)
Istanbul	11.000	40523
Paris **Greater Met. Area**	2.147 11.174	23125
London **London Greater Met. Area**	7.172 13.945	7982
Athens	3.762	30207

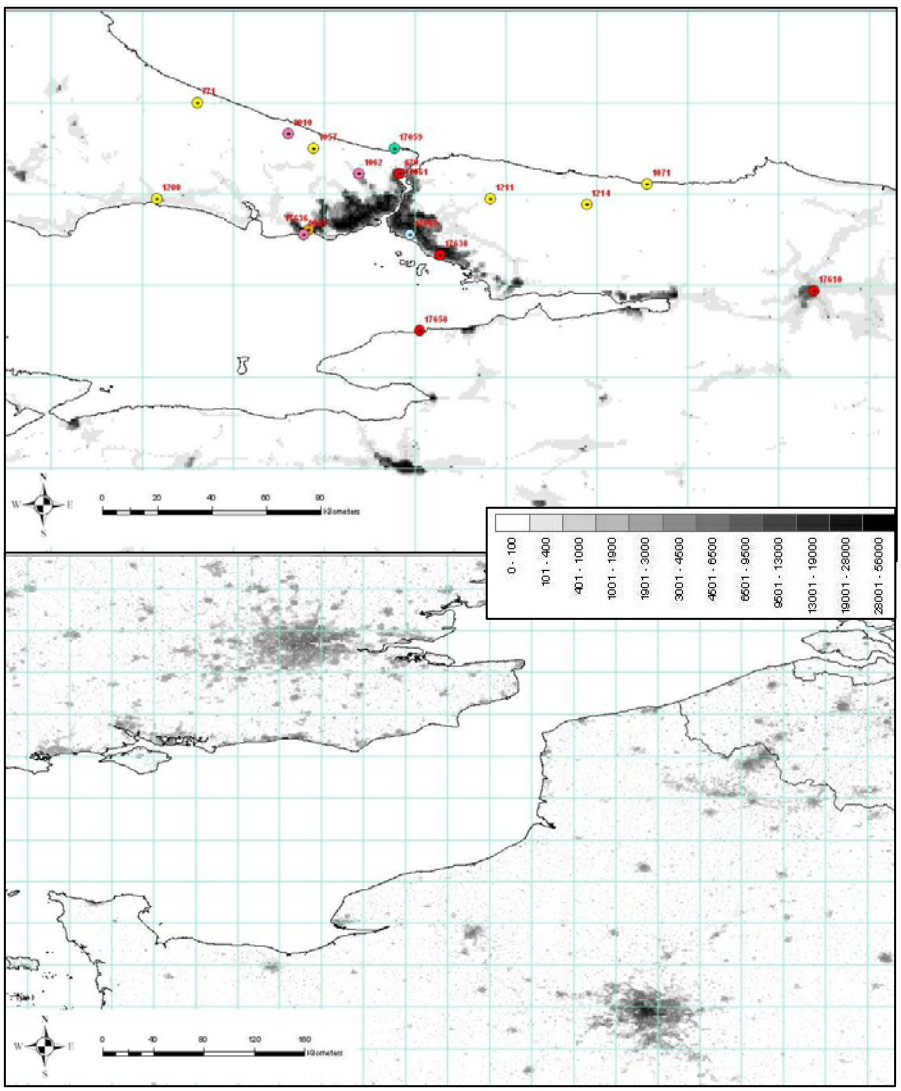

Figure1. Population density per km^2 at large European urban areas.

Table 3 also shows information concerning the general urbanisation trends based on national statistics (www.factbites.com/topics/). At this table, population growth rate

is the average annual percent change in the population, resulting from a surplus (or deficit) of births over deaths and the balance of migrants entering and leaving a country. The growth rate is a factor in determining how great a burden would be imposed on a country by the changing needs of its people for infrastructure, resources and jobs. It is also a parameter which is associated with urban emissions and how these will change in future years.

Table 3: National trends on population changes.

Population Data	**Turkey**	**France**	**UK**	**Greece**
Population Growth Rate (%)	1.09	0.37	0.28	0.19
Urbanisation (%)				
1975	41.6	73.0	88.7	55.3
2001	66.0	76.0	90.0	60.0
2015	71.8	78.4	90.8	65.1
Pop. Living in Urban Areas (%)				
2003	66.0	76.0	89.0	61.0

The urbanisation rate is based on estimates and projections of urban and rural populations as given by the Population Division of the United Nations Secretariat and published every two years. Urban-rural classification of population in internationally published statistics follows the national census definition, which differs from one country or area to another. National definitions are usually based on criteria that may include any of the following: size of population in a locality, population density, distance between built-up areas, predominant type of economic activity, legal or administrative boundaries and urban characteristics such as specific services and facilities. Population living in urban areas is the actual percentage of people living in urban areas during 2003.

4. ATMOSPHERIC EMISSIONS

For the purpose of this work, and prior to assessing the risk from exposure to air-pollutants, it is essential to associate emissions to air quality. Hence, to assess what are the levels of expected annual concentration. For city of Istanbul the level of emissions are not easily found.

In Figure 2 are illustrated the emissions from NO_x (as NO_2), SO_x (as SO_2), CO and NMVOCs, at the EMEP grid corresponding to the centre of Istanbul. These emissions are examined from several years during 1980 to 2002. The Sectors of Emission Sources as provided by EMEP (Vestreng and Klein 2002 and Vestreng, V. et al., 2004) are as follows and do not include the emissions from Large Point Sources (e.g., power plants or large industries):

1-Combustion in energy & transformation industries, 2-Non-industrial combustion plants, 3-Combustion in manufacturing industry, 4-Production processes, 5-Extraction and distribution of fossil fuels and geothermal energy, 6-Solvent use and other product use, 7-Road Transport, 8-Other mobile sources and machinery, 9-Waste treatment and disposal, 10-Agriculture and 11-Other sources and sinks.

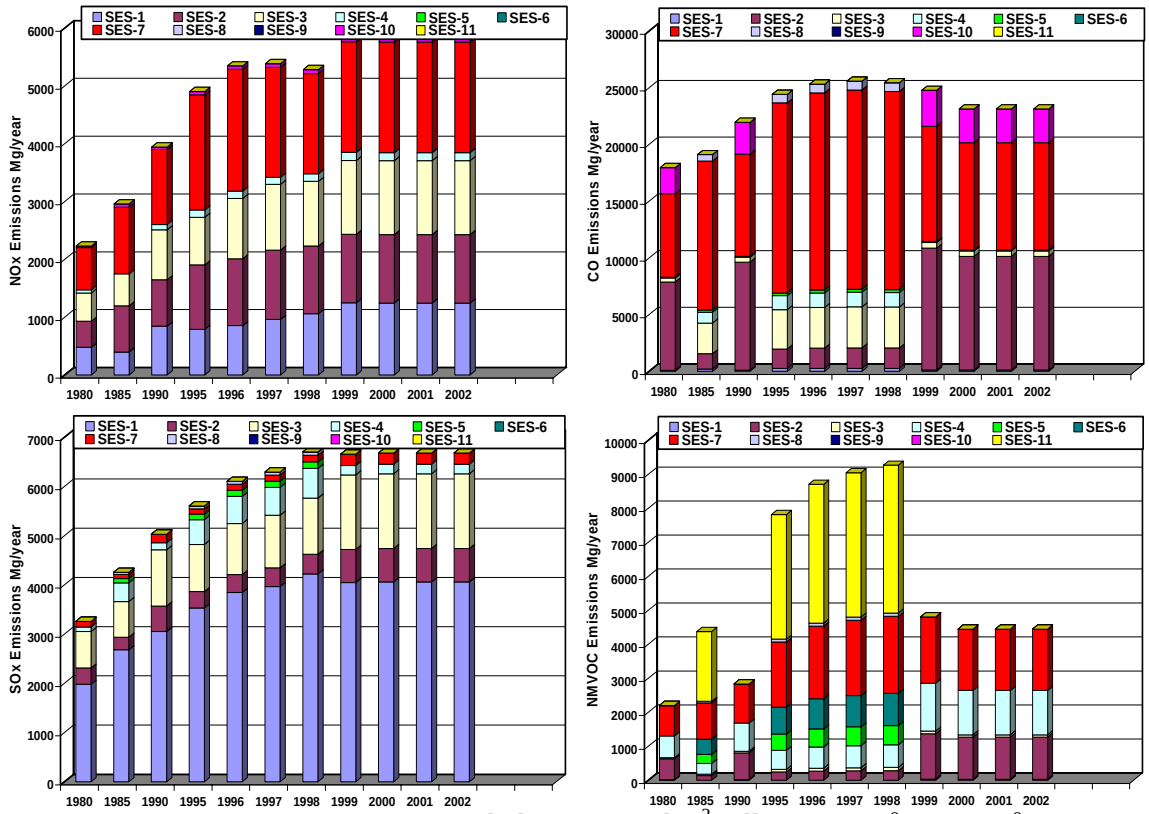

Figure 2. 1980-2002 Emissions at Istanbul in a 50x50 km^2 cell at "28.843^{o}E, 40.823^{o}N"

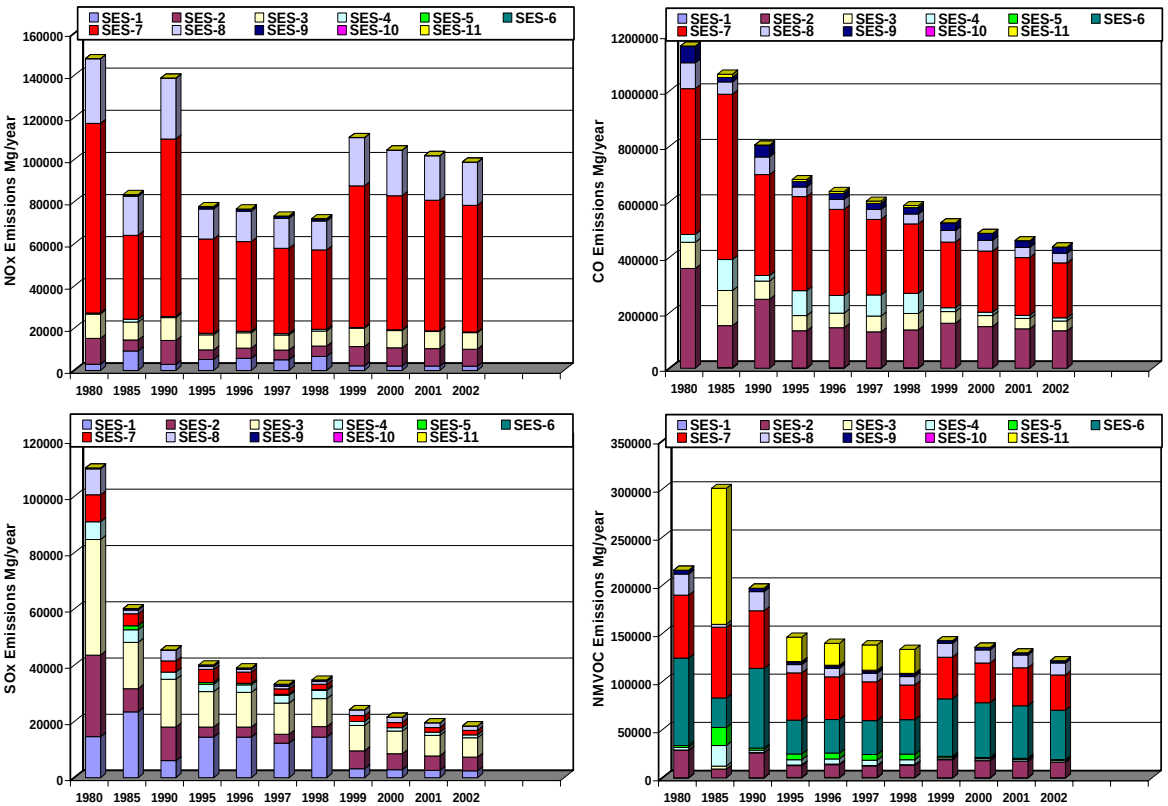

Figure 3. 1980-2002 Emissions at Paris in a 50x50 km^2 cell at "2.046^{o}E, 48.820^{o}N".

It is evident from these figures that traffic is an important source for NO_x and CO, but also the important contribution of combustion in energy & transformation industries for NO_x and SO_x as well as the importance of non-industrial combustion plants for NO_x and CO.

At Figure 3 are shown similar graphs for a similar size grid cell for the city of Paris. Noticeable are first the scale which is 20 times higher for CO and NOx, 10 times for SOx and NMVOCs. Here, again we have the importance of traffic for NOx and CO, but the lower importance of combustion in energy & transformation industries for NO_x and SO_x. Clearly the persistence of SO_x and NO_x emissions at the domain of Istanbul is also an important observation from comparisons in these domains.

Similar comparisons have been carried out for the centre cells of London and Athens. However, since the levels and the scale for these domains are similar the corresponding plots are not included here. Only indicative are shown at Figure4 the levels of total NOx and the traffic NOx emissions in all domains. It is evident from this figure that the percentage attributed to traffic is significantly less than the Paris and London and that the total emissions are significantly lower at Istanbul. Hence, as a first estimate from these comparisons are that the expected concentrations should be significantly those from what observed in those two of Paris and London. It is also expected that significant increases will be noticed when the ratio of 28 cars per 1000 people (State Institute of Statistics, 2005). A trend that is already observed with the recent rates of introducing new cars registrations at the Greater Area of Istanbul.

Despite the fact that the expected concentrations are to be lower, the fact that the population density at several cells at Istanbul are triple of those found in Paris and fact that emissions from traffic are to significantly higher means makes the domain of Istanbul ideal for establishing dose to health effects relationships.

Of significant importance remains the verification that those emission numbers represent reality. The best way of carrying out this process are construction of an emission inventory in higher resolution (1x1 km^2) and the aggregation of cells to a 50x50 km^2 resolution. In the absence of emission data from the open scientific literature the verification process can be carried out from the emission data quoted at www.nationmaster.com. The data are summarised at Table 4.

Table 4. National trends on emissions and concentrations

Emission/AQ Data	**Turkey**	**France**	**UK**	**Greece**
NO_x emissions per capita,	14.1	22.7	26.3	29.8
NO_x emissions per populated area	0.33	0.99	2.76	0.47
NO_x Change 1990-early 2000s (%)	48	-29	-43	11
SO_x emissions per capita	31.3	9.0	16.6	47.7
SO_x emissions per populated area	0.65	1.09	5.37	1.83
SO_x Change 1990-early 2000s (%)	33	-60	-73	4
Urban NO_2 concentration (1995)	9.45	56.61	64.47	64
Urban SO_2 concentration (1995)	87.02	13.89	21.96	34

At the aforementioned table, NO_x and SO_x emissions are expressed as NO_2 and SO_2 respectively. The units are Kg per capita (based on 2000 and 1990 census) and were obtained from OECD (www.oecd.org/dataoecd/11/15/24111692.PDF). For the emissions per populated land area, these are expressed in Gg/km^2. For this parameter were used the total emissions for each country by summarizing emissions data, originally available as a grid map with 1 deg x 1 deg cells. Air pollution is generally greatest in densely populated areas. To take this into account, were used the girded population of the world dataset available from CIESIN and calculated the total land area in each country inhabited with a population density of greater than 5 persons per km^2. This land area was then used as a denominator for the emissions data.

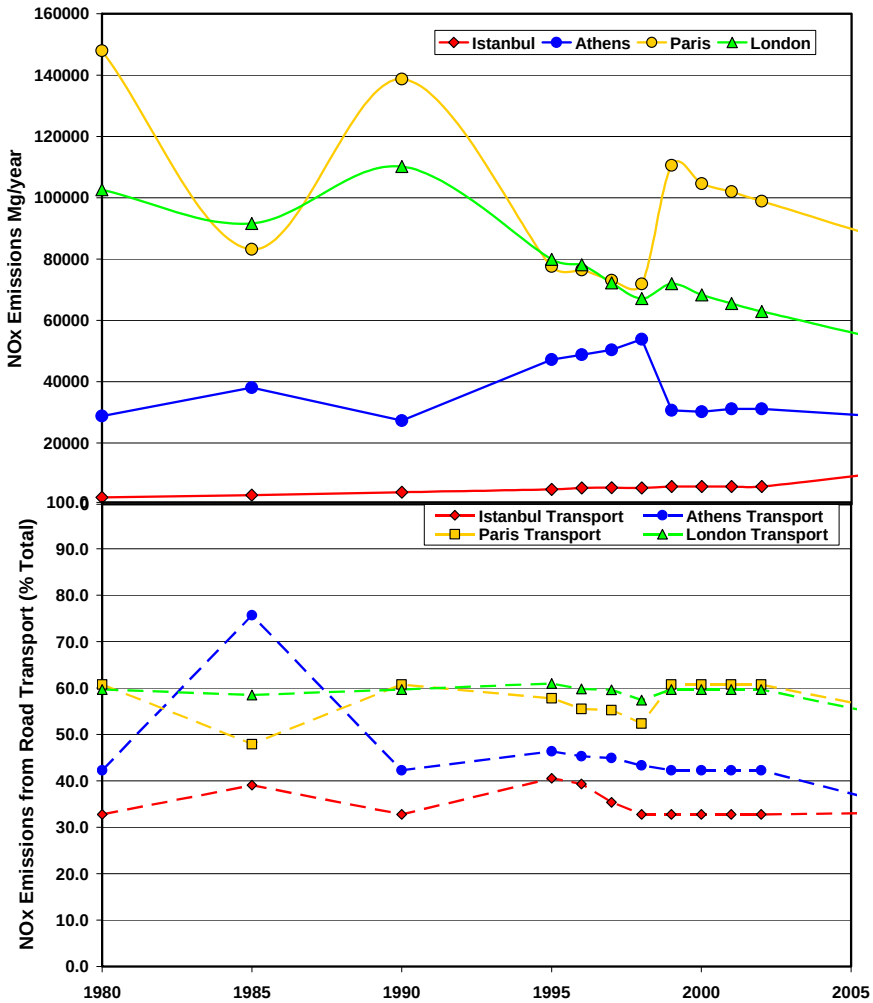

Figure 4. Comparison of NO_x emissions in equal size city cells. Upper graph corresponds to total emissions and the lower graph to the percentage of emissions from road transport.

For urban NO_2 and SO_2 concentration the units used were $\mu g/m^3$. The values were originally collected at the city level. Each nation varied in terms of the number of cities reported, so this data should be used with some caution. Within each country the values have been normalized by city population for the year 1995, then added together to obtain the total concentration for the given country.

It should be stated that in the recent years, the limitations set by the Istanbul Metropolitan Municipality have increased the usage of natural gas and quality coal for heating instead of under-quality coal. This ensured lower CO and SO2 levels especially compared to the previous years. Additionally, the industries within the city were moved to the organized industrial zones located outer parts of Istanbul.

5. PROJECTION OF HEALTH CASES

Systematic air-quality monitoring data are not easily available and for this reason the concentrations for necessary for assessing the health risk are taken from Onkal-Engin et al., 2004. In this study, data were collected at 6 different air monitoring sites, at Kagithane, Besiktas, Esenler, Sariyer, Fatih and Bagcilar. All sites were located on the European side of Istanbul and the population at this area is approximately 30% of the total population. This area has mostly residential areas and some industrial regions. Industrial activity takes place especially in Esenler region. Concentrations were measured by mobile vehicles equipped with air monitoring instruments. The data were collected daily and covered a period of 20 months, from January 2000 to August 2001. According to this work the NO_2 concentration ranged from 58 to 65$\mu g/m^3$.

As noted at section-2, the concentration-response relationships are not readily established for NO_2 from experimental or observational data. For acute effects of NO_2, the evidence comes primarily from human exposure studies. These studies are carried out with relatively small numbers of health volunteers do not provide easily any evidence in a range relevant to current standard setting. Associations have been observed only between NO_2 and mortality in daily time-series studies, but on the basis of present evidence these cannot be attributed only to NO_2 with reasonable certainty. However, since NO_2 is often highly correlated with levels of other ambient pollutants emitted by the same sources or related through complex atmospheric reactions, NO_2 will be used for the purposed of this study as a surrogate for unmeasured traffic related pollutants such as organic and elemental carbon or freshly emitted primary ultra-fine particles (WHO 2003, WHO 2005).

Based on the evidence from several Italian cities for the year 2004 and with urban measuring stations in close proximity to the kerbside the following relationship between concentration and heath effects is established. Compatible data have been produced by several other studies (Katsouyanni et al. 2001, Hoek et al. 2002, Stieb et. al 2002 etc), but for the indicative purposes of this work and because of the close similarity of the climatic conditions during 2004 the data from Figure5 are considered adequate.

Based on the population reported in table 1, the NO_2 concentration reported in reviewed literature (Onkal-Engin et al., 2004) and Figure5, it is reasonable to expect at least 4600 deaths that could be attributed to atmospheric pollution.

The fact that Istanbul has regions with the highest population density in Europe together with fact that the climate allows acute pollution episodes during the year

make this domain ideal for identifying if there are health consequences from atmospheric pollution or not. These studies are beyond the scope of this introductory work. However, prior to the epidemiological studies it will be necessary to carry out detailed monitoring at various locations for several years (Skouloudis, 1997) in particular at hot spots locations according to an emission inventory with high spatial resolutions (at least 1x1 km^2). This will need to be followed by a detailed source apportionment of concentrations according to the methodology developed by AutoOil-2 (Skouloudis 2000, EC DG-ENV 2001).

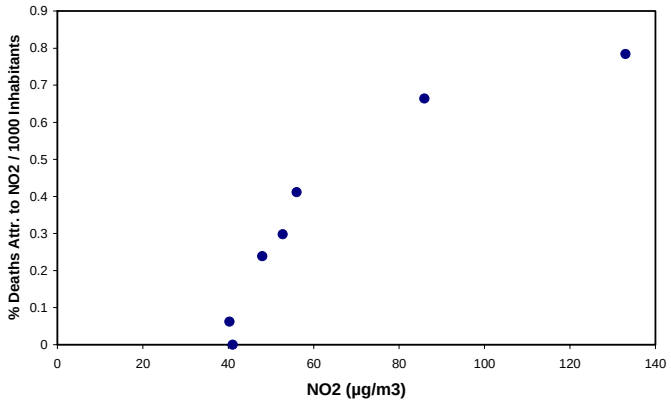

Figure 5. Deaths attributed to atmospheric pollution at Italian cities in 2004.

6. PROSPECTIVES AND FINAL REMARKS

The ultimate goal of any clean air policy is to develop strategies to reduce the risk of adverse effects on human health and the environment as a whole caused by ambient air pollution. With current data structure it is difficult to reveal the link between those effects. It well known from long-term studies that the spatial variation of NO_2 levels within a city and the absence of health data with high temporal resolution (less than days) have weaken the ability to detect effects of atmospheric pollution on population.

On the other hand, measurements from urban background sites and the planning of campaigns in cities with small population density or in areas where emission reductions were carried out such as in the Harvard Six City Study or the American Cancer Society Study have by definition little chance to provide evidence of relating air-pollution doses to health effects.

For these reasons, data from the city of Istanbul with the existence of very susceptible populations, with climatic conditions which are not of the Mediterranean extremes or of the cold European north, are of particular importance in identifying health effects. This city offers the ability to detect effects even if they are infrequent with the low but raising emissions observed in comparison to other European cities where significant emission reductions have been carried out. We may therefore be confronted with situations of identifying thresholds and hence modify the setting standards to protect public health.

Risk reduction strategies are and will continue to be powerful tools in promoting public health. However, these tools have large verification uncertainty when conducted in areas where the benefits are not quantifiable in significant population numbers. The development of such strategies requires not only qualitative, but also quantitative knowledge of relevant effects. For this reason a network for adequately reporting air-quality concentrations is essential. At the same time the geographical attribution of emissions need to be established and verification of exposure should be carried out with air-quality modelling tools.

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AIR QUALITY MONITORING – ESTABLISHING CRITERIA FOR STATIONS CLASSIFICATION

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ABSTRACT

According to the Council Decision 97/101/EC on Exchange of Information, stations should be classified in relation to the type of area where they are located and according to the type of dominant emission sources influencing the air pollutant concentrations at the station.

A detailed methodology was developed for the validation of the classification of Portuguese air quality monitoring stations, through objective criteria to assure a harmonized interpretation of the definitions, from region to region.

In relation to the criteria for area types, best results were found for the population density within a 1km radius in the surroundings of each station. In relation to dominant emission sources, were pointed out criteria based upon several pollutants concentrations.

Key Words: Air Quality, Monitoring, Stations Classification, Emission Sources

1. INTRODUCTION

In the Eighties and Nineties the assessment of air quality within European Members States was based on networks of air quality monitoring stations established according to their specific realities.

More recently, in the Council Directive 96/62/EC of 27 September 1996, was considered necessary to establish a procedure for the exchange of information between the Member States on air quality, in order to help combat pollution and nuisance. That Directive established the framework for assessment and management of ambient air quality on the basis of common methods and criteria. In the so-called Daughter Directives can be found other criteria related with classification and location of sampling points. The Commission Decision 97/101/EC, of 27 January 1997, brought the concept of harmonization to exchange of information and data on ambient air quality in the European Union.

The Portuguese air quality monitoring network includes 73 stations (operating in 2005) managed by regional authorities.

In 2000 and 2001 the Environmental Institute in cooperation with the Faculty of Sciences and Technology of the New University of Lisbon collected information about the meta-information of all the national network stations, in each location (available in a data base at www.qualar.org). After these visits, were performed some adjustments to the stations classification according to the specifications set in the recent legislation. For the most recent stations have been accepted the classifications given by regional authorities.

However, some issues had been raised: there is a necessity of using common criteria to uniformize the process of stations classification; the definitions established on the Commission Decision 2001/752/EC are too vague; and several doubts remained after applying the referred definitions to the existing stations.

All those issues pursuant the development of this study, that aimed to validate and clarify air quality monitoring stations classification, through objective methodologies based upon a common procedure that assure a harmonized interpretation of the definitions, from region to region, in compliance with European legislation. The stations classification must obey to a set of common rules in order to increase the compatibility and comparability of the data transmitted

According to the Annexes of Council Decision 97/101/EC on Exchange of Information, as revised by Commission Decision 2001/752/EC of 17 October 2001, air quality monitoring stations should be classified in relation to the dominant emission sources influencing the air pollutant concentrations at the station:

- Traffic - located such that its pollution level is determined predominantly by the emissions from nearby traffic (roads, motorways, highways);
- Industrial - located such that its pollution level is influenced predominantly by emissions from nearby single industrial sources or industrial areas with many sources;
- Background - located such that its pollution level is not influenced significantly by any single source or street, but rather by the integrated contribution from all sources upwind of the station;

and according to the area type where they are located:

- Urban - continuously built-up area;
- Suburban - largely built-up area: continuous settlement of detached buildings mixed with non-urbanised areas (small lakes, woods, agricultural);
- Rural - all areas that do not fulfil the criteria for urban or suburban areas are defined as rural areas.

Two distinct methodologies were identified to validate the stations classification in relation to dominant emission sources and in relation to the type of area.

2. METHODOLOGY

2.1. Validation of air quality monitoring stations by type of area

The validation of stations classification by type of area is based on criteria that allow distinguishing the Urban, Suburban and Rural classes of stations.

All the 51 monitoring stations operating in Portugal in 2003 were considered in the study.

According to the Guidance on the Annexes to Decision 97/101/EC on Exchange of Information as revised by Decision 2001/752/EC (or in short the Guidance on the Annexes), the definitions of area types are based on the distribution/density of buildings. However other elements such as population density, size of the area and land-use information can be taken into consideration when classifying the area in particular for "limit" cases (European Commission - DG Environment, 2002).

Population density in the surrounding area of the station was used as indicator. To verify the classification of the stations some indicators, related with Portuguese territorial administrative levels, were tested. The *freguesia* is the smallest Portuguese territorial administrative unit. It is divided in small statistic areas - the statistic sections and sub-sections - for demographic purposes. The statistic sub-section is the smallest homogenous area within the *freguesia* and corresponds, for example, to the block in urban areas. Thus, three indicators were tested: population density in the *freguesia* where each station is located; population density in the statistic sub-sections; and population density in the circular area of 1 km around the station, based on the smallest territorial unit the statistic sub-section (best results were found for this last indicator).

The following steps were applied:

- get the geographical localizations of all the stations;
- define a circular area with 1 km radius around each station;
- select the statistic sub-sections that are included (or have the majority of their area included) in the circular area with 1 km radius around the station;
- sum the populations and the areas and calculate the respective population densities within the circular area of 1 km radius around each station;

- define limits of population densities that allow distinguishing each one of the three area types (Urban, Suburban and Rural).

Once this methodology is applied it as to be verified, at last, in which of the three intervals fits the population density in 1 km radius around the station, and consequently which is the type of area of the station – Urban, Suburban or Rural.

To distinguish each typology of area types were established limits of population density:

- Rural areas were established as those with a population density less or equal to 500 inhabitants/km^2;
- Suburban areas were established as those with a population density between 500 and 2000 inhabitants/km^2 (or between 500 and 3000 inhabitants/km^2) – once an objective criterion does not exist to distinguish the Urban and Suburban typologies, those two limits were tested and were the ones that fit better to the pre-existing classifications;
- Urban areas were established as those with a population density greater then 2000 inhabitants/km^2 (or greater then 3000 inhabitants/km^2).

For the cases with population density between 2000 and 3000 inhabitants/km^2 the knowledge of the technician of the regional authorities is essential to decide which typology is the most appropriate.

The density population data was obtained from the "2001 Census – XIV Population General Census" (INE, 2001). A Geographical Information System software was used - the ArcGIS 8.3 from ESRI® Arc Map™ 9.0.

2.2. Validation of air quality monitoring stations in relation to dominant emission sources

The validation of stations classification in relation to dominant emission sources is based on criteria that allow distinguishing the classes of Traffic, Industrial and Background. The proposed methodology is based on the analysis of pollutants levels, by studying sets of data from 1995 to 2002, measured in the 43 stations, with annual efficiency grater or equal to 50%.

The data analysis was performed for the pollutants nitrogen dioxide (NO_2), nitrogen monoxide (NO), oxides of nitrogen (NO_x), carbon monoxide (CO), particulate matter (PM_{10}), sulphur dioxide (SO_2), and ozone (O_3).

According to the Guidance on the Annexes, as far as possible and in addition to the general type applying to the station as a whole, it is asked to classify the station as for each of the different pollutants that are measured at the station (at least for the pollutants covered by air quality Directives). It must be kept in mind that a station can be classified differently when considering the different pollutants.

Several statistical indicators and ratios between pollutants were tested. This approach allowed the comparison between statistical parameters and to understand their relation with stations classification. Were pointed out criteria (shown in Table 1) to verify the classification of the stations for different pollutants measured (NO_2, NO, NO_x, CO, SO_2), and criteria to apply to the station as a whole (based on the classification for each pollutant, ratios NO/NO_2, NO/O_3, NO_2/O_3, and criteria for

O_3). These criteria consist in pollutant concentrations, with which is made a comparison to verify if they are frequently exceeded by the concentrations measured in each station.

The stations classification by pollutant in one of the classes Traffic, Industrial or Background is done as it follows:

- for each year and each pollutant a station belongs to one of the two classes shown in Table 1 if in the majority of the referred parameters is shown compliance with a typology, otherwise belongs to the background typology;
- the final typology for each pollutant is the one that prevail in the majority of the years in analysis.

Table 1. Criteria to verify stations classification in relation to the dominant emission sources, by each pollutant

Pollutant	Parameter	Traffic typology if the concentration ($\mu g/m^3$) is:
NO_2	Annual average (hourly basis)	>30
	Percentile 50 (hourly basis)	>20
	Percentile 98/ Percentile 50	<3,5
NO	Annual average (hourly basis)	>25
	Annual maximum (annual average from 0 to 23 hours)	>45
	Annual average (annual average from 0 to 23 hours)	>20
	Annual minimum (annual average from 0 to 23 hours)	>5
	Annual minimum (annual average from 13 to 16 hours)	>10
NO_x	Annual average (hourly basis)	>50
CO	Annual average (8-hourly basis)	>450
	Percentile 50 (daily basis)	>500
	Annual maximum (annual average from 0 to 23 hours)	>700
	Annual average (annual average from 0 to 23 hours)	>450
	Annual minimum (annual average from 12 to 15 hours)	>300
	Maximum-Minimum (annual average from 0 to 23 hours)	>400
Pollutant	Parameter	Industrial typology if the concentration ($\mu g/m^3$) is:
SO_2	Annual maximum (hourly basis)	>400
	25º Annual maximum (hourly basis)	>175
	Annual average (hourly basis)	>13
	Percentile 98 (hourly basis)	>40
	Percentile 50 (hourly basis)	>6
	4º Annual maximum (daily basis)	>60

The global validation of stations classification as a whole is based on the classification obtained for each pollutant (defined as previously indicated, with criteria presented in Table 1), criteria based on ratios between pollutants and criteria for ozone, as shown in Table 2.

Table 2. Criteria to verify the global classification of stations in relation to the dominant emission sources

Pollutant	Parameter	Traffic typology if the concentration (expressed in $\mu g/m^3$) is:
O_3	Annual average (hourly basis)	<35
	Percentile 50 (hourly basis)	<35
	Summer annual average (hourly basis)	<45
Ratios between pollutants	Annual average NO/ Annual average NO_2	>0,8
	Annual average NO/ Annual average O_3	>0,6
	Annual average NO_2/ Annual average O_3	>0,8

A station as a whole is globally classified as Traffic if the concentrations measured show compliance with that typology criteria (based on the classification for each pollutant, ratios between pollutants, and criteria for O_3, as shown before), otherwise that station would be classified as Background. In the cases where some doubts still remaining, a more detailed analysis is necessary (including localization criteria). The Industrial typology depends only on the classification obtained for SO_2.

If a station has simultaneously traffic and industrial influence is necessary to get more information to decide, once the different station types are mutually exclusive as they reflect the influence of the predominant or prevailing emissions.

3. RESULTS AND DISCUSSION

3.1. Validation of air quality monitoring stations by type of area

In Table 3 is shown the current stations classification, the values of population density in the circular area of 1km in the surroundings of the station, and at last the classifications obtained after applying, to this indicator, the limits defined in the methodology. This methodology was applied to the 51 monitoring stations operating in Portugal in 2003, however, to resume the Table 3 contents, are only shown the stations for which were obtained a different classification from the current one.

The application of the developed methodologies pointed out several potentially wrong classified stations in terms of type of area:

- for six of the 51 stations considered were obtained different classifications from those that are in use (their current classification doesn't fulfil the criteria for their area type, for what, another classification is better applied);
- for other five, some doubts remain on the classification between the typologies Urban and Suburban (their population densities are between the 2000 and 3000 inhab./km^2; in these cases the knowledge of the technicians from the regional authorities is essential to determine the most correct classification);
- for all the other stations were obtained the same classifications as the current ones.

Table 3. Results obtained for stations classification by type of area

Zone	Station name	Current classification by area type	Population density in the circular area of 1km radius (inhab./ km^2)	Proposed classification according to the circular area of 1 km radius around the station	
				Case A	Case B
Porto Litoral	Ermesinde	Suburban	7573	Urban	Urban
Porto Litoral	Custóias	Suburban	2353	Urban	Suburban
Porto Litoral	Baguim	Suburban	3034	Urban	Urban
Vale do Ave	Santo Tirso	Urban	2209	Urban	Suburban
Z. I. Estarreja	Avanca	Rural	685	Suburban	Suburban
Coimbra	Av. Fernão Magalhães	Urban	2029	Urban	Suburban
AML Norte	Alfragide	Suburban	6337	Urban	Urban
AML Norte	Loures	Urban	2452	Urban	Suburban
AML Sul	Paio Pires	Urban	2652	Urban	Suburban
Alentejo Litoral	Monte Chãos	Suburban	4	Rural	Rural
Alentejo Litoral	Santiago do Cacém	Urban	1094	Suburban	Suburban
Legend: Limits for typologies intervals: Case A - Rural ≤500, Suburban]500;2000], Urban >2000 (inhab./km^2) Case B - Rural ≤500, Suburban]500;3000], Urban >3000 (inhab./km^2)					

3.2.Validation of air quality monitoring stations in relation to dominant emission sources

Trough the application of the methodology exposed in the previous section (for each of the 43 stations in analysis and for each of the years with data) is obtained the classification for each pollutant (NO_2, NO_x, NO, CO and SO_2) and for the station as a whole. Those classifications are obtained in an annual basis, i. e. for each year in analysis, and in the end is made an aggregation of information, resulting the final evaluation for each station.

In Table 4 can be found the results for global stations classification, only for all the cases where some doubts were raised in relation to the current typology, i. e. for the cases for which the global classification can be different from the current one. In order to resume the Table 4 contents, only that short list of the main results is presented (instead of the results obtained for all the stations). The results obtained for each station are aggregated for all the years with data.

The application of the developed methodologies pointed out several potentially wrong classifications in terms of dominant emission sources:

- in relation to the classification per pollutant, some stations were classified differently for different pollutants;
- in relation to the global classification of stations as a whole, doubts were raised in thirteen situations:
  - in four Background stations was detected traffic influence for some pollutants, however, it is not sufficient to determine the change of the global classification into Traffic typology;
  - two of the Industrial stations didn't validate, for more then a half of the years in analysis, the criteria defined for this typology;
  - one Industrial station has some traffic influence, however, the dominant emission source is still the industrial one;
  - in three Traffic stations the SO_2 levels shown industrial influence, however, traffic is the dominant emission source;
  - three of the Traffic stations measured low concentrations of pollutants associated to traffic influence.

Table 4. Results obtained for global stations classification in relation to dominant emission sources

Current classification	Station name	Classification by pollutant					Other criteria				Reached global class.
		NO_2	NO_x	NO	CO	SO_2	Ratio NO/NO_2	Ratio NO/O_3	Ratio NO_2/O_3	O_3	
Background	Ermesinde	T	T	B	-	B	B	B	T	T	Back./ Traffic
	Leça do Bailio	T	T	B	B	B	B	B	B	B	
	Chelas	T	T	B	B	B	B	-	-	-	
	Alfragide	T	T	B	T	B	B	B	B	B	
Industrial	Lavradio	T	T	B	B	I	B	T	T	B	Ind./ Traffic
	Monte Chãos	B	B	B	-	B	B	B	B	B	Ind./ Back.
	Santiago do Cacém	B	B	B	-	B	B	B	B	B	
Traffic	Rua dos Bragas	T	T	T	T	I	B	T	T	T	Traffic/ Ind.
	Entrecampos	T	T	T	T	I	T	T	T	T	
	Hospital Velho	B	T	B	T	I	B	T	T	T	
	Câmara Municipal	B	B	B	B	-	B	-	-	-	Traffic/ Back.
	Quebedo	T	B	B	B	B	B	-	-	-	
	Afonso III	B	B	B	T	B	B	B	B	B	

Legend: abbreviations of stations classification: T–Traffic; I–Industrial; B–Background;
abbreviations of global classification: class.–classification, Ind.-Industrial, Back.-Background.

4. CONCLUSIONS

This study aimed to develop objective methodologies that allowed the validation of air quality monitoring stations classification, according to the requirements of Council Decision 97/101/EC. Those common procedures assure a harmonized interpretation of the definitions of European legislation, from region to region.

Regarding the developed methodology for stations classification by type of area the following relevant aspects should be highlighted:

- the definitions of area types are based on the distribution/density of buildings. However, once that information is not available, was used instead the population density as indicator;
- after testing some indicators the selected one was population density in the circular area of 1 km radius around each station;
- to distinguish each typology of area types were established limits of population density (Rural $\leq$500 inhabitants/km^2, Suburban]500;2000] or]500;3000] inhabitants/km^2, Urban >2000 or >3000 inhabitants/km^2);
- the application of the developed methodologies pointed out several potentially wrong classified stations in terms of type of area: for six of the 51 stations were obtained different classifications from those that are currently in use; for other five, some doubts remain on the classification between the typologies Urban and Suburban;
- the proposed changes of stations classification must be assessed by the technician of environmental regional authorities that know well the stations surroundings.

Regarding the developed methodology for stations classification in relation to dominant emission sources the following relevant aspects should be highlighted:

- to define the criteria that allow to set a station typology, was taken into account the trend of pollutant levels measured since 1995 to 2002 and the current stations typology;
- several statistical indicators were tested and were pointed out criteria to verify the classification of the station for the different pollutants measured (NO_2, NO, NO_x, CO, SO_2), and criteria to apply to the station as a whole (based on the classification for each pollutant, ratios NO/NO_2, NO/O_3, NO_2/O_3, and criteria for O_3);
- the developed methodology was applied to sets of data measured at the stations, from 1995 to 2002, to verify stations classification (global and per pollutant);
- a station as a whole is globally classified as Traffic if the criteria for this typology are validated. Otherwise the global classification will be Background. In the cases were some doubts remain, it will be necessary to perform a more detailed analysis. The Industrial typology depends only on the classification obtained for SO_2. If a station has simultaneously traffic and industrial influence, it is necessary to get more information to decide which of the emission sources is dominant;
- in relation to the classification of the 43 air quality monitoring stations by dominant emission sources, per pollutant, some stations were classified differently for

different pollutants. For the global classification of stations, doubts were raised in thirteen situations.

5. ACKNOWLEDGEMENTS

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BIOMONITORING OF URBAN AND REGIONAL AIR QUALITY IN INDUSTRIALISED AND DEVELOPING COUNTRIES – EXPERIENCES AND PERSPECTIVES

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ABSTRACT

Unrestrained industrialisation and urbanisation have caused serious environmental problems in many developing countries, and despite emission reductions during the last decades, air pollution still represents one of the urgent environmental problems also in highly industrialised countries. In this paper, environmental monitoring using bioindicator plants is presented as an appropriate tool to detect and monitor air pollution effects thus supplementing information gained from conventional pollution monitoring and modelling. The use of bioindicator plants in urban and regional air quality control is illustrated by examples from two major projects dealing with industrial pollution in South America and urban pollution in several European countries. Recommendations for the successful use of bioindicator plants are given and perspectives for future application are discussed.

Key Words: Air Quality, Biomonitoring, Pollution Impact, Industrial Pollution, Urban Pollution

1. INTRODUCTION

Progressive and unrestrained industrialisation and urbanisation, together with insufficient emission control and shortcomings in environmental legislation and implementation of pollution abatement measures have caused serious environmental problems in many emerging nations in Asia, Latin America and Africa. Asian megacities figure among the most polluted cities in the world resulting in high rates of air pollution induced morbidity and mortality (Srivastava and Kumar, 2002; Molina and Molina, 2004; Fang et al., 2005; Gurjar and Lelieveld, 2005). The economic, social and ecological consequences associated with the elevated pollution levels cannot be overseen yet. Various global scenarios indicate that air quality in this region as well as in many other developing countries may further deteriorate rather than improve in the 21st century (Prather et al. 2003). Air pollution and climate change are interrelated and these linkages are considered in integrated policy approaches (EEA, 2004). In order to address the issue of air pollution in developing countries, several initiatives have been taken recently, e.g. the APMA project (www.asiairnet.org) and the Clean Air Initiative for Asian Cities (www.cleanairnet.org/caiasia), among others. But also

in highly industrialised countries, air pollution still represents one of the most urgent environmental problems although in those regions air quality has improved considerably over the last decades. Thus, during the last years, the European Union has been devoting several programmes and directives with an integrated view to improve air quality particularly as to pollutants responsible for acidification, eutrophication and ground-level ozone pollution as well as particulate matter (EU, 1996).

Air quality in urban agglomerations, industrial sites and rural areas may routinely be assessed by emission inventories, modelling and physico-chemical measurements of ambient pollutant concentrations. In many developing countries, however, such monitoring systems are still completely absent or are just in the phase of being set-up. Yet, it should be stressed that such measuring techniques permit to control whether air quality standards set in accordance with national and international legislation are adhered to, but that they do not provide any direct information regarding the possible impact of air pollution on man and environment. That is because the response of organisms to a given pollutant does not only depend on its concentration or dose, but also on a range of predisposing and accompanying factors. Hence, environmental monitoring using bioindicator plants is considered an appropriate tool to detect and monitor air pollution effects supplementing information gained from conventional pollution measurements and modelling. In regions with limited financial and technical resources, biomonitoring using indicator plants also offers the possibility to detect the presence of elevated pollutant levels and to determine the large-scale pattern and temporal changes of pollutant distribution (De Temmerman et al., 2004).

In the present paper, examples from two major projects will be given illustrating the use of bioindicator plants for the assessment and monitoring of air quality in urban agglomerations and industrial areas of developed and developing countries. In the first example, the implementation of a biomonitoring programme in a strongly polluted industrial area in Brazil and the main results obtained from the exposure of various bioindicator species over several years are depicted. The second example describes the use of highly standardised biomonitoring methods at more than 100 sites throughout Europe aiming at assessing and demonstrating the effects of air pollutants in urban agglomerations of eight countries. Finally, recommendations towards the successful application of bioindicators will be given and perspectives for future developments will be discussed.

2. SOME DEFINITIONS AND CONCEPTS

Bioindicators may be defined as “organisms or communities of organisms reacting to environmental factors with changes in their life functions and/or their chemical structure thus permitting to conclude on the state of the environment” (Arndt, 2001). Based on this definition, bioindicators may principally be differentiated into sensitive (or *response*) and accumulative indicators (Figure 1). While the **sensitive indicator** shows distinct biological effects, for example foliar injury, upon the exposure to a pollutant, **accumulative indicators** may show enhanced concentrations of a chemical compound without exhibiting a decreased vitality or visible injury symptoms. The two basic types of bioindicators can be found among **test organisms** which are

used in highly standardised laboratory procedures, **ecological indicators** which provide information on the conditions of whole ecosystems and finally **monitoring organisms** which are generally used for qualitative and quantitative monitoring of environmental conditions, e.g., in air quality control. Procedures which study or sample organisms already present in the ecosystem under investigation are called **passive biomonitoring**, whereas **active biomonitoring** means to introduce the monitoring organisms into the ecosystem under more or less standardised conditions (Arndt et al., 1987; VDI, 1999; Mulgrew and Williams, 2000). Studies applying active monitoring procedures like those presented in this paper generally follow a common methodological approach as displayed in Figure 2.

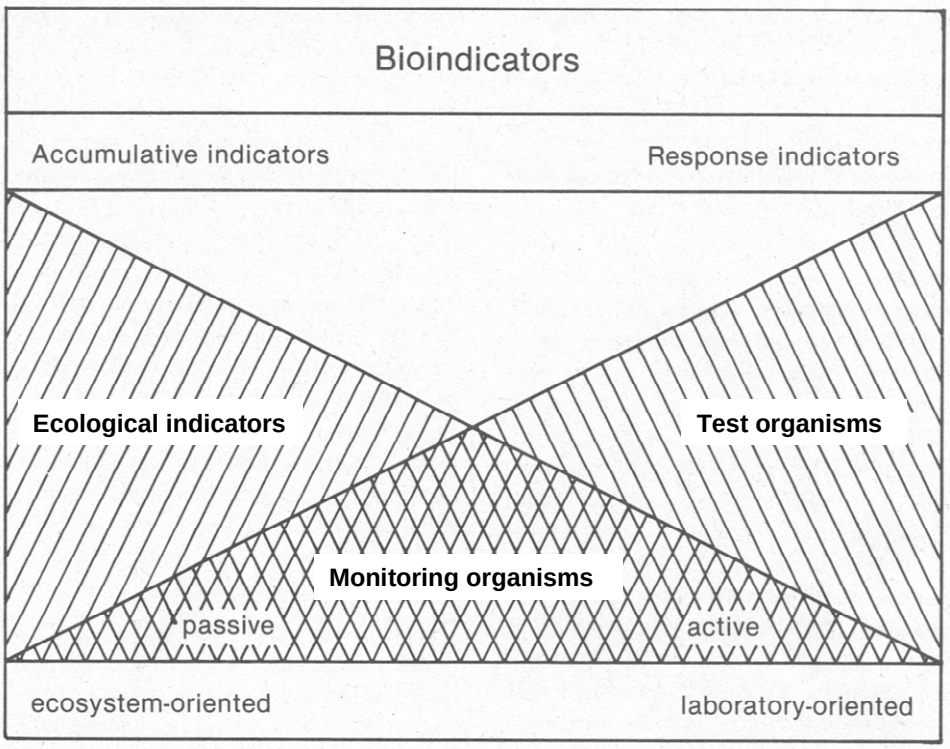

Figure 1. Overview of different biomonitoring procedures (modified after Arndt, 2001)

3. IMPACT OF INDUSTRIAL EMISSIONS ON THE BRAZILIAN ATLANTIC RAIN FOREST

The industrial complex of Cubatão in SE-Brazil is a worldwide known example for the disastrous consequences of unrestrained industrialisation for man and environment representing a typical situation in many developing countries. Since the early 1950s, this complex, one of the largest industrial centres in South America, including steel and fertiliser plants as well as chemical and petrochemical facilities, had been built on the narrow plain between the Atlantic shore and the steep slopes of the coastal mountains. Due to insufficient emission control and the topographic and meteorological characteristics of the region, air pollutants have been transported into the narrow valleys by the prevailing sea-land-breeze for decades causing serious health problems to the local population and strong damage to the Atlantic Forest ecosystem.

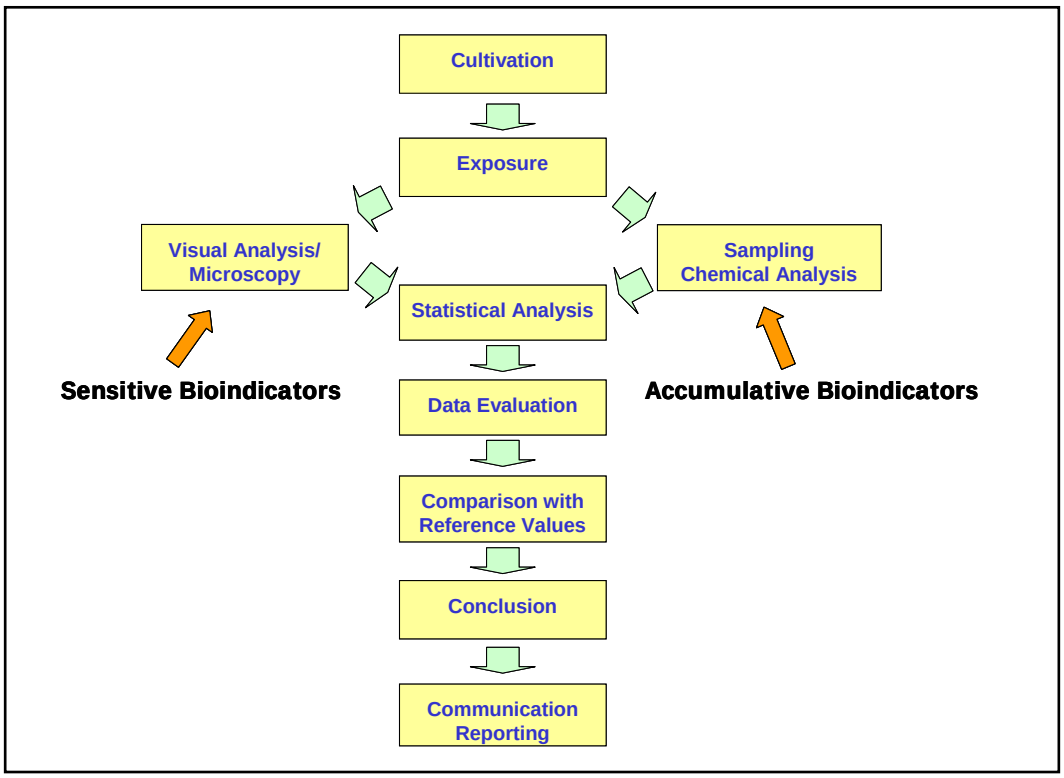

Figure 2. Flow chart on the work steps essential within active biomonitoring studies.

Within the scope of an interdisciplinary research project, bioindication methods were applied to detect the phytotoxic compounds responsible for the forest dieback and to obtain information on the spatial and temporal distribution of the most relevant air pollutants. Data from the exposure of various sensitive and accumulative bioindicator species over several years permitted to delimit distinct sub-areas which were affected by various air pollutants originating from different emission sources. Typical tip necroses on leaves of sensitive plant species like *Gladiolus sp.* and *Hemerocallis sp.* and strongly elevated foliar fluoride concentrations in rye grass (*Lolium multiflorum*), an accumulative indicator plant, were detected in an area downwind from several superphosphate-producing fertiliser plants (Figure 3). The fluoride contents in rye grass reached mean values of more than 100 µg g^{-1} DW which upon ingestion may cause harmful effects on animals. In greater distance to the emission sources and at higher altitudes, by contrast, there was no fluoride impact observed (Klumpp et al., 1996).

Areas close to a petrol refinery, by contrast, were characterised by clearly increased sulphur and nitrogen levels in plants. Particularly strong sulphur accumulation was found in rye grass exposed at intermediate altitudes of the mountain range where high atmospheric concentrations of sulphurous and nitrogenous compounds and high sulphur and nitrogen deposition to soil and vegetation were regularly registered. The latter fact can be explained by the complex atmospheric circulation processes in the area driven by distinct land/sea breeze systems which contribute to prolonged periods of polluted airmasses stagnating in front of the slopes (Vautz et al., 2003).

Ozone-induced injuries on leaves of the sensitive tobacco cultivar Bel-W3 were observed at all exposure sites. Particularly strong ozone damage was recorded at greater distances to the emission sources of primary pollutants and at higher altitudes, whereas only slight foliar injuries occurred at sites close to the factories and in the lowlands. The spatial distribution of phytotoxic ozone levels was found to be triggered by high NOx and VOC emissions originating from the industrial centre itself as well as from the urban agglomeration of São Paulo. By exposure of the sensitive indicators *Urtica urens* and *Petunia sp.*, occurrence of phytotoxic levels of peroxyacetyl nitrate (PAN) in Brazil was proven for the first time (Klumpp et al., 1994; Domingos et al., 1998). This type of pollution was attributed to emissions of volatile organic pollutants from petrochemical plants and from alcohol-fuelled passenger cars. Such detailed information on the intensity and geographical distribution of different gaseous and particulate air pollutants was only possible to be obtained by means of biomonitoring procedures as extensive physico-chemical air monitoring was not feasible in that region due to technical and financial limitations and the very complex terrain and climatic conditions making the installation of dense networks of technical monitoring equipment impossible.

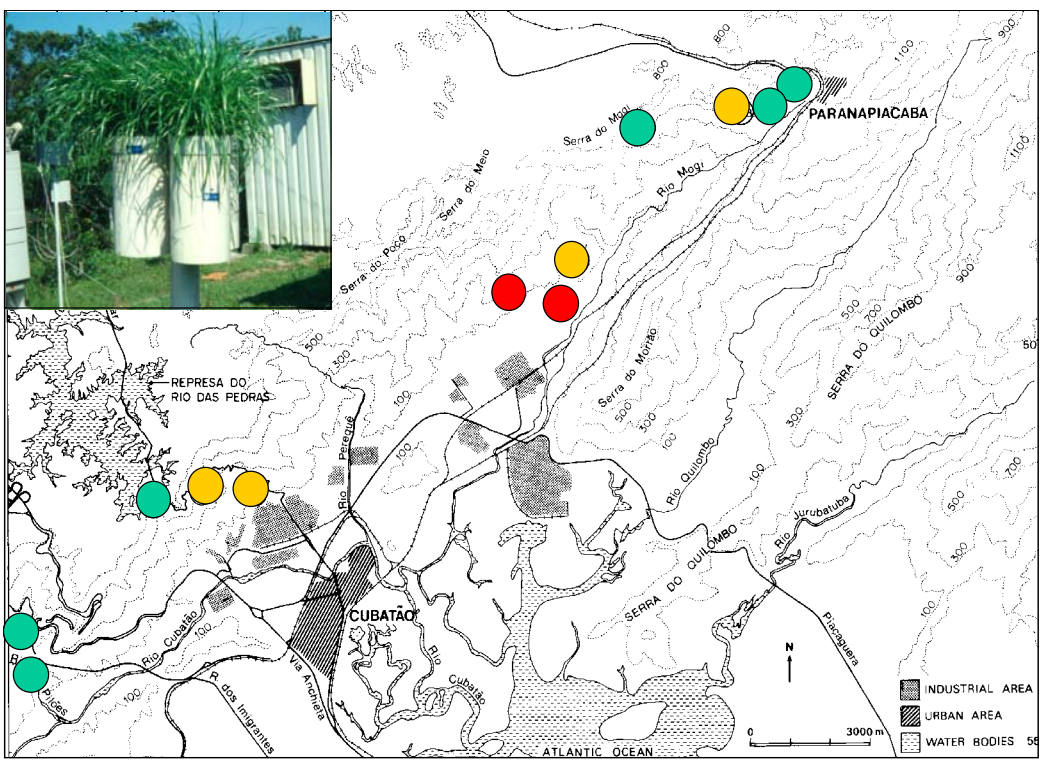

Figure 3. Spatial pattern of fluoride accumulation in exposed rye grass cultures (mean values of 26 exposure periods of 28 days each). Red dots characterise sites with high foliar fluoride concentrations (>100 µg g^{-1} DW); orange dots intermediate levels (20 µg g^{-1} DW$\leq x \leq$100 µg g^{-1} DW) and green dots low levels (<20 µg g^{-1} DW).

4. AIR QUALITY IN URBAN AGGLOMERATIONS IN EUROPE

EuroBionet, the "European Network for the Assessment of Air Quality by the Use of Bioindicator Plants" (www.eurobionet.com) was set up in 1999. In this network of 12 cities and regions in eight European countries, bioindicator plants were used for monitoring air quality and promoting environmental awareness. Communal administrations and research institutes from Edinburgh (GB), Sheffield (GB), Copenhagen (DK), Düsseldorf (D), Nancy (F), Lyon (F), Barcelona (E), Valencia (E), Ditzingen (D), Klagenfurt (A), Verona (I) and Glyfada (GR) took part in the project (Figure 4). Within these cities, local bioindicator networks with more than 100 monitoring stations in total were established and operated over three years. At these stations accumulative and sensitive bioindicator plants (tobacco, rye grass, spiderwort/*Tradescantia* and curly kale) cultivated according to highly standardised procedures were exposed to ambient air in order to assess and to demonstrate the effects of ozone, sulphurous compounds, heavy metals, polycyclic aromatic hydrocarbons and mutagenic substances. The scientific investigations were accompanied by an intensive programme of public relations and environmental education (Klumpp et al., 2004).

Figure 4. Map of Europe showing the partner cities of the network.

The experiments provided numerous data on the spatial and temporal distribution of the effects of air pollutants both within local networks and at the European level. A clear gradient of ozone-induced effects from northern and northwest Europe to southern and central Europe became evident using tobacco plants (*Nicotiana tabacum* cv. Bel-W3). The strongest ozone-induced leaf injuries were observed at the exposure sites in Lyon and Barcelona, while in Edinburgh, Sheffield, Copenhagen and Düsseldorf only weak to moderate ozone impact was registered (Figure 5).

Evaluation of data on ambient ozone concentrations revealed that in the majority of the cities the international threshold and target values for protecting vegetation were exceeded. The Tradescantia micronucleus test for assessing mutagenic effects using *Tradescantia* clone #4430 was carried out for the first time successfully over such a large geographical area. Signs of a raised genotoxic potential were found at sites with high levels of car traffic (Klumpp et al., 2004).

The experiments showed that local 'hotspots' of heavy metal pollution could be verified using the standardised grass culture (*Lolium multiflorum italicum*), and that it was also possible to document the small-scale distribution of the pollution load and short-term changes in emission status. Overall, impact by sulphur and heavy metals was classified as low to moderate, and limit values for feedingstuff were adhered to at most stations. Comparably high heavy metal pollution, however, was noticed in Spanish cities, but a clear drop in lead levels was registered during the course of the project (Figure 6). Antimony proved to be particularly characteristic of traffic-influenced sites. The enrichment of different polycyclic aromatic hydrocarbons (PAH) in curly kale (*Brassica oleracea acephala*) revealed a clear differentiation between urban and reference stations (Klumpp et al., 2004). Overall, the contents lay at an intermediate concentration level typical for urban agglomerations. Furthermore, the studies showed that bioindicator plants are outstandingly useful tools for environmental communication and education as they make the noxious effects of air pollution visible to the everyday life of citizens (Ansel et al., 2004).

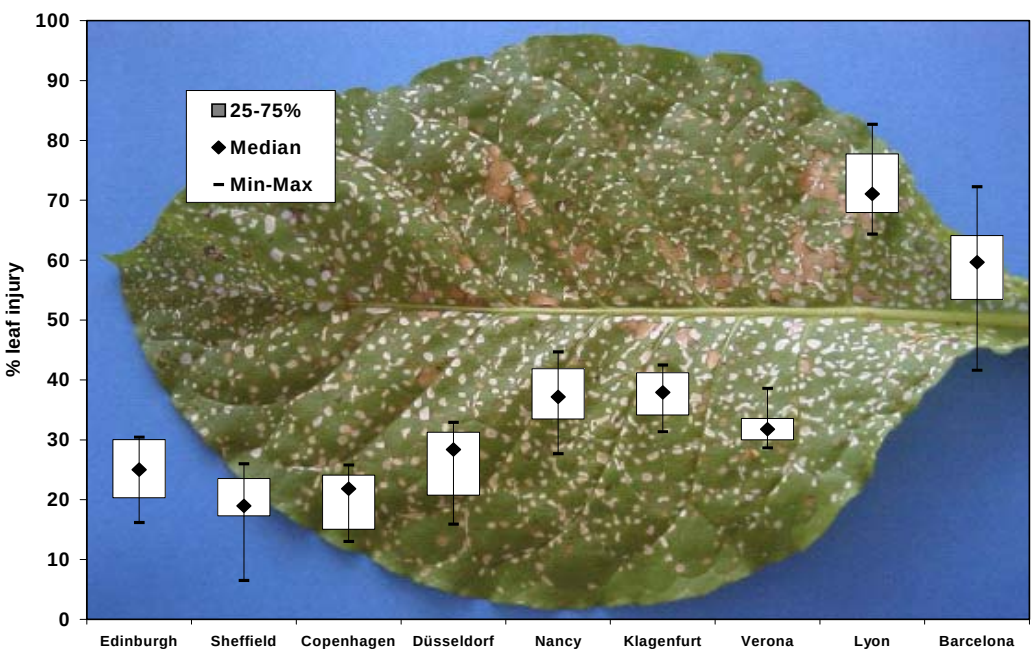

Figure 5. Mean leaf injury degree of tobacco Bel–W3 exposed in nine partner cities of the EuroBionet during eight consecutive bi-weekly periods in 2001.

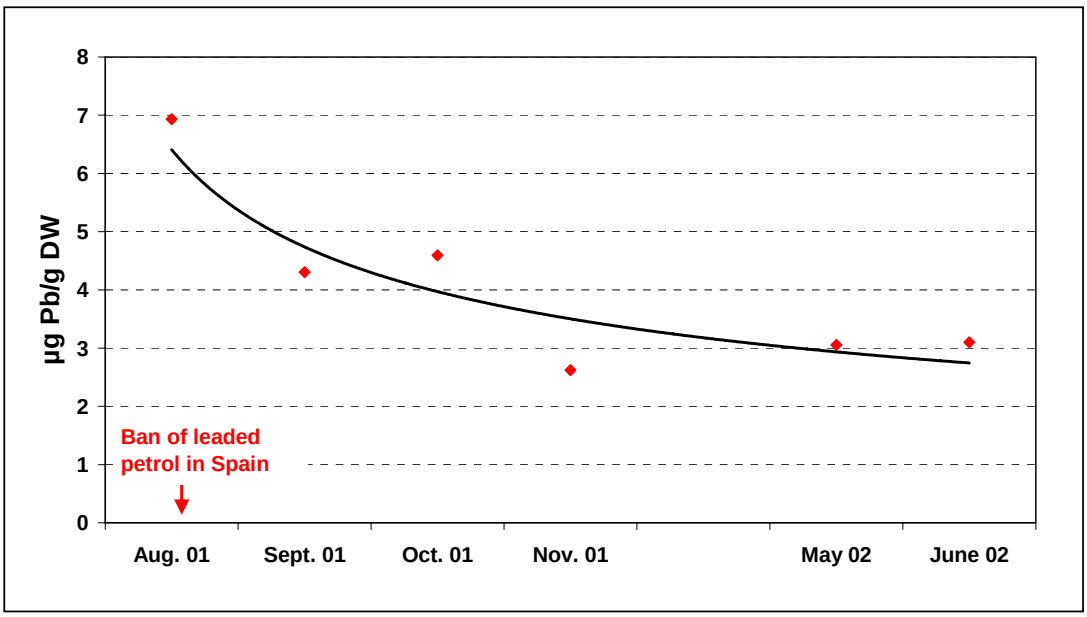

Figure 6. Fall in lead contents of grass cultures (in µg g^{-1} DW) in the Valencia monitoring network after final ban of leaded petrol in Spain in summer 2001.

5. CONCLUSIONS AND PERSPECTIVES

Bioindicators do not measure **ambient pollutant *concentrations***, but indicate **air pollution *effects*** on organisms. They show an integrated response to different pollutants over time and space even in the presence of complex pollutant mixtures. In doing so, they integrate all external (e.g., weather, soil, pests, simultaneous action of other pollutants) and internal factors (e.g., developmental stage, age, nutritional status) in the sense of an overall risk allowing for the estimation of the risk potential concerning the objects to be protected. They may disclose not only acute, but also chronic effects and may concentrate toxic substances to an amount that makes chemical analyses easier. If the bioindicator species is relevant to the food chain, limit values for pollutants can be taken into account.

Many of these attributes render biomonitoring an appropriate means to detect and to monitor air pollution effects thus supplementing information gained from conventional monitoring and modelling. Hence, bioindicators may be employed in i) source-related air pollution monitoring, ii) regional and national/multi-national surveys, iii) ecological long-term monitoring, iv) control of compliance with threshold values, v) environmental impact assessment, vi) air pollution control plans, vii) risk assessment concerning human health or contamination of the food chain, and viii) licensing procedures for new industrial installations, among others. Moreover, biomonitoring may provide data on the presence of phytotoxic levels of air pollutants and their geographical and temporal distribution particularly in developing countries and remote areas where continuous physico-chemical air monitoring is commonly inexistent due to the lack of financial, technical and human resources. Finally, it has been demonstrated that bioindicators are an excellent tool for environmental communication and that they are outstandingly useful in environmental education and awareness raising.
Besides ‘traditional’ pollutants like sulphur dioxide, ozone, fluoride, heavy metals and some hydrocarbons for which well established bioindication methods already

exist, new problems from 'emerging pollutants' will pose a challenge for biomonitoring in the years to come. The increased environmental concentrations of noble metals (like platinum and palladium) which are released as abrasion from catalytic converters are just one prominent example. Other compounds of current interest are a variety of organic substances, including POPs and endocrine disruptors, which constitute a high potential risk for human health. Environmental monitoring of such compounds may be achieved by using accumulative indicators (e.g., standardised grass culture) or through monitoring of the associated mutagenic effects, e.g., by the *Tradescantia* method. Finally, the constantly high deposition rates of nitrogenous compounds like NOx and NHy require modified bioindication methods, which can be employed in local or national monitoring programmes.

Apart from local and regional pollution, long-range transport of air pollutants is giving rise to hemispherical or even global pollution problems with steadily increasing levels even in remote regions far from emission sources (Prather et al., 2003). Such dimensions of air pollution are being addressed by international conventions like the UNECE *Convention on Long-range Transboundary Air Pollution* (www.unece.org/env/lrtap/) or the *Malé Declaration on Control and Prevention of Air Pollution and its Likely Transboundary Effects for South Asia* (www.rrcap.unep.org/issues/air/maledec/). Similarly to European initiatives using bioindicator plants for the assessment of air quality in urban (EuroBionet) and rural areas (ICP Vegetation, icpvegetation.ceh.ac.uk), steps towards supra-regional monitoring programmes using conventional monitoring, passive samplers and/or bioindicators will become necessary to obtain detailed information on the geographical pattern of air pollution problems and their potential impact on agricultural production, biodiversity and human health in developing countries in Latin America, Africa and Asia. Activities like those proposed by the RAPIDC Programme (www.rapidc.org) may serve as an example for this process.

6. ACKNOWLEDGEMENTS

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THE DESIGN OF AN AIR POLLUTION MONITORING NETWORK: ROMA URBAN AREA- ITALY

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ABSTRACT

The study presented in this paper was carried out by the Local Administrative Authorities in order to re-design the air quality monitoring network of the city of Rome (Italy) according to the new European Directive. A territorial analysis of urban area, pollutant and population distribution at macro and micro scale was performed using a statistical approach. Because traffic emissions can be considered the major sources of pollutants in Rome, the methodology proposed took into account not only the population distribution but also its daily fluxes.
Finally, merging the critical state index map and the classified road map, a new air pollution monitoring network was designed.

Key.**Words:** Urban Air Quality, Air Pollution, Monitoring Network.

1. INTRODUCTION

In the last years, problems connected with air quality in great urban areas and with the stresses that the atmospheric pollution cause on the human health have urged the European Community to create a framework to establish criteria for air quality data collection and analytical techniques with particular reference to the location and the minimum number of sampling sites. In particular it has been proposed that air quality monitoring focused on the protection of human health, must be performed in areas where the exposition to the high levels of pollutions is maximum, for a significant period of time and that the areas chosen for monitoring should be representative of other similar areas.
Two different type of station are defined:
Urban/suburban background stations: used to monitor the 'average' air pollution levels (urban background concentration) resulting from transport of air pollutants from outside the urban area and from emissions in the city itself. The stations are, however, not directly influenced by dominating emission sources like traffic or industry .
Traffic stations: located where the level of pollutants is particularly influenced by emissions coming from near roads. This kind of stations are located in areas characterized by an high gradient of concentration.
In Italy the application of EuroAirNet criteria has been entrusted to local administrations; the Latium Region, in which is located the city of Rome, has been

charged therefore, to asses whether the existing monitoring network follows the new criteria either for the number of sites for the different pollutants or for their locations.

2. MAIN TEXT

The Rome Metropolitan Area is located on the west coast of the central Italy, in the Latium Region, along the Tiber River Valley, not too far from the Apennines Range. Rome Municipality, one of the biggest in Europe, covers about 1400Km^2; most of its territory is covered by vegetated and agricultural lands and only the central area is prevalently built as evident in figure 1 where land use map of the Roman municipality territory is shown.

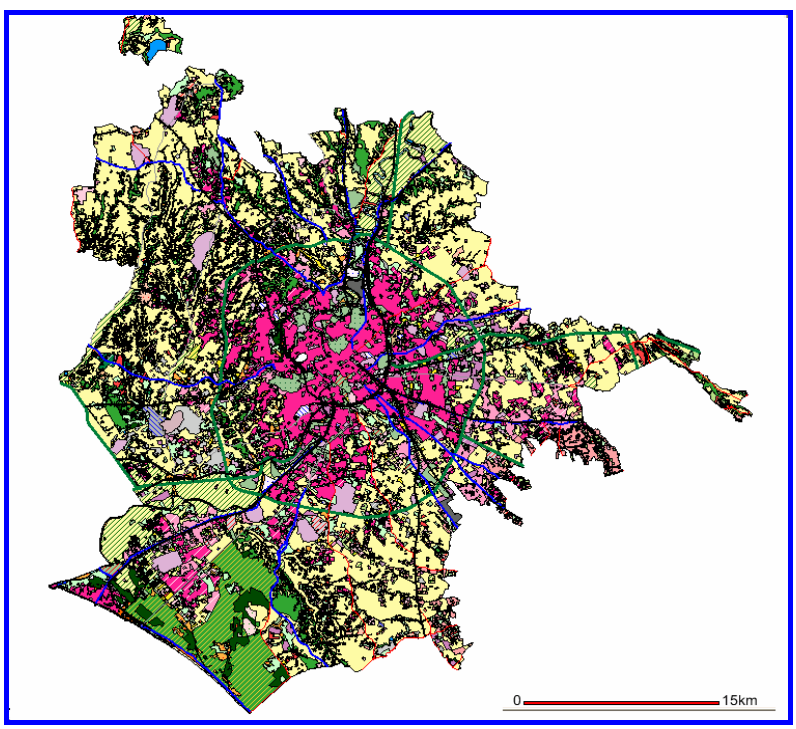

Figure 1. Land Use map of the roman territory. In magenta urban areas, in yellow crops, in different green tones vegetation cover are shown. The roads network is in blue but the green circle is the GRA.

The Great Ring Road (GRA, Grande Raccordo Anulare), with about 20 km of diameter, marks the boundary of the densely populated urban area; moreover in this central area, it is possible to recognized, along the main historic roman roads and XIX century villas, areas dedicated to natural parks (i.d. Appia Antica sub-urban park). Administrative, political and services are the main Rome activities, including transport and all assets related to tourism; these activities are particularly concentrated in the central area within the GRA where 80% of the populations (about 2 750 000 inhabitans) lives (Table1).

In the territory of Rome Municipality, traffic emissions represent the main pollutant source: more then 2.000.000 vehicles per day travel along the city roads. Any major

industrial or thermoelectric plant are located in the surrounding areas and the amount of pollutants produced by domestic heating is in any case negligible.
According to the European directive EuroAirNet, the Italian legislation (*DM 60/2002)* points out that both pollutant concentrations and *exposure* of people to the air pollution have to be considered when a monitoring network will be designed.

Table 1. Census data

AREA	km^2	inhabitans	Working population
outside GRA	1055	604564	100277
inside GRA	327	2145747	853226
ROME	*1382*	*2750311*	*953503*
% inside GRA	**23,67**	**78,02**	**89,48**

In this work, consequently, the geographic distribution of pollutants in the city of Rome and the population density data were both used to identify the areas were these values are both above the average; these, of course, will be the most suitable areas for the location of the monitoring stations.
In a previous study realized by the local regional administration (DGR n. 767 del 1 agosto 2003), in order to divide the territory in air quality homogeneous sub-areas, a multi-task decision model was applied. Considering the high values of pollutants measured, their heterogeneity, the extension and the high number of inhabitants of the territory, the studied area was divided in 164 sub-areas, taking into account:

- the spatial distribution of resident populations as proxy of the amount of pollutants due to domestic heating,
- the traffic emission data,
- air quality maps computed by the regional monitoring authority
- pollutants data (Benzene, Ozone, NO_2) derived by several diffusive sampler campaigns carried out by Roman Municipality

For each sub-areas, an air quality index was computed and the entire territory was then classified to obtained an air quality index map in which the values range between 1 (lower level of air pollution - higher air quality) and 4 (higher level of air pollution – lower air quality).

The resulting map (figure 2a) has been considered as the starting point to evaluate the distribution of pollutants in the city of Rome.

Data derived by the general census of inhabitants/housing and of industrial/shopping activities held in 2001 was used to prepare population density maps (figure 2b,2c) paying particular attention in setting apart the amount of resident population (people that lives in the area) and working population (people that are in the area only during the working hours). It is important to notice that Rome territory is divided into 5808 census sections, each one with different surface but almost the same amount of inhabitants: the surface of the section range between $1200m^2$ and 60 Km^2, with a mean value of 230.000 m^2.

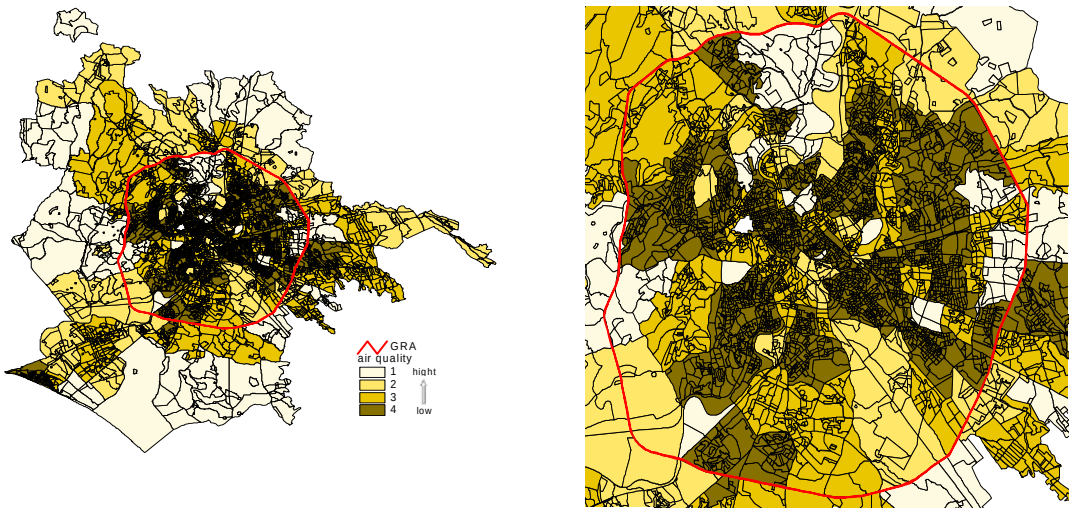

Figure 2a. Air quality map of Roman Municipality; on the right, inside GRA area

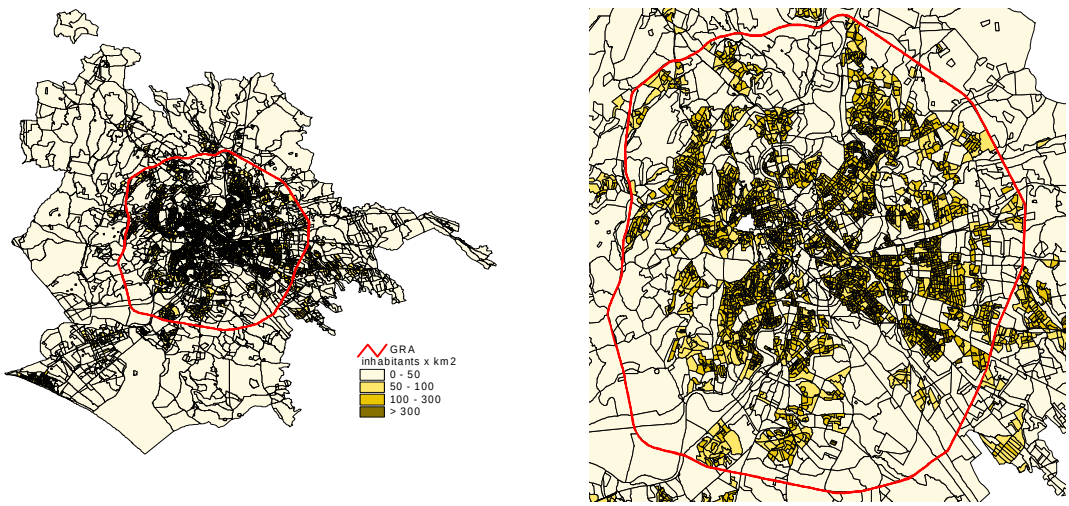

Figure 2b. Resident population in the Roman Municipality; on the right, inside GRA area

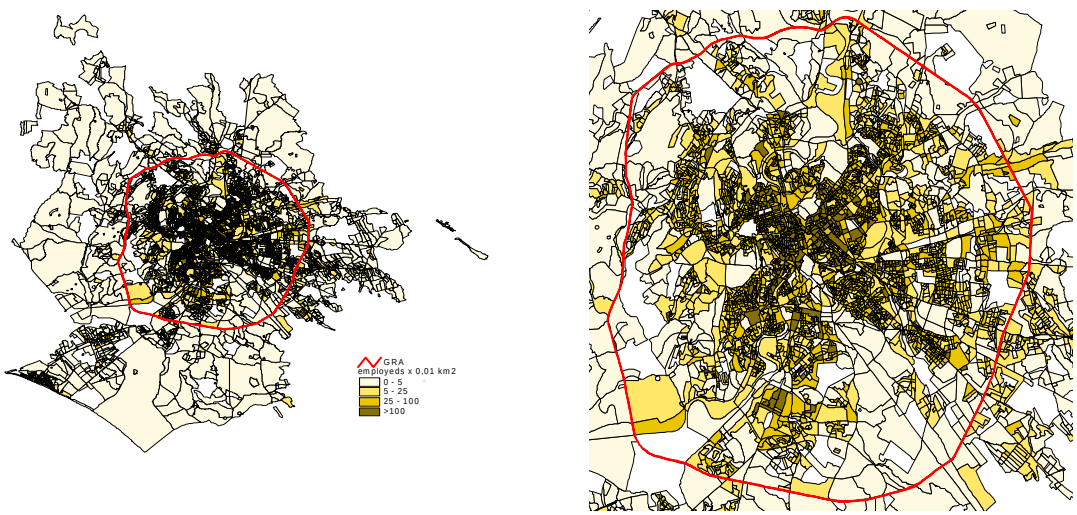

Figure 2c. Working population in the Roman Municipality; on the right, inside GRA area

The territorial analysis of Roman urban area was performed using a statistical approach, taking into account not only the population distribution but also its daily fluxes. The air quality map and population distribution maps of figure 2 emphasize that the inner area is the most polluted and also the most densely populated, as the census data in table 1 underline; for this reason this study has been focused on the area limited by the GRA;

As shown in the details of the figure 2, maps can only give a qualitative description of the level of pollutants since the data were not computed on homogeneous surface units. In order to avoid this incongruity it was necessary to standardize input data.
A regular grid of 500mx500m was overlaid on the map of Roman Urban Area and for each cell the percentage of residential population and the percentage of population working in that area were derived by census data. 5525 cells were thus obtained, 1308 of which are within the GRA area. Census data related to resident and working population of each cell were also normalized to their maximum value, this means that all the value were compressed in the range between 0 and 1.
Since the aim of this study was focused to the human health, the pollutants value for each cell was also extrapolated by urban air quality map, paying attention to use the maximum between the values present in that cell.
In order to calculate the new critical state index map, both census data (resident + working people) were then weighted with the air quality indexes. Even if the new index for each cell can range between 0 and 8, for the cells within the GRA, the value varies between 0 and 7.04, the mean value is equal to 0.29 and standard deviation 0.76 (see table 2). To obtain a map similar to the air quality map used as input, the critical state indexes were clustered around 4 territorial classes (figure 3), considering the mean value and its standard deviation (table 2).

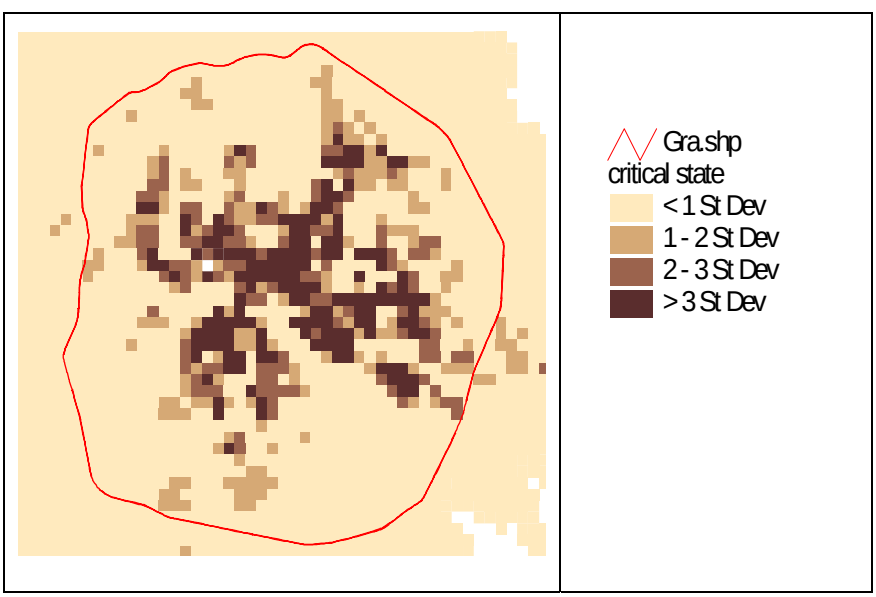

Figure 3. Critical State index map

Class 1, that shows the values closer to the mean, covers more the 65% of the entire territory while the other classes show values between 9 and 13% . In order to

understand how the critical state index map can be used to design the monitoring network, the relations between this map and census data were underlined in figure 4, where percentage of resident and working people for each class are shown.

Table 2. Critical state index classifications in the territory inside the GRA

Class interval	**Class**	**N cells**	Minimum	Maximum	Mean	standard deviation
total distribution		**1308**	**0**	**7,04**	**0,29**	**0,76**
< mean + 1 St Dev	**1**	856	0	1,04	0,09	0,20
1 - 2 St Dev	**2**	178	1,05	1,8	1,4	0,21
2 - 3 St Dev	**3**	117	1,81	2,59	2,19	0,23
>3 St Dev	**4**	157	2,6	7,04	3,72	0,89

The area classified as low critical collects only 20% of resident population and 19% of workers although it is the widest one; as the critical state index grows the population density increases: in class 4, highest critical state index, 40% of resident population and 50 % of workers are present in the 12% of the territory (figure 4) .

The critical state index can be used also to summarize the air quality index, as shown in figure 5. Class 1 presents all the air quality indices, while in the other classes, only air quality index 3 and 4 are present. For this reason is necessary to perform further investigation before selecting the monitoring station sites, according to the European criteria, in the territory classified as class 1.

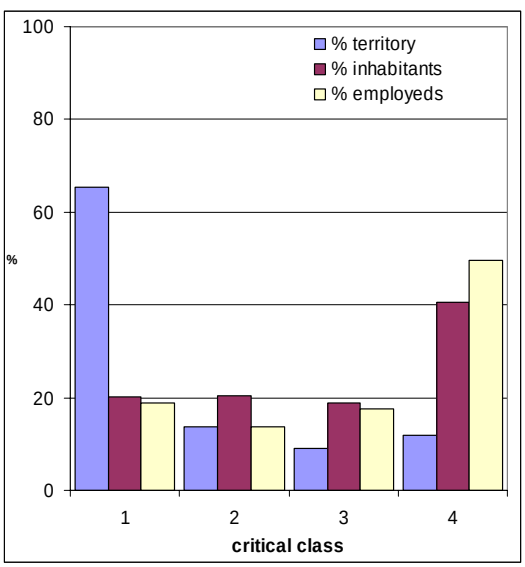

Figure 4. Critical State index Vs. population and territory distribution

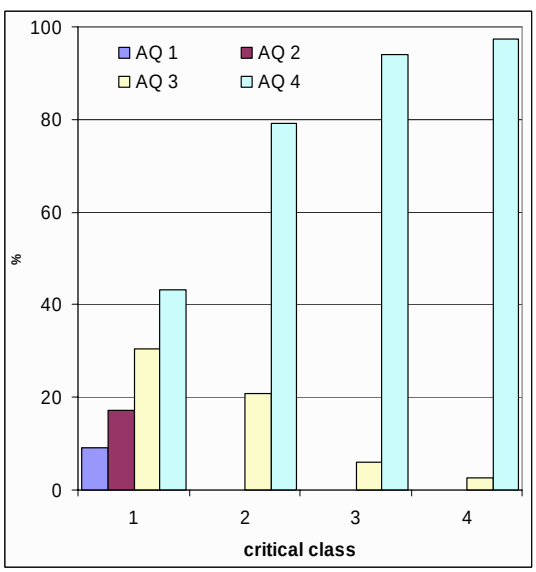

Figure 5. Critical State index Vs. Air Quality index class

The critical state index map can not be used to discriminate the areas where traffic and/or background stations have to be localized. To solve this problem, a new

analysis, based on private and public vehicular traffic emissions, evaluated by Società del Comune di Roma STA (Società Trasporti Autoveicolari) in 1999, was performed.

This set of data has been built estimating the emissions of CO, NO, Benzene, PM 10 and VOC for each segments of the main city roads covered daily by private vehicles. Also this data set was classified using the mean value and its standard deviation to obtain 4 classes; in figure 6 each main road of the city network is mapped using 4 different thickness lines. This representation easily emphasizes the area where traffic pollution is higher and therefore it can be used to locate the traffic monitoring stations.

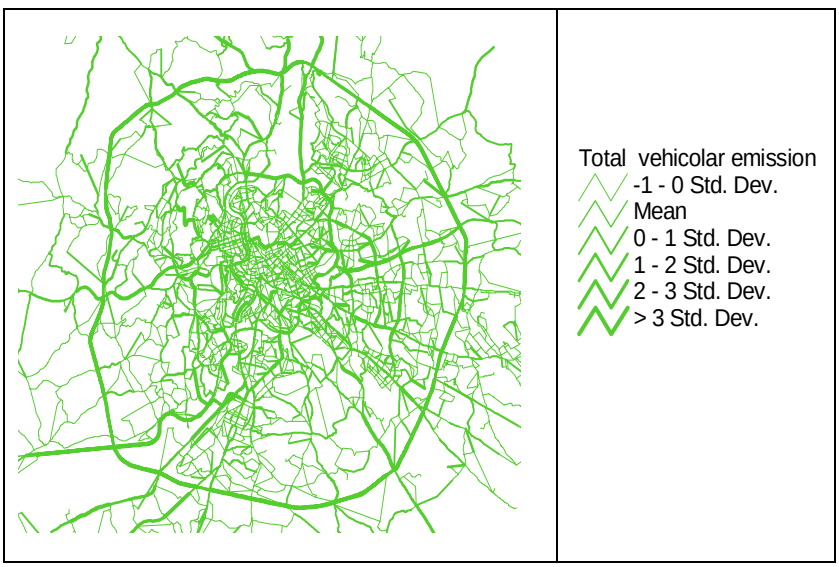

Figure 6. Total vehicular emissions on the road network of Rome

About 100 roads were selected from the roman road network and two different buffer of 35m and 150m were plotted around the main road direction. The first buffer was used to select areas where the traffic stations can be located, since in this area pollutants are only due to traffic emission coming either from the main road or from minor roads with high traffic flux . The buffer of 150m was used to select the areas where traffic emissions were not significant and the level of pollutant could be related to " all different windward sources" *(European Decision 2001/752/CE).*

In order to extract areas in which the different types of monitoring stations can be located, the roads map was, finally, overlaid to the critical state map. (fig. 7).

Moreover this procedure allowed to verify the effectiveness of the positions of the existing monitoring stations. The monitoring network of the roman territory seems to follow the European criteria, particularly concerning macro-scale criteria. The majority of the station is actually located in the critical areas but at the same time almost one station is located also in an other critical index class. On the other hand, the typology of the monitoring station differs from E.U. criteria: there are too many

traffic stations (6/10), few background stations and only one urban background station is present.

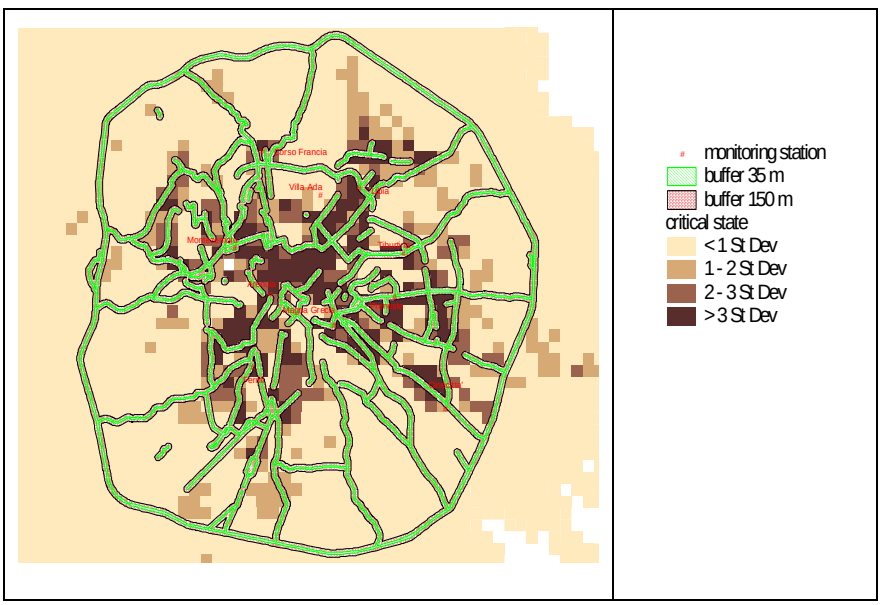

Figure 7. Monitoring stations map of Rome obtained overlaying roads network to critical state index map

On the basis of the results thus obtained, the regional government decided to re-locate some stations and to add further background stations to built a new network fitted to the peculiar urban structure of the city. Three different type of monitoring stations are thus selected:

- Traffic: to monitoring high level of pollutant due to vehicular traffic on the main root,
- Traffic Oriented: to measure the pollutants in areas strongly related to vehicular traffic,
- Urban/Residential Background: to measure an average level of pollutant in the city centre and in the suburban residential area.

The UE criteria require that the locations in which the measurements are carried out should be representative of few hundreds (200) square meters for traffic oriented stations and several square kilometres for urban background. The latter type of stations are the most important since they are representative of the exposition of the majority of population.

Traffic oriented type was introduced to take into account the significance of different pollutant measures. Traffic stations are locate to verify hourly values of NO2 e CO while traffic oriented are devoted to daily and annual mean values of PM10 and benzene.

Following the suggestions given by this study, the new complete monitoring network is designed according to the scheme:

- 2 background stations in the area with critical state index class 4
- 1 background stations in the area with critical state index class 3
- 1 background stations in the area with critical state index class 2

- 1 background stations in the area with critical state index class 1
- 1 urban background station
- 3 traffic oriented stations in the area with critical state index class 4 and 3 (daily values)
- 2 traffic stations in the area with critical state index class 4 and 3 (hourly values)

In order to single out the right location of the monitoring station at micro-scale a further selecting tool was supplied by digital orto photo (scale 1:10000) of the city of Rome. Overlaying the digital ortophoto on the critical state maps and the classified roads network (fig.8) it was possible to verify if the areas selected followed the criteria established by regional monitoring authority, as shows in Figure 6.

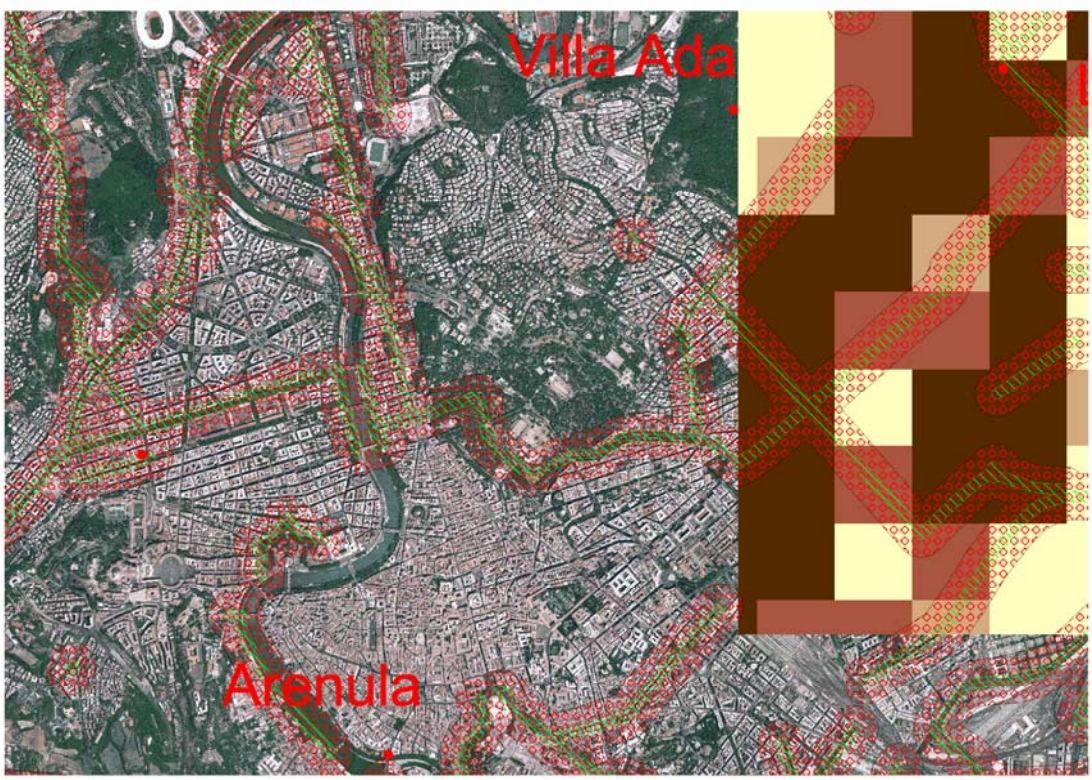

Figure 8. Buffer areas along the roads overlay to the ortophoto and to critical state index map used for microscale analysis.

3. CONCLUSION

In this paper a methodology to design an air pollution monitoring network integrating pollutants concentration data and territorial analysis has been presented. A statistical approach was used to process air quality map, census data and pollutants data derived by existing monitoring stations. Data coming from different sources were normalized and referred to the same territorial unit. This method allowed the production of a critical state index map. To select the areas more suitable for monitoring station locations, pollutants distribution due to vehicular traffic was also

taken into account. According to European Criteria a new monitoring network was planned also using for microscale territorial analysis several orto-photos of the city.
The new monitoring lay-out required some effort in order to ensure that the type and the dimension of the monitoring network should be compatible with the economic resources, including running and maintenance.

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ASSESSMENT OF AMBIENT AIR QUALITY IN ESKISEHIR, TURKEY

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ABSTRACT

In this study, air quality in Eskisehir was evaluated in terms of such pollutants as SO_2, PM, NO_2 and O_3. SO_2 and PM concentration levels in Eskisehir have been monitored since 1986 and these data were provided from the national ambient air monitoring network. Ambient NO_2 levels since January 2004 and ambient ozone levels since November 2004 have been monitored by use of passive samplers in the study area of this work. All these data were considered for ambient air quality assessment. Concentration relationship between pollutants themselves and the relationship between concentrations and meteorological parameters were discussed. Additionally, monitored data were compared against the limit values in the regulations.

Key Words: Air Quality, Sulphur Dioxide, Nitrogen Dioxide, Ozone, Particulate Matter

1. INTRODUCTION

Urban air pollution and its impact on urban air quality is a widely recognized problem. Many cities in the world are exposed to high levels of air pollution. The two most important reasons of local and global changes in the air quality are population and urbanization.

The current situation of the air quality in the world indicates that SO_2 maintains a downward trend, NO_2 maintains levels very close to those of World Health Organization (WHO), while as PM is a major problem in almost all Asian countries exceeding 300 $\mu g/m^3$ in many cities and ozone shows average values that exceed the selected guideline values demonstrating that it is a global problem (Baldasano et al., 2003).

Air quality in urban areas continues to be a growing concern in terms of its health and environmental impacts. Different sources of urban air pollution such as road traffic, heating and industry, with the road traffic being a dominant source also increase by the rate of increase in population and urbanization.

Major urban air pollutants, including sulphur dioxide (SO_2), nitrogen dioxide (NO_2), particulate matter (PM) and ozone (O_3) emitted to the atmosphere are subject to mixing, transport and transformation processes. Chemical interactions can produce harmful pollutants such as nitrogen dioxide which evolves from the oxidation of nitric oxide by ozone. Photochemical reactions can lead to ozone which is an extremely reactive chemical that has been shown to reduce visibility and have harmful effects on human health, commercial crops, and natural areas. It is also one of the most important gaseous component of photochemical smog. High levels of PM are significantly associated with adverse health effects, ecosystem damage, and degraded visibility (Wise and Comrie, 2005). SO_2 originating particularly from the combustion of sulphur-containing fossil fuels (principally coal and heavy oils) has also negative effects on human health, vegetation and some materials (MPAP, 2004).

Scientific researches have shown that long-term exposure to these pollutants above a specific level may cause effects which may differ from those mentioned above. Therefore, most of the countries in the world have established air quality regulations such as WHO, the European Union Air Quality Framework and Daughter Directives, the UK Air Quality Strategy (Lim et al., 2005). In this case, monitoring studies gain more importance in order to observe the effectiveness of air quality control regulations, improve air quality management efforts and detect long-term air quality trends.

The existing air quality information in Turkey is either limited to only a few pollutants or is not spatially and/or temporally representative of the current situation due to rapid growth of the urban areas. There are national air quality standards established for such pollutants as SO_2, NO_2, PM, O_3, etc.

Although SO_2 and PM have been monitored at multiple points within the Turkish ambient air monitoring network, other pollutants such as NO_x and O_3 could have been monitored at only a limited number of points. The expansion of the national ambient air monitoring network and adding new components to this network tasks require large investments and additional operational expenses. Therefore, there is an urgent need of adopting inexpensive, simple and reliable methods for air quality monitoring in Turkey. This need can be fulfilled by such methods as passive sampling which is simple, inexpensive and provide possibility for the determination of pollutant distribution over a large area.

A few air quality monitoring studies were carried out in Eskisehir in the past except the monitoring of SO_2 and PM by monitoring network since 1986. In 1990–1995, NO_2 measurements were carried out at Anadolu University Yunusemre Campus by Air Pollution Research Group at Chemical Engineering Department. Proceeding NO_2, O_3 and BTX monitoring studies that were carried out in 2003 and 2004 were conducted discontinuously.

In this study; (a) monitoring results of the pollutants SO_2, NO_2, PM and O_3 in Eskisehir were presented, (b) collected data were compared with the regulations of different countries (Turkey, WHO, EPA, etc.) and also with those of other national

cities, (c) the relationship between related pollutants such as NO_2 and ozone, and also between atmospheric concentrations of the pollutants and meteorological parameters (temperature, wind) were determined.

2. MATERIALS AND METHODS

In this study, air quality in Eskisehir was identified by the monitoring results of main pollutants such as SO_2, NO_2, PM and O_3. Eskisehir is a rapidly developing intermediate size Turkish city, situated in the Northwest of the Central Anatolia, with a population of approximately 500,000 inhabitants. Mainly the traffic and heating are considered responsible for the pollution in the city. After 1998, natural gas has been introduced for domestic heating purposes by the 50 % of the residencies in the city.

SO_2 and PM have been included in the Turkish ambient air monitoring network for two points in Eskisehir. Because NO_2 and O_3 were not included in that monitoring network, later attempt has been found necessary to monitor spatial and temporal distributions of these pollutants in the urban area of Eskisehir. For this purpose, passive sampling method has been applied since January 2004 for NO_2, and since November 2004 for O_3. Six sampling points were selected from different sites of the city. Because NO_2 is mostly originated from the traffic, all the sampling points were selected in a way to have different levels of traffic density in accordance with results of emission inventory study carried out for Eskisehir (Cinar, 2003). Ozone monitoring has been started at the same sampling points to observe the relationship between NO_2 and ozone concentrations. An automatic ozone analyser was available at one sampling point (Anadolu University Iki Eylul Campus) to monitor daily and hourly changes in the O_3 concentrations.

Figure 1 shows the study area and sampling points on the map given for Eskisehir.

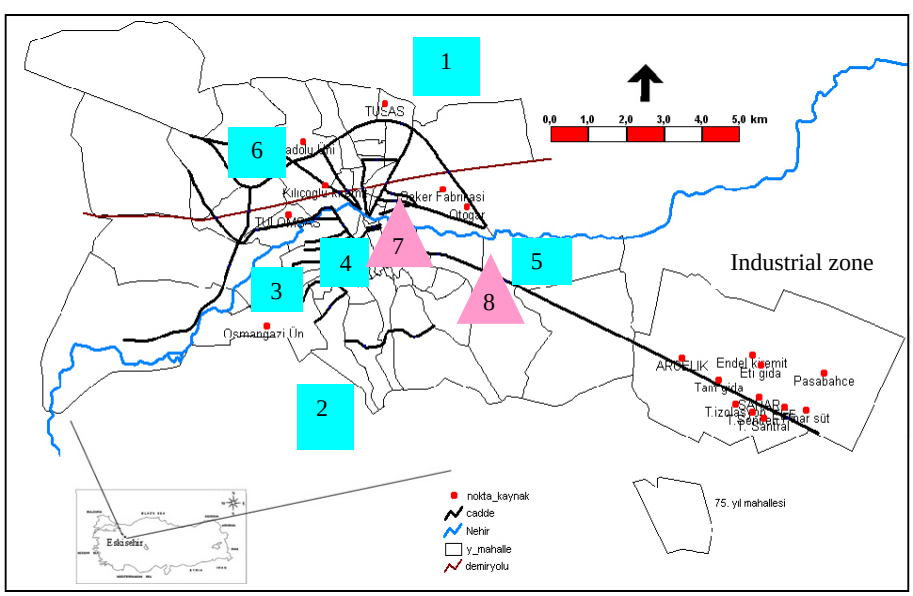

Figure 1. Study area and sampling points

NO_2 & O_3 : (1) Anadolu Univ.Iki Eylul Campus, (2) Universite Evleri, (3) Ataturk Boulevard (4) M. Kemal Ataturk Street,(5) Cifteler Street, (6) Tepebasi
SO_2& PM :(7) Koprubasi, (8) Cifteler Street

Measurements for collecting weekly average data were carried out at six sampling points for both NO_2 and ozone by using passive sampling method. Following the sampling, analyses of the samples were conducted by using spectrophotometric method for NO_2 and ion chromatographic method for ozone. Concentration data for SO_2 and PM were gathered from national ambient air monitoring network (State Institute of Statistics, SIS).

Observed pollutant concentrations were compared with Turkish and other international air quality standards. The relationship between NO_2 and ozone concentrations was determined by sampling these two pollutants at the same point and during same period. By using the concentration data particularly for ozone, the relationship between atmospheric concentrations and some meteorological parameters (temperature, wind etc.) were also determined.

3. RESULTS AND DISCUSSION

Figure 2 presents annual emissions of the pollutants and their source contributions in percentages for Eskisehir.

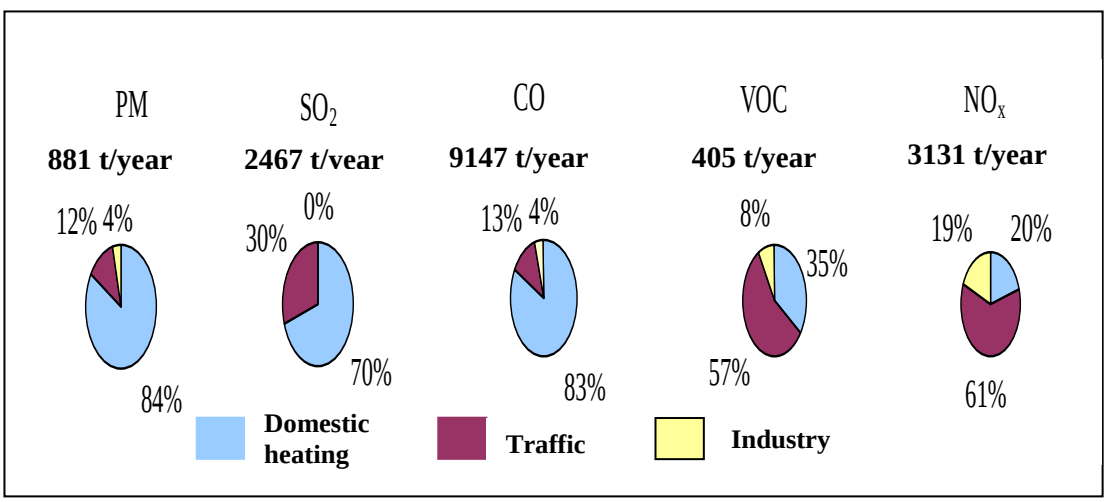

Figure 2. Emissions and sources of ambient air pollutants for Eskisehir

Annual PM and SO_2 trends between 1992-2001 for Eskisehir are indicated in Figure 3. Figure 4 shows monthly PM and SO_2 concentrations for 2002.

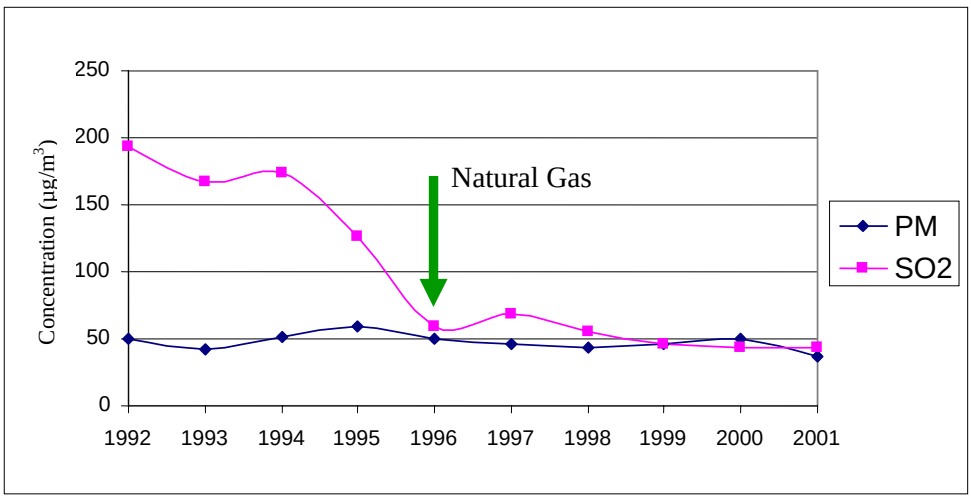

Figure 3. SO_2 and PM trends for the period 1992-2001

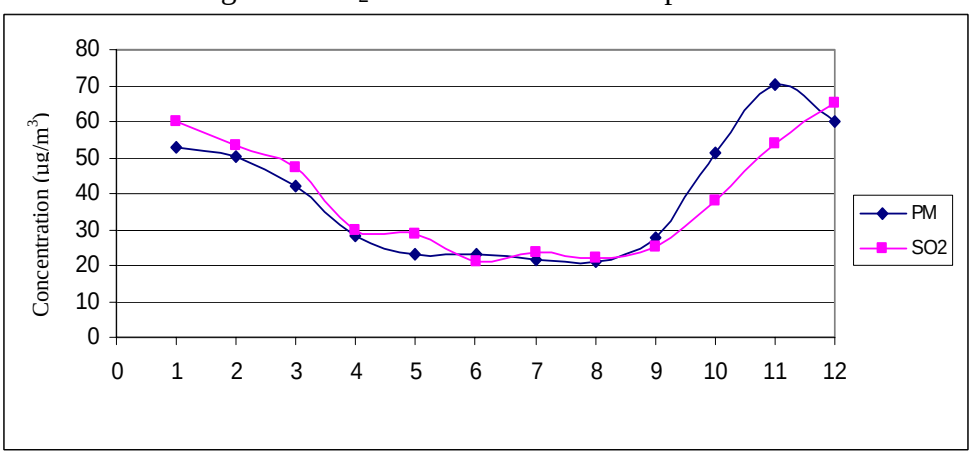

Figure 4. Monthly variations in PM and SO_2 concentrations in 2002

Figure 5 and Figure 6 show the variation in the monthly average NO_2 and ozone concentrations, respectively, at 6 sampling points for the years 2004 and 2005.

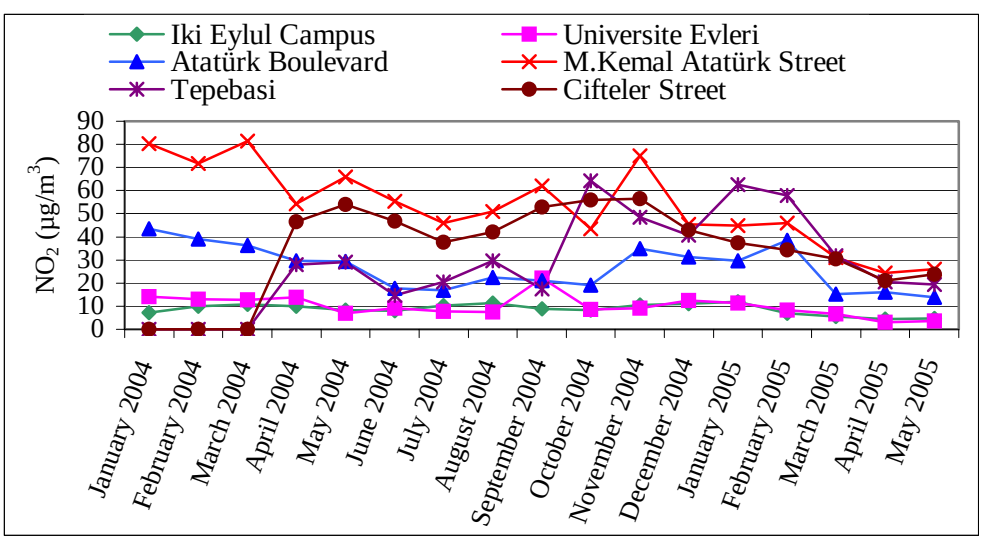

Figure 5. Monthly NO_2 averages for the period 2004-2005

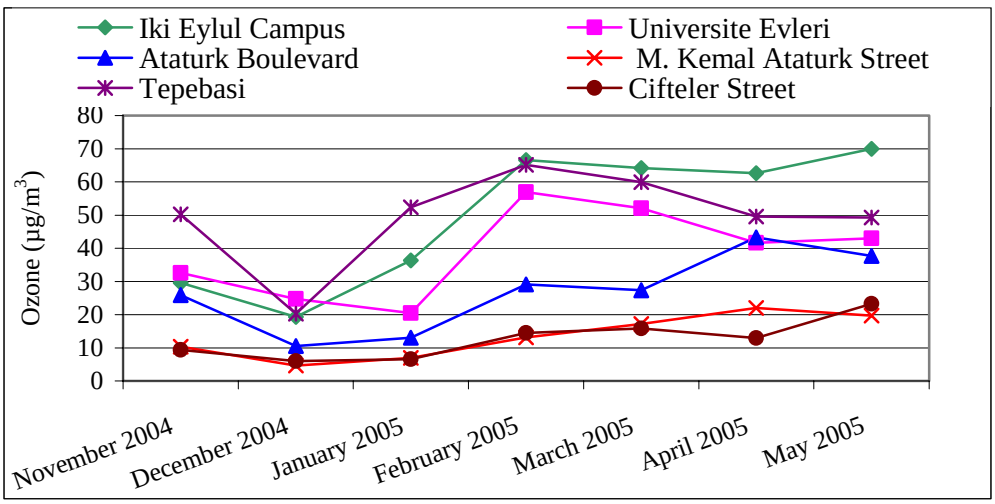

Figure 6. Monthly ozone averages for the period 2004-2005

Monitored data are being compared for the year 2004 with the national and international regulation standards in Table 1.

Table 1. Comparison of the data for SO_2, NO_2, O_3 and PM during 2004 with the national and international regulations in units of µg/m^3

Pollutant	Monitored data	Turkish Limits		WHO guidelines	EC regulations	EPA regulations
		Short term	Long term			
SO_2	51	400	150	125(24 h) 50(annual)	125(24 h) 50 (long-term)	365(24 h) 80(annual)
NO_2	32.66*	300	100	200(1 h) 40(annual)	50 (long-term)	100 (annual)
O_3	147**	240(1 h)	-	120(8 h)	-	235(1 h) 157(8 h)
PM_{10}	38	300	150	-	80(annual)	50(annual) 150(24 h)

*This data represents annual average value (2004) measured in the six sampling points
** Maximum hourly ozone concentration measured between April & June 2005

Figure 7 shows a typical relationship between NO_2 and ozone concentrations recorded at Anadolu University Iki Eylul Campus. Correlation between NO_2 and ozone concentrations is indicated in Figure 8. As expected, there is a reverse relationship between the two pollutant levels. When NO_2 concentrations are high (especially in the city centre), ozone levels are prevailing at low levels and when ozone concentrations are high (especially far away from the city centre), NO_2 levels are found low.

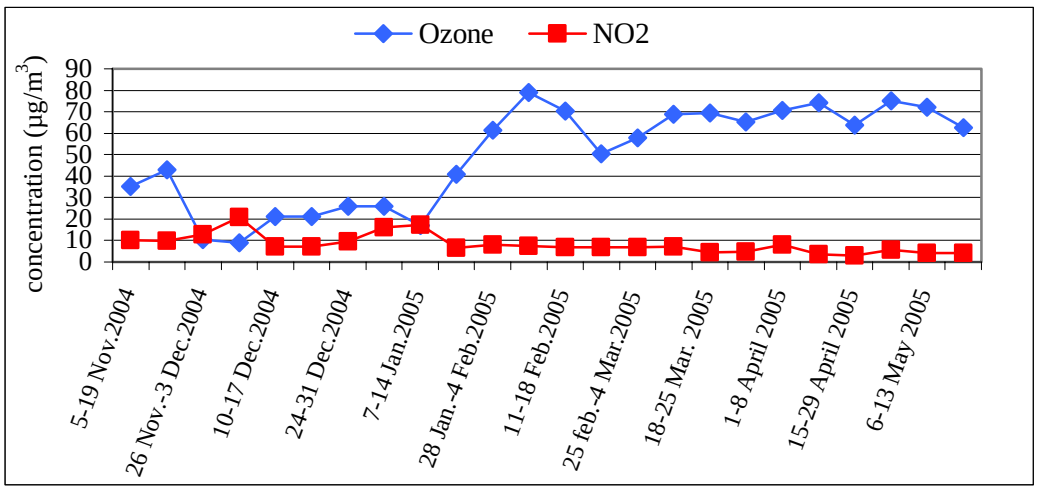

Figure 7. Relationship between NO_2 and ozone at Iki Eylul Campus

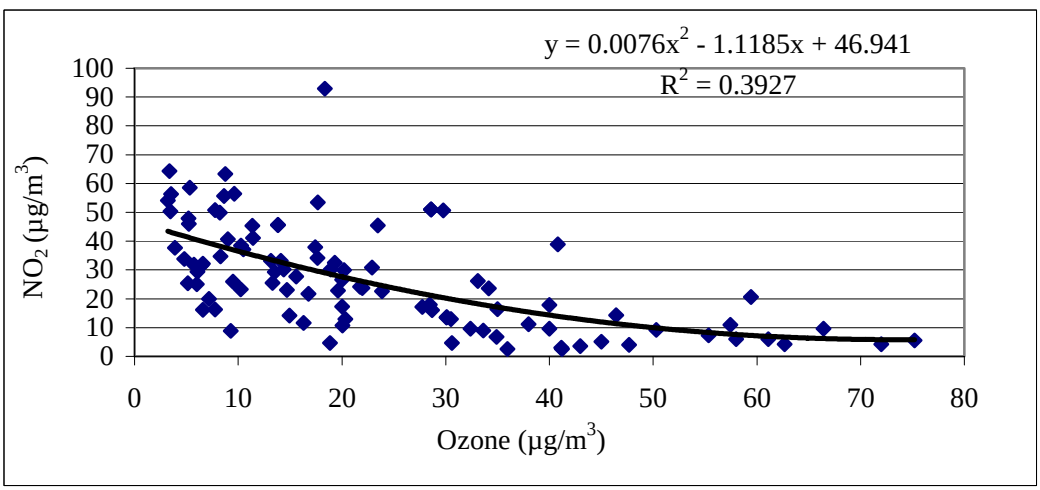

Figure 8. Correlation between atmospheric NO_2 & ozone concentrations in Eskisehir

Figure 9 indicates the changes in ozone values during a typical day for winter (January) and summer (June) seasons and, the temperatures given in Figures 9a and 9b belong to same hours. As is well known, ozone season starts in April. Figure 10 indicates maximum daily ozone concentrations during April 2005 and maximum values varied between 96-140 µg/m^3. Maximum ozone concentrations which were lower in previous months in winter season increased up to 155 µg/m^3 in June. As is expected, this value may increase to a much higher level during summer season.

4. CONCLUSION

In this study, the levels of SO_2, PM, NO_2 and O_3 were discussed for the identification of air quality in Eskisehir. Appearently, domestic heating is responsible for SO_2, PM and CO pollution, while traffic is responsible for NO_x and VOC pollution. Industry is the less important source for urban air pollution in Eskisehir.

At the start of 2000s, Eskisehir community started using natural gas in their fuel-mixes for residential heating and industrial productions. Since then, there has been a significant decrease in SO_2 from 200-250 µg/m^3 to below 50 µg/m^3 and in PM from 140-150 µg/m^3 to below 40 µg/m^3. For the year 2004, average concentration values for SO_2 and PM were 51 and 38 µg/m^3, respectively. Monthly average NO_2 and O_3 concentrations were found to vary between 3-81 µg/m^3 and 5-70 µg/m^3, respectively.

The percentage of population exposed to NO_2 concentrations at levels between 60-100 µg/m^3 is 24 % in Western Countries, 15 % in Middle and East European Countries and 18 % as the world average. This study indicated that 29 % of Eskisehir's population was exposed to high NO_2 levels in 2004. But, since the railway system has started for public transportation in the city, at the end of 2004, NO_2 concentration levels, especially in the city centre, have decreased by an average ratio of 45 %.

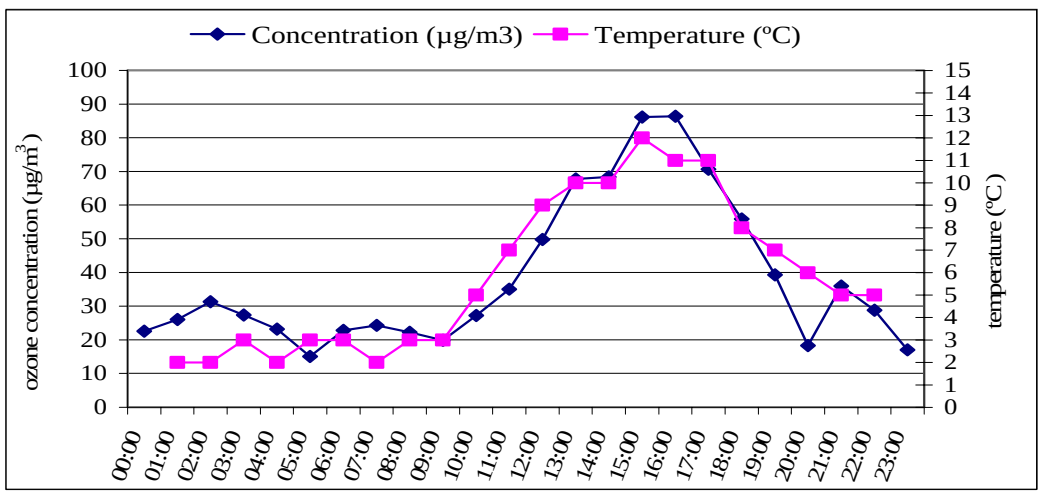

Figure 9.a) Hourly ozone concentration and temperature values corresponding to 01.01.2005

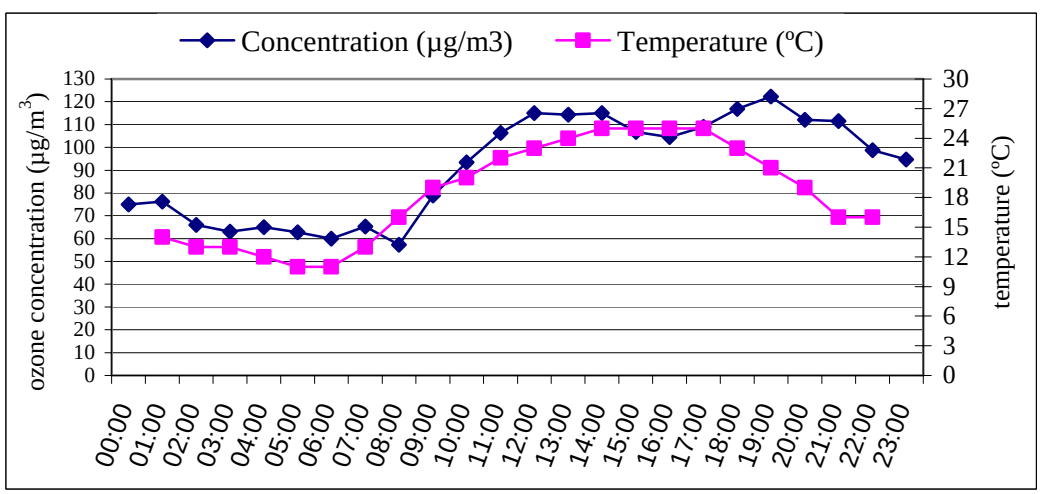

Figure 9.b) Hourly ozone concentration and temperature values corresponding to 13.06.2005

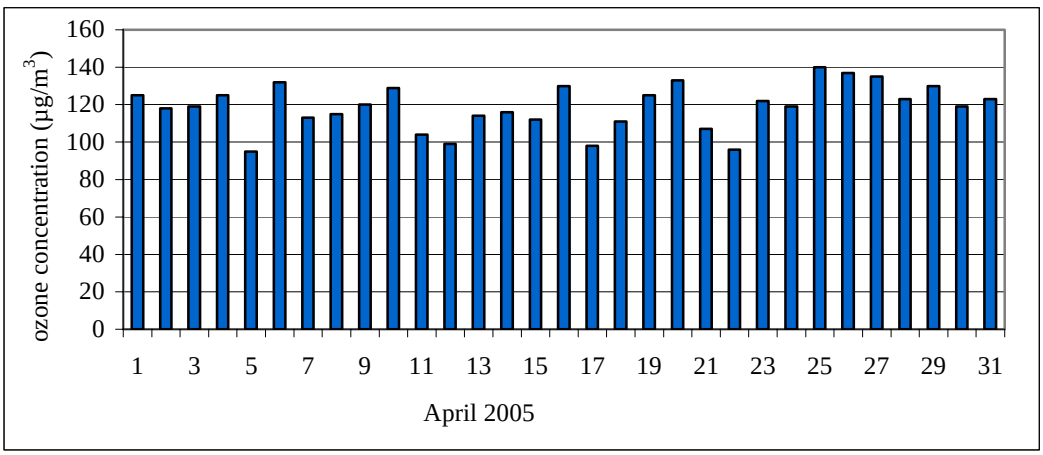

Figure 10. Daily maximum ozone concentrations at the beginning of ozone season (April 2005)

Hourly changes in the O_3 concentrations were monitored at a single sampling point in winter and summer seasons by automatic ozone analyser. The levels in winter were lower than that in summer season. Regarding the effects of meteorological parameters investigated, an increase was observed in the concentration levels with the increase in temperature. For summer season, two peaks are noticeable. Morning peaks, prevailing during morning to noon hours, occurs when calm or northeast wind direction is dominant. However, afternoon peaks correspond to northwest-west wind direction. When this profile is compared with the ozone concentration, it can be said that till noon hours local effects can be dominant but in the afternoon, pollutant transport by the northwest-west direction seems dominant.

Reverse relationship exists between NO_2 and O_3 concentrations. In the city centre, NO_2 levels were high while O_3 levels were low and in the regions far away from the city centre, O_3 levels were high while NO_2 levels were low.

For the year 2004, NO_2, O_3 and PM levels never exceeded national and international limit values. But, SO_2 concentration (51 µg/m^3) not exceeding the current Turkish limit value (150 µg/m^3), was slightly above the WHO and EC limit value of 50 µg/m^3.

When the measurement results are compared against those from other national cities such as Istanbul and Ankara, it can be noted that average annual NO_2 concentration prevails at 33 µg/m^3 level in Eskisehir, while it is around 40 µg/m^3 in Ankara, and monthly NO_2 concentration is 60-80 µg/m^3 in Istanbul. Winter season O_3 value for Eskisehir is around 30 µg/m^3 and 20 µg/m^3 in Ankara. The levels of NO_2 and O_3 concentrations in those cities are more or less the same.

5. ACKNOWLEDGEMENTS

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MODELING UNCERTAINTY ESTIMATION PROCEDURES FOR AIR QUALITY ASSESSMENT

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ABSTRACT

This work has a two-fold objective: a review of the current existent methodologies to estimate modelling uncertainty; the preparation of some guidelines for this modelling uncertainty estimation, which can be used by local and regional authorities responsible for air quality management. Examples of modelling uncertainty estimation, using statistical analysis and the European Directives quality indicators, are presented and discussed.

Key Words: Air Quality, Modelling, Uncertainty, Quality Indicators

1. INTRODUCTION

Air quality models are powerful tools to predict the fate of pollutant gases or aerosols upon their release into the atmosphere. Dispersion is primarily controlled by turbulence, which is random by nature, thus cannot be precisely described or predicted by means of basic statistical properties. As a result, there is spatial and temporal variability that naturally occurs in the observed concentration field. On the other hand, uncertainty in the model results can also be due to factors such as errors in the input data and model formulation. Because of the effects of uncertainty and its inherent randomness, it is not possible for an air quality model to ever be "perfect", and there is always a base amount of scatter that cannot be removed (Chang and Hanna, 2004). Nevertheless, air quality models need to be properly evaluated before their predictions can be used with confidence, since model results often influence decisions that have large public to models health and economic consequences. Therefore information about uncertainties associated application is as important as their resulted data, and should be correctly estimated and interpreted. The uncertainty concept is one of the crucial points of Quality Assurance/Quality Control (QA/QC) procedures that should provide quantitative information about the modelling precision, identifying the uncertainty sources and their potential reduction. The present European legislation defines the requirements of QA/QC procedures for air quality modelling, including the definition of Quality Objectives as an acceptability measure, to guarantee they indicate a good model performance and reliable modelling results for decision makers. However, a practical application of these requirements and interpretation of the uncertainty analysis results based on the recommended methodology is difficult, and in some cases incomprehensible for non-expert users. The development of a consistent procedure for the uncertainty evaluation is still a challenge for the scientific community.

2. MODEL UNCERTAINITY ESTIMATION METHODOLOGIES

Uncertainty analysis is defined by Morgan and Henrion (1990) as the computation of the total uncertainty induced in the output by quantified uncertainty in the inputs and model, and the attributes of the relative importance of the input uncertainties in terms of their contributions. Thus, total model uncertainty can be defined by the sum of the model uncertainty, variability and uncertainty on input data. Uncertainties associated with model formulation may be due to erroneous or incomplete representation of the dynamic and chemistry of the atmosphere, incommensurability, numerical solution techniques, and choice of modelling domain and grid structure. Uncertainties in input data are described in terms of emissions, observational data, meteorology, chemistry and model resolution. Variability refers to stochastic atmospheric and anthropogenic processes. It contributes to uncertainties discussed previously, like those associated with emissions estimation and representations of chemistry and meteorology.

The total model uncertainty can be determined by comparison between observations and model predictions through the application of data Quality Indicators, which reflect the ability of a model to simulate real world phenomena. Besides being difficult to define quantitative Quality Indicators for model evaluation, applications of such indicators help to understand model limitations and provide a support for model intercomparison.

There can be three components to the evaluation of air quality models: scientific, statistical and operational (Chang and Hanna, 2004). In a scientific evaluation, the model algorithms, physics, assumptions and codes are examined in detail for their accuracy, efficiency and sensitivity. This exercise usually requires in-depth knowledge of the model. For statistical evaluation, model predictions are examined to see how well they match observations. The operational evaluation component mainly considers issues related to the user-friendliness of the model (user's guide, user interface, etc). This work will focus mainly on scientific and statistical model evaluation and on the estimation of the total uncertainty.

2.1 Sensitivity analysis

Uncertainties in modelling systems are often studied using sensitivity analysis procedures. It is assumed that a model consists of a set of equations with m dependent or "output" variables and n independent variables plus input parameters. The sensitivity coefficient can be defined as the ratio of the fractional change in an output variable to the corresponding fractional change in an input variable. The combined effects of variations in multiple input parameters can be estimated by assuming that there are no correlations among variables and there are no nonlinear effects, giving the result that the total fractional uncertainty in a given dependent or "output" variable is the square root of the sum of the squares of each individual sensitivity coefficient.

Nevertheless, this sensitivity coefficient approach has problems for large scale photochemical grid models with input parameters exhibiting relatively large uncertainties for systems that are nonlinear and input variables strongly correlated. Advanced mathematical procedures and software systems have been developed allowing sensitivity coefficients to be evaluated for more complex modelling systems (e.g. Carmichael et al., 1997; Saltelli et al., 2000).

2.2 Statistical analysis

Uncertainties can be characterized and air quality model evaluation can be determined by statistical analysis, where model predictions are examined to see how well they match observations. Many scientists have carried out discussion on the evaluation of air quality models and on the development of general evaluation methods; however, standard evaluation procedures and also performance standards still do not exist. Traditionally, model predictions are directly compared to observations, but this direct comparison method may cause misleading results because uncertainties in observations and model predictions arise from different sources (Chang and Hanna, 2004).

As already mentioned, the uncertainty in observations may be due to random turbulence in the atmosphere and measurements errors, whereas the uncertainty in model predictions may be due to input data errors and model physics. Hanna et al. (1993) recommended a set of quantitative statistical performance measures for evaluating models, which have been widely used in many studies (e.g. Nappo and Essa, 2001; Ichikawa and Sada, 2002) and have been adopted as a common European model evaluation framework (Olesen, 2001). Table 1 presents the main statistical parameters used as quality indicators in these studies.

Table 1. Quality indicators for air quality model performance evaluation

Quality indicators	Formula	Observations	Ideal value
Correlation coefficient	$r = \left[\frac{\sum_{i=1}^{N}(Co_i - \overline{Co})(Cp_i - \overline{Cp})}{\sigma_O \sigma_P}\right]$	Co and Cp are the concentration observed and predicted $\overline{Co}$ and $\overline{Cp}$ are the averaged concentration observed and predicted	1.0
Fractional bias	$Fb = \frac{\overline{Co} - \overline{Cp}}{0.5(\overline{Co} + \overline{Cp})}$		0.0
Root mean squared error	$RMS = \sqrt{\sum_{i=1}^{N}(Co_i - Cp_i)^2}$	σ_O and σ_P are the standard deviations of observations and predictions Co_i and Cp_i are the observed and predicted concentration in monitoring station ''i''; n the total number of monitoring stations.	0.0
Normalized standard deviation	$NSD = \frac{\sigma Cp}{\sigma Co}$		1.0
Normalized mean square error	$NMSE = \frac{\overline{(Co - Cp)^2}}{\overline{CoCp}}$		0.0
Average normalized absolute bias	$ANB = \left(\frac{\overline{\lvert Co - Cp \rvert}}{Co}\right)$		
Geometric mean bias	$MG = \exp(\overline{\ln Co} - \overline{\ln Cp})$		1.0
Geometric variance	$VG = \exp\left[(\overline{\ln Co} - \overline{\ln Cp})^2\right]$		1.0
Fraction of predictions within a factor of 2 of observations	$0.5 \le \frac{Cp}{Co} \le 2.0$		1.0

Since the distribution is close to log-normal for most atmospheric pollutant concentrations, the linear measures FB and NMSE may be overlay influenced by

infrequently occurring high observed and/or predicted concentrations, whereas the logarithmic measures MG and VG may provide a more balanced treatment of extreme high and low values. Nevertheless, MG and VG may be overly influenced by extremely low values, near the instrument thresholds and are undefined for zero values. FAC2 is the most robust measure, because it is not overly influenced by outliers. FB and MG are measures of mean relative bias and indicate only systematic errors, whereas NMSE and VG are measures of mean relative scatter and reflect both systematic and unsystematic (random) errors. The correlation coefficient (r) reflects the linear relationship between two variables and is thus insensitive to either an additive or a multiplicative factor. Some authors recommend this parameter when large-scale models with gridded fields are involved (McNally and Tesche, 1993). Elbir (2003) proposed a statistical analysis that included the index of agreement (d), which determines the degree to which magnitudes and signs of the observed value about mean observed value are related to the predicted deviation about mean predicted value, and allows for sensitivity toward difference in observed and predicted values as well as proportionality changes. Studies conducted by Sivacoumar and Thanasekaran (1999) and Karppinen et al. (2000) also established the usefulness of the index of agreement and other above-mentioned statistical parameters for evaluating model performance. The referred index of agreement (d) is defined as follows:

$$d = 1 - \frac{\sum_{i=1}^{N} (Cp_i - Co_i)^2}{\sum_{i=1}^{N} \left(\left| Cp_i - \overline{Co} \right| + \left| Co_i - \overline{Co} \right| \right)^2} \quad (1)$$

considering the same definitions of variables of Table 1. The index of agreement varies from 0.0 (theoretical minimum) to 1.0 (perfect agreement between observed and predicted values) and gives the degree to which model predictions are error free. To show how this statistical analysis methodology could be applied to a test case, an air quality model performance evaluation was conducted to an application of two air quality models to an ozone episode occurred in Portugal, in 2001. A 48 hours simulation was performed for Continental Portugal, over a gridded domain with 10 km horizontal resolution, using CHIMERE and CAMx models, aiming to estimate hourly ozone concentrations (Ferreira et al., 2004). Models performance was evaluated for 5 air quality monitoring stations, three of them considered as background stations and two located in industrial areas. Results of the referred analysis are summarised in Table 2. It must be stressed that the correlation coefficient is one of the most important parameters, as it reflects the ability of the models to simulate measured data, and, based on the results presented in Table 2, its values reveal a little better behaviour of CAMx model. The values obtained for the bias, reported by FB, ANB and MG, reflect the differences between average observed and simulated results. Considering that these three parameters contribute with the same kind of information, only one of them is, in fact, required for a statistical analysis of modelling results. RMSE and NMSE give information about the errors obtained within the observed-predicted pairs of results, but RMSE does not ignore the range of the variable in cause, ozone concentration, which in some cases could lead to incorrect interpretations of the results of this parameter. Thus, a normalized form of the parameter, NMSE, could be in such cases more adequate. FB and MG obtained values for CHIMERE are closer to the ideal values, 0 and 1

respectively, than the correspondent results for CAMx, meaning that systematic errors are higher in CAMx simulation results.

Table 2. Statistical analysis results for CHIMERE and CAMx simulation.

Parameter	Average for all stations		Average for background stations	
	CHIMERE	CAMx	CHIMERE	CAMx
r	0.52	0.62	0.56	0.70
Fb	-0.16	0.28	-0.19	0.20
RMS	49.10	51.15	43.14	42.66
NSD	1.12	0.77	1.13	0.84
NMSE	0.27	0.45	0.25	0.34
ANB	1.06	0.52	1.26	0.53
MG	0.76	1.44	0.73	1.48
VG	1.16	1.16	1.21	1.19
FAC2	1.19	0.77	1.24	0.84
d	0.71	0.69	0.78	0.79

However, both modelling applications have systematic and random errors as indicated by VG results. The parameters MG and VG are, in some way, useless, since they are sensitive to very low concentrations, which occur at night during the application example. Therefore, these parameters should be carefully used in such an evaluation. Regarding FAC2 and d, similar results were obtained for both models. Based on the ideas pointed out, it can be concluded that every statistical parameter plays a role in the evaluation of model performance and uncertainties estimation, but some of them could be considered more important, useful and required for such an analysis, namely, the correlation coefficient (r), the fractional bias (FB), the root mean square error (RMSE) (without forgetting its accounting on the magnitude of the studied variable), and the normalised mean square error (NMSE). For EPA regulatory applications, the primary objective is to evaluate how well an air quality model simulates the maximum one-hour averaged concentration anywhere on the sampling network. USEPA (1996) presents a compilation of a series of photochemical model validation exercises focused on the model's ability to predict the domain-wide peak ozone concentration and the concentrations at all locations with observed ozone data above 60 ppb. These quality indicators are described in Table 3, including the ideal values, which are merely indicative, once they were defined based on tests performed. Table 4 presents the EPA quality indicators that were also computed for the application described above.

Table 3. EPA's quality indicators for air quality model performance evaluation

Quality indicators	EPA	Ideal values
Normalized accuracy of the maximum 1h concentration unpaired in space and time	$A_u = 100\left(\frac{Co_{max} - Cp_{max}}{Cp_{max}}\right)$	± 15-20%
Normalized bias test	$D = \frac{1}{N}\sum_{i=1}^{N}\frac{Co_i - Cp_i}{Co_i}$	± 0.05-0.15
Gross error of all pairs Co > 60 ppb	$E = \frac{1}{N}\sum_{i=1}^{N}\frac{Co_i - Cp_i}{Co_i}$	± 30-35%

Table 4. EPA quality indicators obtained for CHIMERE and CAMx simulation

Parameter	Average for all stations		Average for background stations	
	CHIMERE	CAMx	CHIMERE	CAMx
Au	18.0	46.6	10.1	26.5
D	-0.8	0.1	-1.1	0.1
E	0.0	0.1	0.0	0.1

This group of parameters complements the previous analysis, since it evaluates the model capability to simulate peaks, which is particularly important for the evaluation of atmospheric pollutants episodes, like the example exposed.
Another way to evaluate model performance in a stochastic framework is to assume that the observed concentration is simply a random sample taken from the probability density function (PDF) of the predicted concentration, which can be estimated by such techniques as higher-order turbulence closure schemes and Monte Carlo analysis (Chang and Hanna, 2004). Several authors already applied the Monte Carlo method for different urban/regional scale models (e.g. Moore and Londergan, 2001; Beekmann and Derognat, 2003). This method is also the most commonly used to estimate uncertainties in model input variables, since it has a quite simple principle and it can applied to a complete set of more than 100 input parameters and it allows use of standards nonparametric statistical tests concerning confidence intervals (Ang and Tang, 1984; Borrego et al., 2004). In summary, multiple performance measures and methods should be applied and considered in any model evaluation exercise, as each measure/method has advantages and disadvantages and there is not a single method that is universally applicable to all conditions.

2.3 Model uncertainty according to the EU Directives

The Framework Directive (FWD) and Daughter Directives establish requirements for air quality modelling, including the definition of the Modelling Quality Objectives, as a measure of modelling results acceptability. In this context, the uncertainty for modelling and objective estimation is defined as the maximum deviation of the measured and calculated concentration levels, over the period for calculating the appropriate threshold, without taking into account the timing of the events. The quality objectives defined for each quality indicator are listed in Table 5.

Table 5. Modelling Quality objectives established by EU Directives

Pollutant	Quality Indicator	Quality Objective	Directive
SO_2, NO_2, NO_x	Hourly mean	50-60%	1999/30/EC
	Daily mean	50%	
	Annual mean	30%	
PM, Pb	Annual mean	50%	
CO	8-hour mean	50%	2000/69/EC
Benzene	Annual mean	50%	
Ozone	8-hour daily mean	50%	2002/03/EC
	1-hour average	50%	

Model quality measures described in the EU Directives are interpreted as the relative maximum error without timing (RME), which is the largest concentration difference of all percentile (p) differences normalized by the respective measured value.

$$RME = \frac{\max(|Co_p - Cp_p|)}{Co_{p\max(Co_p - Cp_p)}} \tag{2}$$

The question of timing is relevant for those hourly and daily limits, or target values, which are defined as a number of allowed exceedances of a given threshold concentration. Besides that, the model quality objectives for the allowed uncertainty are given as a relative uncertainty, without clear guidance on how to calculate this relative uncertainty. It could be assumed that the respective measured value shall be used to normalize the absolute difference between the maximum deviation of the measured and calculated concentration levels. Another possibility would be to take the maximum relative deviation, but this approach could shift the emphasis to the very low measured concentration ranges, where usually the largest relative deviations between observations and calculations occur, which could be the main reason for non-compliance of annual mean values accuracy requirements. Besides that, other problems of the interpretation of the model accuracy requirements, according to the EU Directives could occur since there are no differences between a short-term and long-term model application accuracy analysis, being the first one in advantage due to the number of paired-in-time results. An alternative model error measure was already proposed by Stern and Flemming (2004), defining the quality indicator as the concentration difference at the percentile corresponding to the allowed number of exceedances of the limit value normalized by the observation (RPE).

$$RPE = \frac{|Co_p - Cp_p|}{Co_p}, \; p \tag{3}$$

This measure is more robust than the error defined in the EU Directive and also evaluates the model performance in the high concentration ranges, but without the sensitivity to outliers. Since the model accuracy is examined in the concentration range of the limit values, there is also a direct link to the EU Directives. In order to test and illustrate these model accuracy measures, a one-year simulation of the chemistry-transport model CHIMERE was used. CHIMERE was applied in the regional scale mode, covering Portugal with a resolution of 10 km for the entire year 2001 (Borrego et al., 2005). The model results were compared with measured data from 23 sites of the national air quality monitoring network according to the EU directives thresholds. In Table 6 is presented an average of the relative maximum error (RME) and the relative error at the percentile that correspond to the allowed number of exceedings of the limit value threshold (RPE) for the background and all the monitoring sites, for each pollutant indicator defined by the EU Directives. Concerning the hourly and daily averages indicators, the analysis of the relative maximum error (RME) defined by the EU directives reveals that it is calculated at the highest measured value.

Table 6. Average of RME and RPE for the background and all the monitoring sites, for each pollutant indicator defined by the EU Directives

Pollutant	EU Directives indicators	RME (%)*	Percentile (P)	RPE (%)*	RPE (%)**
SO_2	Human health protection (hourly mean)	79	99.73 (25^{th} max 1h mean)	34	40
	Human health protection (daily mean)	66	99.18 (4^{th} max 24h mean)	57	69
	Vegetation protection	33	annual mean	33	46
	Vegetation protection	44	winter mean	44	58
NO_2	Human heath protection (hourly mean)	81	99.79 (19^{th} max 1h mean)	39	48
	Human heath protection	47	annual average	47	50
O_3	Human heath protection (8h running daily mean)	69	93.15 (26^{th} max 8h daily mean)	16	35
	Vegetation protection	71	AOT40	49	65

*considering only background monitoring stations; ** considering all monitoring stations

In these cases, the assessment of the model accuracy depends on the model performance in a concentration range having an extremely small probability. This also means that the model accuracy assessment could probably be based on an outlier concentration caused by an error of the monitoring unit or an extreme weather situation. In fact, and in opposite to the RME, the alternative model error measure proposed (RPE) shows a quite total compliance with the legislation accuracy requirement of 50% for all the pollutants indicators. These conclusions are in agreement with other model evaluation studies with similar or even higher complexity (Stern and Flemming, 2004; Hass et al., 2003). The analysis of Table 6 reveals also the problem of the heterogeneity of the observed concentration fields and the importance of selecting the adequate and representative monitoring sites for model resolution, since it is impossible for a grid model to simulate all stations with the required accuracy. In spite of the European Air Quality monitoring network (EUROAIRNET) considers that both spatial and temporal representativeness of monitoring stations should be addressed in uncertainty estimation procedures, in order to guarantee a more accurate comparison with air quality standards, the Daughter Directives say nothing about the monitoring stations representativeness and the selection of criteria for the number and type of stations to be used on model accuracy evaluation. Nevertheless, there is a need for pre-selecting the stations to be used for model evaluation and that should be relied on the sites classification or on the prior knowledge of the air quality regime of the measurement sites (based on daily mean and the daily variation of each pollutant). Besides the monitoring stations representativeness, there is absence of any guidance in the EU Directives about measurement inaccuracy and incomplete data coverage that should all be taken into account in the context of a model evaluation. Regarding to data coverage, the EU Directives require a minimum of 90 % data coverage of the hourly or daily values. In fact, this is another model accuracy check problem since in the past the data coverage of the Portuguese stations was mostly below 90%.

3. CONCLUSIONS

A systematic description of the modelling uncertainty analysis methodologies, based on bibliography review, was performed and discussed. Examples of air quality modelling uncertainty estimation at regional scale were presented, taking into account the review of the current existent scientific and legislated methodologies.
The statistical analysis suggested to evaluate model performance and to estimate uncertainties comprises a set of parameters, giving information about the ability of the model to predict the tendency of observed values, errors on the simulation of average and peak observed concentrations, and type of errors (systematic or unsystematic). From the application exercise, it was concluded that despite all parameters are important, it is possible to define a subset of parameters able to reproduce the general uncertainties estimation, comprising the correlation coefficient, the fractional bias and the root and normalized mean square errors. Parameters that reflect the capability to simulate peaks should be taken into consideration in air pollution episodes simulation. Concerning the quality indicators defined by EU directives, the results show that the legislated uncertainty estimation measures are ambiguous and inadequate in several aspects, mainly in what concerns the error measures for hourly and daily indicators based on the highest observed concentration. A relative error at the percentile correspondent to the allowed number of exceedances of the limit value was suggested and tested, showing that is more robust and also evaluates the model performance as required. Besides that, the EU directives do not give rules on how to deal with monitoring stations representativeness on model evaluation, an important issue to guarantee the correct information about measured or predicted exceedances of thresholds values.

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THE DOAS METHODOLOGY FOR AIR POLLUTION STUDY AND INVESTIGATION IN INDUSTRIAL AND URBAN AREAS

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ABSTRACT

Object of this study is the versatility of a remote sensing measurement system through experimental survey of the levels of primary and secondary pollutants in urban and industrial Italian areas.
Data on NO_2, O_3, benzene and toluene are measured and discussed after intensive measurement campaign in different seasonal period by means of two Differential Optical Absorption Spectroscopy systems installed at ground level and on the roof of the ISPESL Mobile Laboratory, respectively.

Key Words: DOAS, Air Pollution, Secondary Pollution, Photochemical Smog

1. INTRODUCTION

In order to improve the air quality in Europe the European Commission issued some directive with regard to acceptable levels of a range of gaseous pollutants species as SO_2, NO, NO_2, O_3 and benzene (Commission European Communities, 1996). In particular, measurements of ozone and benzene represent nowadays a very important target in the atmospheric studies due to the different sources and health effects of both the gaseous species. Ozone has important adverse health and environmental effects such as respiratory irritation: chemically, it is the primary constituent of smog but it is not emitted directly into the air by specific sources but created by photochemical reactions involving sunlight, nitrogen oxides and volatile organic compounds (VOC) (Morales et al., 2004).
Among the different method used to analyze these compounds the technique involving open-path spectroscopy is ideal for monitoring pollutants for their advantages over classical methods and point-source analyzers (Avino et al., 2002).
The Differential Optical Absorption Spectroscopy (DOAS) is one of the most versatile optical techniques for the determination of air pollutants. DOAS is an useful measuring technique for routine work to control air quality and pollution emissions but also for applications in air pollution studies (Platt et al., 1979; Platt and Perner, 1980).
The DOAS is a remote-sensing analytical technique finding strong consents as demonstrated by numerous paper published during these last years. The DOAS analytical method is based on the UV and Vis light absorption (from 240 nm to 340 nm) of species with fine vibrational structures like SO_2, NO_2, ozone, nitrous acid,

formaldehyde, benzene and toluene; the Lambert-Beer's law regulates the relationship between the adsorbed light intensity and the concentration of each species.
The DOAS system is constituted from the following parts: a light source, a receiver, a spectrophotometer equipped with an optical fiber and a computer for the system management (data elaboration and data storage). The light source is a Xenon lamp (at high pressure and 150W): a transmitter sends the light to the receiver that transmits the beam through the optical fiber in the analyzer (Figure 1).
The absorption spectra of each monitored chemical species are acquired at their relative typical wavelength ranges; subsequently, the interferences are eliminated by comparison with the reference spectra.
This technique furnishes the concentrations related to a portion atmospheric environment varying also for some kilometers. In fact, these "integrated" concentrations represent the average area pollution level better than the measurements obtained by traditional analyzers which are considered "punctual".

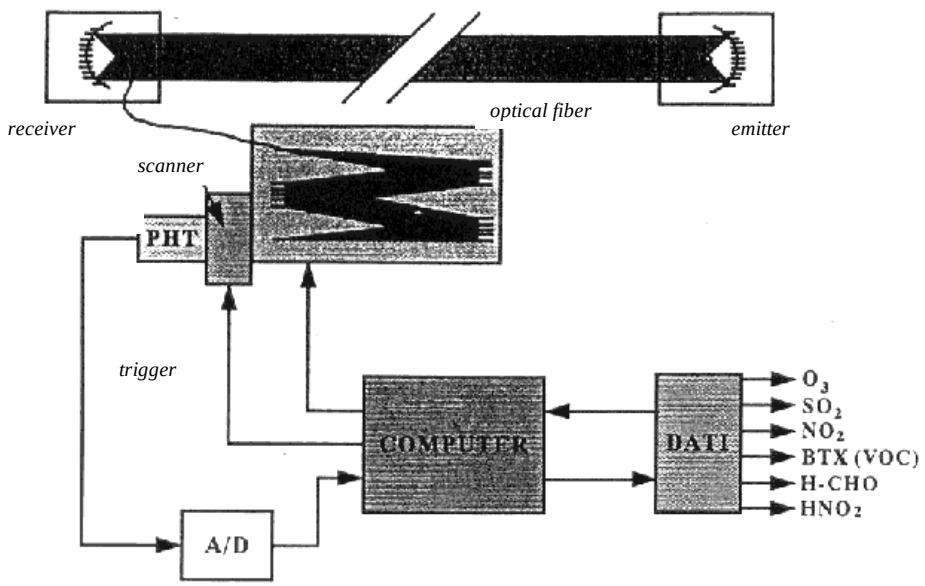

Figure 1. Flow-scheme of a DOAS system

The constituents investigated with DOAS technique include sulphur dioxide (SO_2), nitrogen dioxide (NO_2), nitrous acid (HNO_2), formaldehyde (HCHO), ozone (O_3), ammonia, mercury and aromatic hydrocarbons.
This papers reports measurements of NO_2, O_3, benzene and toluene carried out in downtown Rome during a springtime and in an industrial site during a wintertime by means of DOAS system installed at ground level and above a roof of the ISPESL Mobile Laboratory.

2. EXPERIMENTAL

The first DOAS system (mod. AR 500, Opsis, Sweden) has been installed at the

ISPESL monitoring station located in downtown Rome (near St. Maria Maggiore Cathedral) at about 10 m above ground level in an urban zone characterized by high density of autovehicular traffic. The second similar DOAS system was installed on the roof of the ISPESL Mobile Laboratory in an area at high density of industrial activity and the measurements can be considered at ground level: the site is close to a city at high density of anthropogenic activities (strong industrial emissions) and located in front of the sea.
For both instruments the analytical parameters are almost the same. The distance between emitter and receptor ranged between 200 and 250 m (this terms influences the sensitivity of the measures).
The absorbance of light from the emitter is continuously measured within the wavelength range 240-350 nm to determine several compounds (Table 1). The aromatic hydrocarbons are detected in the wavelength range between 250 and 290 nm where the major interfering gases are oxygen, ozone and sulphur dioxide; around 100 spectra per second are collected in this wavelength range and stored in a register with 1000 channels with a resolution of better than 0.05 nm. The concentrations of air pollutants are automatically calculated from the absorbance values in according with Lambert-Beer's law (Brocco et al., 1997).
Spectra are required on an average time of 7 min for the system located in downtown Rome, and 5 min for the system sited in the industrial site.

Table 1. Operative conditions of the DOAS system

Pollutant	λ (nm)	Time (min)	SD (μg/m^3)
SO_2	270-380	1	0.5-2.0
NO_2	398-450	1	1.5-2.0
O_3	250-320	5	3.2-5.0
Benzene	240-310	1	3.5-6.0
Toluene	240-310	1	4.5-6.5
Nitrous acid	320-380	7	0.3-0.4
Formaldehyde	270-340	5	0.5-1.0

3. RESULTS

The data for nitrous acid, NO_2, O_3, benzene and toluene concentrations as measured by the two long-path DOAS systems during different seasonal periods in various areas are extensively discussed. All the data are hourly averaged from measures carried out every 5 min of sampling intervals.
In Figures 2 and 3 are provided spectra of the average hourly benzene and toluene concentrations in the two locations investigated.
The situation of the benzene pollutant, especially in urban areas, is really changed during this last decade. At the beginning of the years '90's, the benzene coming from autovehicular, industrial and anthropogenic emissions was present in atmosphere with concentrations among 40 and 80 μg/m^3. For both its toxicological characteristics (suspect carcinogenic for human) and chemical stability, such compound has constituted an element of constant hygienic-sanitary interest since many years.

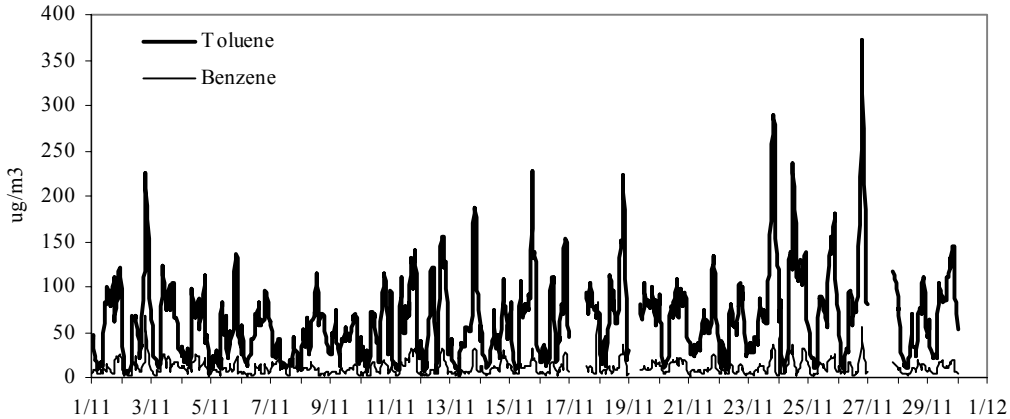

Figure 2. Hourly average concentrations of benzene and toluene measured in November 1999 in downtown Rome with the DOAS system.

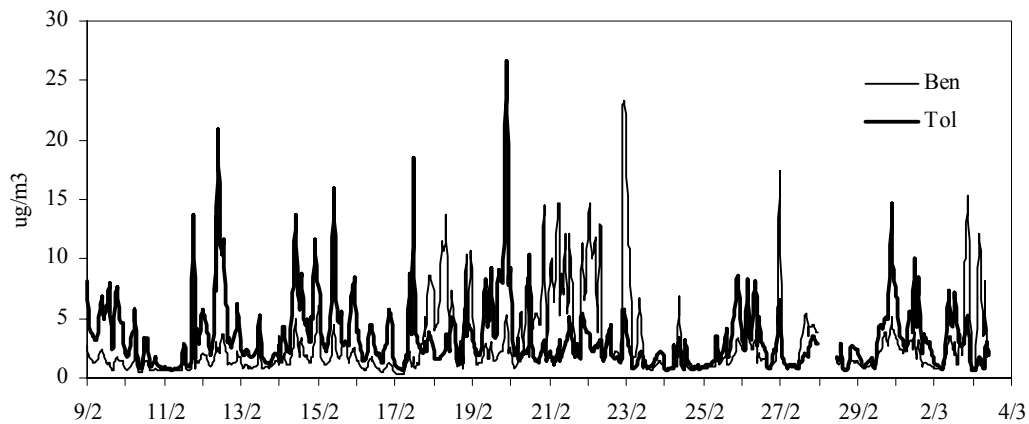

Figure 3. Hourly average concentrations of benzene and toluene measured in February 2000 in an industrial site with the DOAS system.

It is interesting to notice that during this decade there was a slight but clear decrease of benzene concentration in atmosphere also for the introduction in the Italian lifestyle of the use of the green fuel. And this reduction can be seen in the figure referring to the urban situation (Figure 2): benzene and toluene has the same trend and the ratio is almost constant around 3-5 time in according with those reported in literature.

In Figures 4 and 5 are reported the average hourly concentrations of nitrous acid measured in October 2002 and January 2003. During the month of October, because of the elevated solar irradiation the nitrous acid formed for heterogeneous reaction of NO_2 with H_2O, photo-dissociates itself producing OH radicals: consequently, the concentrations reach modest values ranging between some micrograms and 6-8 $\mu g/m^3$. In the winter period the concentration levels of nitrous acid are notably more elevated up to 40 $\mu g/m^3$. Also this compound has an important hygienic-sanitary interest being a gas phase mutagen and a precursor to nitrosoamines.

In Figure 6 are reported the average hourly concentrations of O_3 in winter period in an industrial site overlooking the sea. This characteristic results interesting when the histograms are examined: in fact, comparing the concentration values with those determined in other urban areas during the day, it can be evidenced nighttimes ozone peaks of the same order of magnitude of those diurnal. This circumstance can be made possible by the presence of meteorological conditions related to phenomena proper of sea places such as the breezes.
In Figure 7 are reported the hourly average NO_2 concentrations measured in a winter month in the industrial area, where the production of nitrogen oxides is more massive. It can be noted how the concentration values trend respects the characteristics of NO_2 secondary pollutant: there are peaks in the warmest hours of the day (e.g., when the solar irradiation and the photochemical activity are greater) except in two cases (i.e., 5th and 6th of December) when a contribution of extraordinary emission intervenes underlined clearly by the histograms.

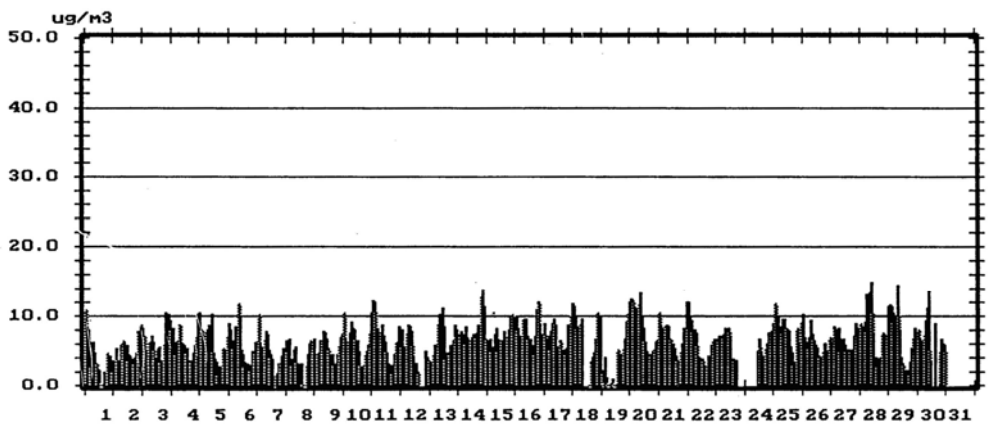

Figure 4. Hourly average concentrations of nitrous acid measured in October 2002 in downtown Rome with the DOAS system.

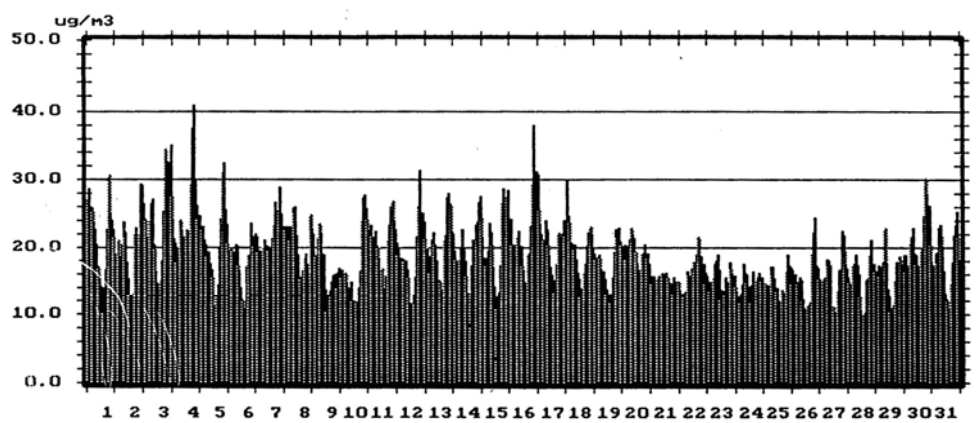

Figure 5. Hourly average concentrations of nitrous acid measured in January 2003 in downtown Rome with the DOAS system.

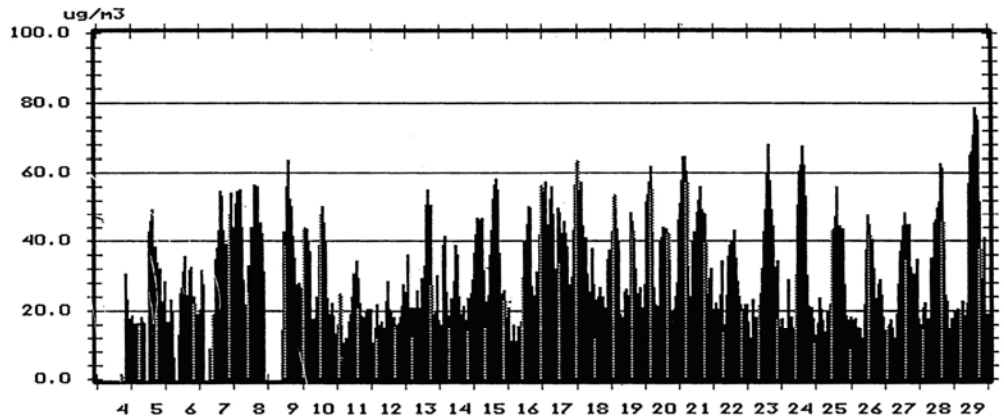

Figure 6. Hourly average concentrations of ozone measured in February 2000 in an industrial site with the DOAS system.

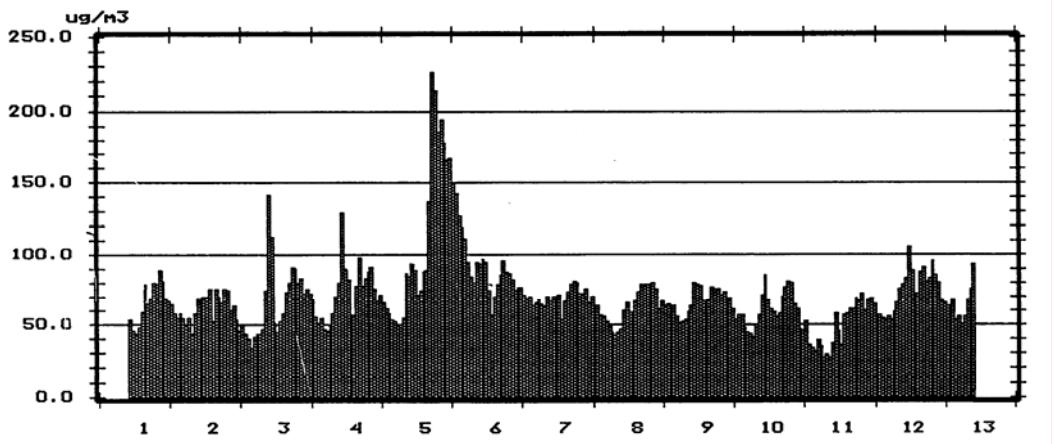

Figure 7. Hourly average concentrations of NO_2 measured in December 2002 in downtown Rome with the DOAS system.

It is evidenced that the secondary pollution, and in particular that derived from NO_2 and ozone, is not influenced by emission intensity and consequently assumes homogenous values in the entire urban area (Avino, 2004).

4. CONCLUSION

The DOAS technique is an advanced measurement system useful for integrating information coming from monitoring networks: furthermore, it allows to investigate and understand the complex mechanisms of formation and transformation of atmospheric pollutants through the contemporary measurements of gaseous primary and secondary species. In this way the representation of the air pollution is more correct than using automatic analyzers.
The results obtained take in account the spatial-temporal variations of the pollutant concentrations due to both the atmospheric dishomogeneity and the contributions of sources not directly present in the areas considered.

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CONTINUOUS SEMI-VOLATILE FRACTION MEASUREMENT IN PM_{10} AND $PM_{2.5}$

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ABSTRACT

Different studies have shown that the semi-volatile fraction of $PM_{2.5}$ accounts for 20%…50% of the total $PM_{2.5}$ mass. Semi-Volatiles account for a lower but significant percentage of PM_{10} mass. To determine the appropriate PM_x mass it is important to measure not only the non-volatile fraction but also the semi-volatile content. Semi-volatiles can be lost from filter samples due to the on-going sampling, to gas-solid or even fluid-solid reactions. Also during the conditioning before weighing volatile compounds might be lost. Particulate monitors have used heated sample probes to prevent condensation, but by doing so, they can lose the semi-volatile fraction by heating up the sample. As a result, the data obtained often reflects measurements that have poor semi-volatile capture and PM values are therefore underestimated. With a newly developed real time OPC instrument employing non heated and heated probe sample cycles in the same instrument, it is possible to get a value of PM_x including Volatiles and to calculate a correction (location) factor for existing measurements as well as providing information about particle size distribution within the mass sample. This paper will show results from field tests in US and Germany and results from comparison with other real time and filter analysis. Results support higher PM values, better semi-volatile capture and the potential to calculate a correction factor.

Key Words: PM10, PM2.5, SVC, Semi-Volatiles

1. INTRODUCTION

Current methods of measurement of particulate matter only give a limited amount of information about particles in ambient air. For a better understanding of the possible impact of particles on human health we need information about the mass, size, concentration and composition of particulate matter. Available technologies have limitations with respect to these parameters.

In addition, information about temporal changes is required, making real time measurement desirable. Such data collection is cost effective and provides better source analysis and better understanding of the relationship of particulates measurement to processes occurring in the atmosphere. This information has the

potential to improve our understanding of causality and epidemiology and potential also for better prediction of episodes which may impact on human health.

Much of the data available only provides mean mass values, giving no information about size, distribution and concentration of particles.

A high mass value could come from a few coarse particles or from a huge amount of small particles.

Much of the existing data has been collected using filter methods with direct gravimetric measurement but no temporal information or ral time methods. The commonly used real time technologies have been based on Beta Attenuation Technology, Tapered Element Oscillating Microbalance TEOM (and FDMS), and Optical Particle Counters (OPC). Results are obtained from radiation attenuation, frequency of microbalance oscillation and orthogonal light scatter respectively.

Fine particulate mass in the atmosphere includes non-volatile components such as sulfate, crustal material and elemental carbon which (within instrument resolution) can be easily captured by a variety of techniques. However, also included in the fine particulate matter is semi-volatile matter.

Examples of semi-volatile particles include ammonium nitrate, ammonium sulphate, some organic material and water which is much more demanding to monitor (Eatough et al., 2003)

Different studies (Ten Brink, 2004) have shown that the semi-volatile fraction of $PM_{2.5}$ accounts for 20%...50% of the total $PM_{2.5}$ mass. Semi-volatiles account for a lower but significant percentage of PM_{10} mass. To determine the appropriate PM value, it is important to measure not only the non-volatile fraction but also the semi-volatile content. This importance increases as the focus on smaller particles measurement increases.

Semi-volatiles can be lost from filter samples due to the on-going sampling, to gas-solid or even fluid-solid reactions. Also during the conditioning before weighing semi-volatile compounds may be lost.

Dust monitors using heated sample probes to prevent condensation may lose the semi-volatile fraction by heating the sample.

As a result of the limitations of sampling methods, the data obtained often reflects measurements that have poor semi-volatile capture and PM values are therefore underestimated.

It is necessary to improve the technologies available to increase the efficiency of particulate capture as well as to determine the aerosol mass, size distribution and

concentration in combination/addition with different speciation technologies to get insight into the composition of particulate matter.

In this paper we present for discussion the results of two studies and propose that the results support the notion that using non heated probes results in higher Particulate Mass Sample Readings and that this higher reading can be explained by better captured of semi-volatile compounds.

The use of heated and non heated measurement cycles within the same instrument, can provide valuable indicative measures of the proportion of semi-volatiles in any given site in a cost effective and efficient manner. It is possible that this data can be used to calculate a site specific correction factor for other data. By incorporating this into an OPC based instrument additional useful information is obtained about particle size distribution within the overall mass measurement.

2. METHOD

Optical Particle Counter (particle counting with the method or orthogonal light scattering) instruments are widely used to measure particle counts and mass of ambient aerosols. Optical Technology draws on the principles of classic MIE theory.

The GRIMM monitors for this trial use light scattering technology for single particle counts in which a semiconductor laser serves as the light source. The ambient air to be analysed is drawn into the unit via an internal volume controlled pump at a rate of 1.2 litres/minute. The pump also generates the necessary clean sheath air which is filtered and passes through the sheath air regulator back to the optical chamber. This is to ensure that no dust contamination comes in contact with the laser-optic assembly. This particle free airflow is also used for the reference zero test during the auto-calibration.

The inlet air is usually unaltered prior to introduction to the light scattering chamber. The scattered signal from each particle passing through the laser beam is collected at approximately 90^{o} by a mirror and transferred to a recipient diode. The Grimm optical system measures the scattered light at 90 deg. to the incident beam from individual particles as they pass through the optical system and therefore changes in the refractive index of the particles, by any altered parameters, has minimum or no effect on the measurement. After a corresponding reinforcement, the signal of the diode is recorded with a multi-channel size classifier. A pulse height analyzer then classifies the signal transmitted in each channel. These counts are stored in the data storage card for future analysis.
To prevent condensation, the monitor incorporates a special sample probe drying system and does not alter the sample.

The new generation OPC instrument has been designed so that it can operate with the sample inlet probe unheated or heated and the results of both measurements are processed and the difference calculated.

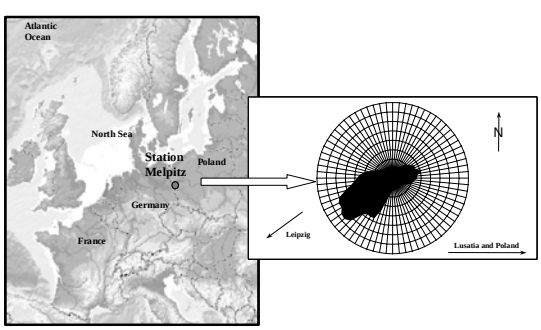
The instrument first measures the total amount of particles (including semi-volatiles in the ambient air with the standard non heated probe and obtains PM 10 and PM 2.5 values. The sample inlet is then heated to 100 C stripping Semi-Volatiles and in the second measurement the Non-Volatile fraction is calculated.

The difference between the two results is the semi volatile fraction of the ambient air. By processing both cycles, it is possible to get the mass value of the semi volatile fraction. The system is mobile and is installed in a robust weatherproof housing. This allows for mobile measuring campaigns, hotspot measuring or source apportionment. Three field tests were conducted.

The first field test was conducted by the Brigham Young University and the DRI in 2003. There were two field campaigns, the first in July 2003 in Roubidoux,CA and the second in December 2003 in Fresno, CA. Two OPC instruments using heated (to 100 C) and non heated probe measurements were compared to RAMS (Real Time Ambient Mass Sampler ; a TEOM (using a sample inlet heat of 50^{o}), a differential TEOM and a TEOM FDMS system.

In the third field test (conducted by the Troposphaeren Institut in Leipzig, Germany) the results from a single OPC unit using 10 minute cycles of heated and non heated probe data collections were compared to the results of High Volume Sampler Collection and the results of further chemical analysis of the High Volume Filter Sample.

The OPC with the nan heated and heated sample inlet were compared against three co-located High Volume Sampler Digitel DAH80 equipped with a PM_{10}, a $PM_{2.5}$ and a PM_1 sample head. The location for the field test was the Melpitz Research Station of the Troposphaeren Institut in Leipzig. This site was well suited for the field test because it is located in a plain with a rural background. The main wind direction is south-west bringing Atlantic air with emissions from middle Europe. The second wind direction is east. This brings mostly dry air from high pressure areas with heavy anthropogenetic pollution from the countries in eastern Europe.

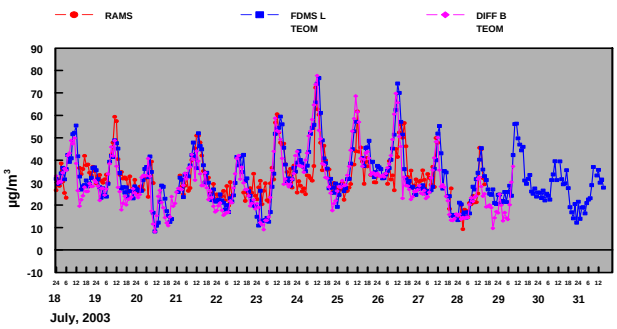


Measuring was conducted in the time from February 26 to April 26, 2004 for a total of 88 days. The daily mean temperatures were ranging from -2 to 18^{o}C. Weather conditions were changing frequently.

3. RESULTS AND DISCUSSION

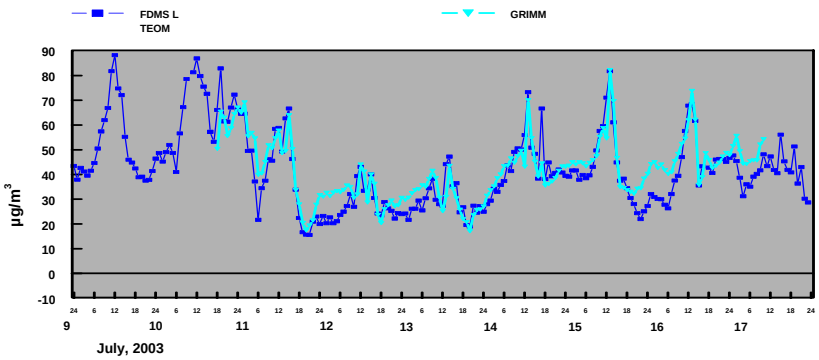
3.1 Roubidoux Study

The measurement of $PM_{2.5}$ by the GRIMM monitor in Roubidoux was evaluated by comparison with the RAMS, FDMS and Differential TEOM, each of which were in agreement with each other, and each of which have been shown to measure total fine particulate mass, including both the nonvolatile and semi-volatile components (Grover et al., 2004). However, each of these instruments uses a Nafion dryer in the inlet stream and does not measure the fine particulate water content. The comparisons between these three instruments has been

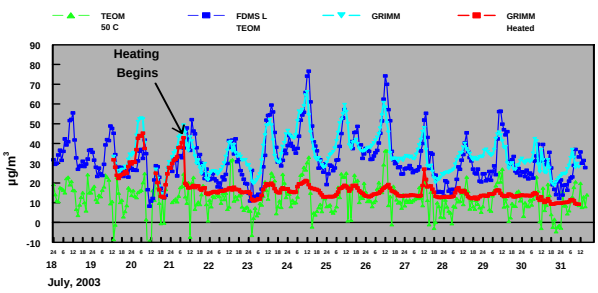


previously given (Grover et. al, 2004). For the purposes of this paper, the GRIMM monitor is compared to the average result obtained with these three instruments. This comparison is shown for data obtained during July 2003 at Rubidoux, CA during two different time periods. During the first time period from 11-17 July FDMS and Differential TEOM data were obtained, but no RAMS data were available. During the 20-30 July period data were available from all three comparison instruments.

Peaks in the $PM_{2.5}$ concentrations generally occurred during the mid-day period for each sampling day. This was a time of significant secondary ammonium nitrate and semi-volatile organic material formation. Relative humidity was general low during this mid-day time period. The GRIMM and comparison monitor results are in good agreement during these periods of low relative humidity, Indicating that the protocols used to convert the GRIMM monitor volume distribution data to a $PM_{2.5}$ mass concentration are robust.



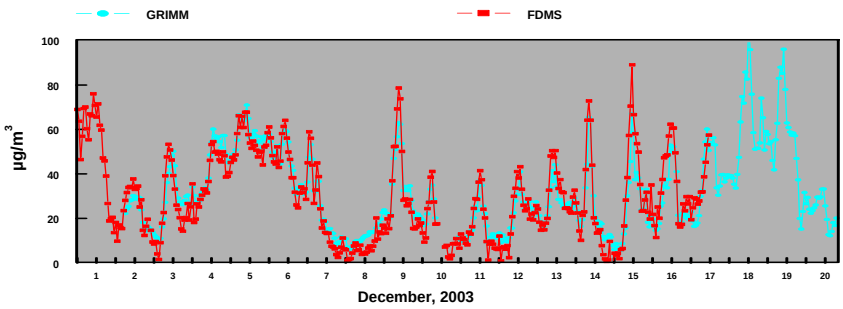
Additional information on mass measurement by the GRIMM monitor were obtained by comparison of the GRIMM monitor results with those obtained with a conventional TEOM monitor operating at 50 ^{o}C and a GRIMM monitor with a inlet heated to 50 ^{o}C. These data are compared to the conventional GRIMM results. As expected, both the heated TEOM and heated GRIMM results give $PM_{2.5}$ measurements which are lower than obtained with the other instruments. This can be attributed to the loss of some of the semi-volatile ammonium nitrate



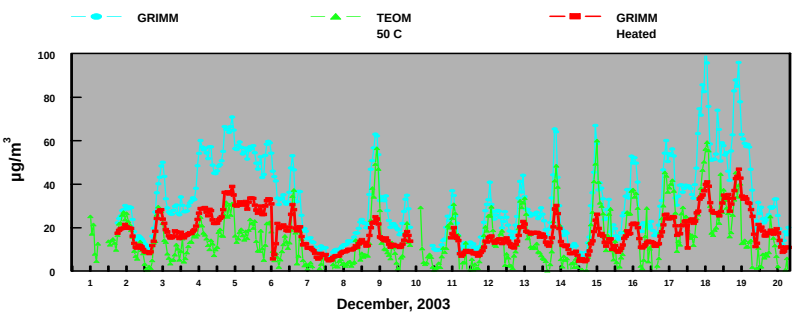
and semi-volatile organic material from the sampled particles at the elevated temperature. The 50 °C TEOM monitor results tend to be somewhat lower than the GRIMM measurements and to have greater diurnal variability. This can probably be attributed to the retention of particles on the heated filter of the TEOM monitor with subsequent continued loss over time as the composition of the sampled aerosol changes. The difference between the unheated GRIMM and comparison samplers which has been attributed above to the measurement of fine particulate water content by the GRIMM monitor is not evident in the heated GRIMM monitor results. This is expected at the elevated temperature of the sampled aerosols in the heated GRIMM monitor.

3.2 Fresno Study

The results obtained in the study at Fresno, CA in December 2003 present results for the GRIMM monitor, the heated GRIMM monitor, the FDMS and Differential TEOM monitors for the first two weeks of the study. The comparison among the various samplers for the data at Fresno are similar to the results seen at Roubidoux.



However, the diurnal pattern in the data is quite different. High concentrations of $PM_{2.5}$ were seen each evening. This can be attributed to a combination of the development of an inversion layer in the early evening, together with the contribution of evening rush hour and wood smoke emissions to the $PM_{2.5}$ present at Fresno.



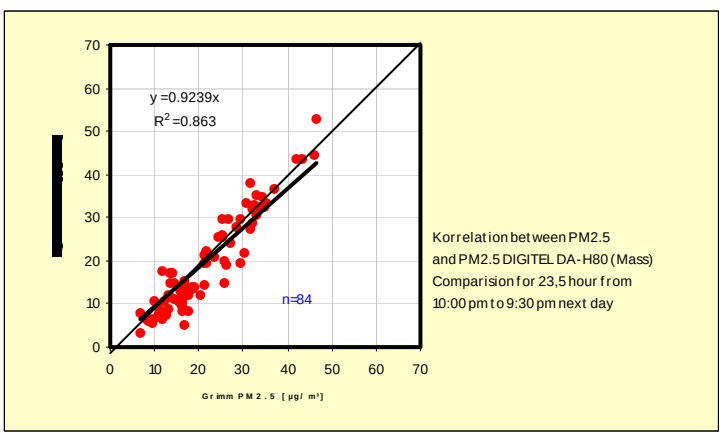
Generally low concentrations are seen during the day. The GRIMM and comparison monitors often give comparable results for both the mid-day and early evening time periods, Important exceptions to this pattern are seen during the prolonged inversion present during December 3 - 6, when the GRIMM monitor was frequently higher than the comparison data in the evening. This is also the time of significant ammonium nitrate formation. Another time period of interest is the early evening data for December 12 and 15. During these two time periods the comparison FDMS data was higher than the GRIMM monitor data by 10 to 15 $\mu g/m^3$ for just 2 or three hours close to midnight. The reasons for this observed difference are not now know. Consistent with results obtained in Roubidoux, the GRIMM monitor with a heated inlet measures significantly less material, presumable not accounting for the particle bound water and much of the semi-volatile ammonium nitrate and semi-volatile organic material.

3.3 Leipzig Study

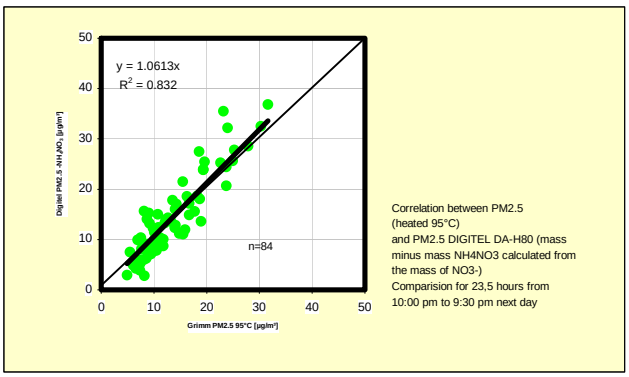
Troposphaeren Institut in Leipzig, Germany

For the field test the OPC with heated and non heated sample inlet were operated in a continuous mode with measuring interval of 10 minutes. The values for PM_{10}, $PM_{2.5}$ and PM1 have been monitored simultaneously. With the High Volume Sampler (HVS) DIGITEL-DHA-80 (30 m³/h flow rate) samples for PM_{10}, $PM_{2.5}$ and PM_1 have been collected on a quartz fibre filter for gravimetric mass measurement and consecutive chemical analysis. Samples have been taken for 23.5 hours (from 10:00h to 9:30h the following day). Of special interest was the amount of NO_3^- and NH_4^+ in the ambient dust. For the comparison a total of 88 filters ware available.

Comparison was made for the PMx values (OPC with non heated sample inlet, gravimetric mass from the HVS filters). A further comparison has been done for the PMx values from the heated OPC with the mass values from the HVS but with subtracted amount for NO_3NH_4, obtained from the chemical analysis.



The comparison showed a good correlation for the PM_x values from the non heated OPC and the values from the HVS. The measurements from the OPC in the 10 minute interval have shown a high temporal resolution of the changing atmospheric conditions. Furthermore the comparison of the values obtained from the OPC with the heated sample inlet and mass values from the HVS without the amount of NO_3NH_4 also showed a good correlation. The results show that the semi volatile fraction changes rapidly and therefore a fixed correction factor cannot be applied broadly.



4. SUMMARY

Measurement of particulate matter in ambient air should be reliable, accurate and sensitive. Information about mass, size, particle composition and temporal patterns is needed for better understanding about the implications for epidemiology and health.

One obstacle to the collection of complete samples has been the potential loss of semi-volatile compounds in filter methods with time and pre-conditioning before weighing of samples. One limitation of most real time methods has been the use of heated sample probes losing volatiles. The significance of this loss increases as the focus on particles less than $PM_{2.5}$ increase. The results of the US field study comparing the Grimm OPC In Non Heated and Heated Sample modes with RAMS and TEOM, TEOM FDMS support the hypothesis that the non heated sample inlet instruments such as the GRIMM OPC used in this study minimise volatile loss as the measurements with the heated probe samples are consistently lower.

The Leipzig study comparing results of Heated and Non heated cycles of measurement with High Volume Sampler mass measurement and subsequent sample speciation, support that volatile loss is the reason for these lower results.

Running heated and unheated instruments side by side at one site can give an estimate of the amount of volatiles on a continuous basis.

We propose that incorporating the capacity to run heated and non heated probe sampling cycles in a portable OPC instrument can provide better volatile capture in the Non heated cycle as well as information about particle mass values and size distribution. Also the comparative results can be used to calculate a correction or location factor for estimating the volatile fraction in the ambient air in a cost effective manner, especially for field companies, hotspot measurement or source apportionment.

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FUZZY ASSESSMENT OF HUMAN-HEALTH RISKS

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ABSTRACT

Uncertainty of input data creates fuzzy conditions for assessing and forecasting ecological risk and risks associated with human health due to environmental pollution. Many uncertainties are difficult to eliminate and they do not have structure so that it could be modeled or described by probabilities and probability processes. With this work a formalism of fuzzy sets was applied to model and assess the risk of carcinogenesis and additional mortality associated with air pollution. With this formalism it is possible to handle uncertainty by means of its modeling. A formulated approach makes it possible to assess the extent of expert confidence that the risk of carcinogenicity (risk of additional mortality) does not exceed some definite value that can be presented both as an accurate and fuzzy number. As an example is examined the risk associated with ten carcinogens; formaldehyde, lead, hexavalent chromium, benzpyrene, benzene, cadmium, nickel, arsenic, acetyldehyde, and carbon tetrachloride. For these three assessments were carried out for 'pessimistic', 'expected' and 'optimistic' scenarios at ten big industrial centers of Russia. For each scenario, the confidence degree that the risk does not exceed the chosen value was also calculated.

Key Words: Human Health Risk, Air Pollution, Fuzzy Logic

1. INTRODUCTION

In the process of decision making for minimizing the risks associated with pollution of the environment we run into one common problem – uncertainty of the input data that creates fuzzy conditions for assessments and forecasting. In striving to make these assessments more reliable, various development scenarios connected with the change of the exposure levels, the volume of emission and the set of harmful substances emitted to the environment are usually generated, and then the assessment of ecological risk and human health risk is conducted to realize hypothetical scenarios. The optimistic scenarios improve the condition of the environment and cut down the risk to human health, but the pessimistic ones make it worse, including the case where the environment is brought to the edge of full degradation.

This work is particularly devoted to the substantiation of the acceptability of fuzzy-set descriptions for assessing human health risk and environmental managing. Though probability as a tool for risk modeling was established a relatively long time ago, fuzzy sets as a tool for the research of ecological risk and human health risk is unusual and new, and this remark is true for many countries worldwide. In spite of the fact that the main focus of attention in this paper is the assessment of carcinogenesis risk associated with harmful chemicals in the atmosphere, the presented approach can be successfully applied for other tasks on environmental risk assessment and management.

2. ASSESSMENT OF THE HUMAN-HEALTH RISK

Human health risk assessment during the analysis of the atmospheric air presupposes the fulfillment of four main stages namely: (1) Hazard identification; (2) Exposure assessment; (3) 'Dose-response' assessment and (4) Risk characterization. In identifying hazard, first of all it is necessary to take into account the factors that are capable of exerting an adverse effect on human health. As applied to the assessment of the air-quality in towns, this stage in the work implies an inventory of industrial effluents, accounting and recording of the chemical substances that are used for industrial and other purposes, etc. In this stage, sampling screening investigations of the atmosphere of towns can be carried out to reveal those hazards that can be overlooked while constructing an emission inventory.

The second stage, for exposure assessment, consists of obtaining the information on actual doses to which population groups are exposed. Usually, this information is provided, first, by the data of air monitoring and, then, from results of calculations. Laboratory measurements carried out in conformity with the active normative monitoring-related documents can provide objective information on the state of the atmosphere. However, these data encompass only a portion of the chemical substances that are actually present in the atmosphere and are related to a particular observation station. Unfortunately the number of these stations is always insufficient and it is difficult to generalize based on vague spatial interpolation. Moreover, these investigations allow one to obtain only an integral estimate of the concentration of chemical substances from all of the sources of emission. The identification of these sources is usually carried out on the basis of expert approaches. Therefore, the authenticity of the results of these works greatly depends on the qualification of the expert. Computational methods allow one to construct a fully adequate model of the contamination of the atmosphere with the possibility of evaluating the concentration of impurity at any point of the space investigated. At the same time, the accuracy of calculations depends on two basic aspects: the quality of the initial information and the model selected.

The dose-response function establishes the quantitative relationship between the value of the exposure and the additional morbidity or mortality. For defining this function, one can use the data of the experiments on animals or, what happens less often, epidemiological researches in which groups of exposed humans are involved. It should be noted that there are many different dose-response relationships taking into account the probability that the various toxic effects can arise depending on the levels and the routes of exposure. Risks for a given substance cannot be defined with some degree of belief until quantitative dose-response relationships are obtained, even if it is well known that the substance is hazardous to human health. If the substance in question belongs to carcinogens, the aim of defining the response for a dose consists in establishing the relationship between the dose of the chemical and the probability of the carcinogenesis effect. Assessment of the response for a dose implies the extrapolation from the large doses and the exposures obtained in the epidemiological investigations to the doses and the exposures that will be expected under the contact of a human with a given substance in the environment. For extrapolation from the large doses to the small ones various researches use multi-step models with different number of steps, the loggit-model (US EPA,1999), etc.

In that way, taking into account all the factors leading to the fuzzy assessments, the exposure scenarios used for risk assessments can be combined into the one united scenario in the form of the triangle number, where three points might be marked out: the minimal possible exposure and the minimal possible risk associated with this exposure (correspondingly $LAIE_{min}$; r_{min}), the most expected ($\overline{LAIE}$; $\bar{r}$) and the maximum possible ($LAIE_{max}$; r_{max}) values of the exposure and the risk. In particular for assessment of the carcinogenesis risk and the additional mortality caused by cancer, it is possible to apply the additive models in which the total effect of the impact of all the carcinogens in the atmosphere is defined as a superposition of the effects caused by each carcinogen:

$$\underline{R} = \sum_{(i)} \underline{\alpha_i} \times \underline{LAIE_i} = \sum_{(i)} \underline{\beta_i} \times \underline{CCA_i}, \qquad (1)$$

where, all the values in eq 1 have a form of the triangle numbers, $\underline{\alpha_i}$,, $\underline{\beta_i}$ are the constants, defined by the dose-response function and the exposure conditions. Model additivity is based on the application of the linier dose-response relationship assuming that the exposure level is not high.

3. RISK ASSESMENTS WITH FUZZY SETS AND ESTIMATE OF CONFIDENCE OBTAINED

If all of the parameters in (1) have 'fuzzyness', i.e. their exact value is unknown then the triangle numbers with the function form shown in Figure 1 is expediently used. These numbers model the following statement: 'parameter A is approximately equal to $\bar{a}$ and identically located in the interval of [a_{min}, a_{max}]'. The chosen description permits the taking of the parameter interval [a_{min}, a_{max}] as an input information for risk assessment where the most expected value is $\bar{a}$, so the appropriate triangle

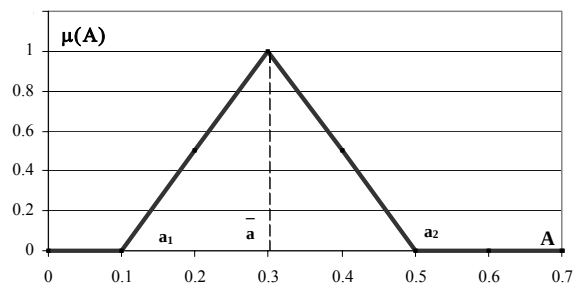

Figure 1. Triangle number A for, exposure, risk of carconogenesis, duration of exposure, etc.

number $\underline{A}$ = (a_{min}, $\bar{a}$, a_{max}) is constructed. Further, we will call the parameters (a_{min}, $\bar{a}$, a_{max}) valuable points of the fuzzy triangle number $\underline{A}$.

Often the subjective probabilities of realizing appropriate scenarios of input data ('pessimistic', 'normal' and 'optimistic') are prescribed to these points. As we can not operate with probabilities whose values we cannot determine or assign, in the process of risk assessment and analysis, the conception of fortuity is substituted for the conception of expectancy and capability.

Assign the following set of fuzzy numbers for assessment of carcinigenesis risk and risk of death associated with cancer:

$\underline{\beta} = (\beta_{min}, \bar{\beta}, \beta_{max})$ – risk assessor cannot exactly estimate either a dose-response relationship, or an inhalation exposure. In the case of assessment of inhalation exposure, uncertainties are caused by its duration, as well as the diversity and the vagueness of the assigned parameters of the exposure scenarios, whereas for the dose-response relationship, as a rule there is a blurriness of the values of unit risks. For all that, a hypothesis concerning threshold action of carcinogens, accepted or rejected by an expert, influences essentially on risk assessment. In this connection, it should be noted that the hypothesis regarding a non-threshold action of carcinogens accepted by Environment Protection Agencies as well as a linear extrapolation from large doses to small ones in a dose-response relationship, has a conventional nature, and there is not enough epidemiological evidence for its acceptance or its decline.

$\underline{CCA_i} = (CCA_{i\ min}, \overline{CCA_i}, CCA_{i\ max})$ – a risk assessor can not exactly assess the concentration of carcinogen averaged for the exposure duration (for example, the reconstruction of emission and dispersal of carcinogens in the atmosphere in the past can be performed very uncertainly; the same can be said regarding the prediction of concentration in the future).

$\underline{R} = (R_{min}, \overline{R_i}, R_{max})$ – a risk assessor forecasts the range of varying the risk of carcinogenesis caused by inhalation exposure. In the case where the survival of people taken ill with cancer is allowed for, definition of coefficient β, formula (1) gives fuzzy set assessments of risk of death caused by carcinogens in the atmosphere. It should noted that when one of the parameters $\underline{A}$ is known exactly, then the fuzzy number $\underline{A}$ reduces to the real number A for which the following conditions are valid $a_{min} = \bar{a} = a_{max}$. But for all that, the main point of method remains the same.

Establishing the suitable level of discretization of α in the interval of belonging [0,1], we can reconstruct the resulting fuzzy number $\underline{R}$ by means of approximation of its function of belonging μ_R with a broken line passing through the interval points. Often it is possible to reduce $\underline{R}$ to a triangle form where we confine the calculations considering only valuable points of fuzzy numbers of input data.

An important problem arising in the case of the application of a fuzzy set methodology consists of an evaluation of the confidence degree of an expert that carcinogenesis (or additional mortality) risk does not exceed definite criterion value R_{th}, that can be given in the form of a fuzzy or accurate number.

For simplicity in Figure 2 the function of belonging $\underline{R}$ and the criterion value R_{th} in the form of accurate number is presented. The point where the function of belonging crosses the straight line $r = R_{th}$ is a point with ordinate α_1. Choose an arbitrary level of belonging α and define corresponding interval $[R_1;R_2]$. For $\alpha > \alpha_1$ $R_1 > R_{th}$, the point $r = R_{th}$ locates beyond the interval $[R_1;R_2]$, and our confidence that risk does not exceed R_{th}, equals zero. It is appropriate to name the level α_1 as a lower bound of a confidence domain. For $0 \le \alpha \le \alpha_1$ the point $r = R_{th}$ locates inside the interval $[R_1;R_2]$. As all realizations R for the given level of α are equally possible, then the

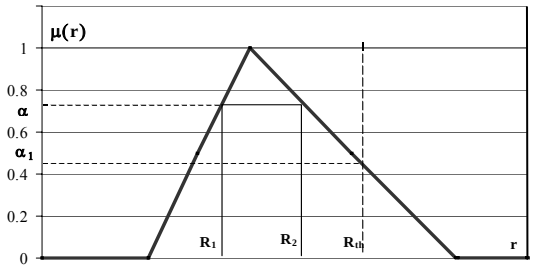

Figure 2. Risk level of R and the criterion of R_{th} .

degree of confidence $\Psi(\alpha)$, that risk does not exceed the value R_{th} represents a geometrical probability of the event that the value of risk R is inside the interval $[R_1; R_{th}]$. Then the total value of the confidence degree that the risk does not exceed the value R_{th} will be equal to:

$$CONF = \int_0^{\alpha_1} \Psi(\alpha) d\alpha \qquad (2)$$

In the important case where the limitation $\underline{R_{th}}$ is defined exactly by the level R_{th}, the function $\Psi(\alpha)$ can be presented in the form:

$$\Psi(\alpha) = \begin{cases} 0 & , \text{ for } R_{th} < R_1 \\ \dfrac{R_{th} - R_1}{R_2 - R_1} & , \text{ for } R_1 \le R_{th} \le R_2 \\ 1 & , \text{ for } R_{th} > R_2 \end{cases}, \quad \alpha = [0, 1]. \qquad (3)$$

To collect all the necessary input data for assessment of the function we need two values of the inverse function $\mu_{NPV}^{-1}(\alpha_1)$. The first one is R_{th} (by definition of the upper bound of risk domain α_1), and denote the second value - R_{th}'. In a similar way denote R_{min} and R_{max} – for two values of the inverse function $\mu_{NPV}^{-1}(0)$. Denote also indication $\overline{R}$ - for the most expected value of $\underline{R}$. Taking into account eqs 2-3 the expression for the confidence degree CONF has the following form:

$$CONF = \begin{cases} 0, & R_{th} < R_{min} \\ \dfrac{R_{th} - R_{min}}{R_{max} - R_{min}} - \dfrac{R_{th} - \overline{R}}{R_{max} - R_{min}} \times \ln\left[\dfrac{\overline{R} - R_{th}}{\overline{R} - R_{min}}\right], & R_{min} \le R_{th} < \overline{R} \\ \dfrac{R_{th} - R_{min}}{R_{max} - R_{min}} - \dfrac{R_{th} - \overline{R}}{R_{max} - R_{min}} \times \ln\left[\dfrac{R_{th} - \overline{R}}{R_{max} - \overline{R}}\right], & \overline{R} \le R_{th} < R_{max} \\ 1, & R_{th} \ge R_{max} \end{cases} \qquad (4)$$

We analyze the expression described by eq 4 for three particular cases:

For $R_{th}= R_{min}$ $R = 0$, $\alpha_1 = 0$, $R_{th}' = R_{max}$, then the limit transition in (4) gives CONF = 0. In other words the degree of confidence that risk does not exceed $R_{th,}$ equals zero and the degree of confidence that risk is higher then R_{th} equals unity.

For $R_{th} = R_{th}' = \overline{R}$ (average confidence) $\alpha_1 = 1$, the limit transition in (4) gives CONF = $(R_{max} - \overline{R})/(R_{max} - R_{min})$.

For $R_{th} = R_{max}$ (extremely high confidence) $\alpha_1 = 0$, $R_{th}' = 0$, and limit transaction in (4) gives CONF = 1.

Hence, a degree of confidence CONF varies from 0 to 1. In accordance with preferences the risk assessor or decision-maker can classify the values of CONF, selecting for themselves the interval of unacceptable values of a degree of confidence. It is possible to introduce more detail gradation of function CONF. For example, if we introduce the variable 'Degree of confidence' with its own term-set of values {Negligible, Low, Medium, Relatively high, Unacceptable} then every assessor or decision-maker can perform their independent description of corresponding fuzzy sub-sets by assigning five functions of belonging μ_*(CONF).

If all of the parameters that are used for risk assessment have interval symmetry then the assessment of risk itself (R) can be reduced to interval symmetrical form. Define $\overline{R}$ as average expected value of R, Δ is scattering of $\underline{R}$ from average value, i.e. $\Delta = \overline{R} - R_{min} = R_{max} - \overline{R}$, $\underline{R} = (\overline{R} - \Delta; \overline{R}; \overline{R} + \Delta)$. Introduce the coefficient of assessment stability:

$$\lambda = (\overline{R} - R_{th}) / \Delta . \qquad (5)$$

It is clear the closer the value of stability coefficient λ to ± 1, the more reliable the assessment of risk and decision made on its basis that will be achieved. For $\lambda = \pm 1$ the assessments can be used without any risk of mistaken decision. Turning to another variable λ in eq 4 it is easy to derive the following expression for the function CONF:

$$\mathrm{CONF} = \begin{cases} 0, & \lambda \le -1 \\ \left(1 + \lambda - \lambda \times \ln(|\lambda|)\right)/2, & |\lambda| < 1 \\ 1, & \lambda \ge 1 \end{cases} \qquad (6)$$

The confidence achieves 80% and more values if $|\lambda| \ge 0.2$. For $\lambda \to -1$ the function CONF tends to zero, and. the confidence increases that the counter event is true, i.e. risk exceeds the given value.

4. AN EXAMPLE OF FUZZY SET ASSESSMENT FOR THE RISK CARCINOGENESIS AT TEN MAIN TOWNS OF RUSSIA

For analyzing the exposure to dangerous chemicals contained in the atmosphere, the initial data were taken from the Russian Weather Service (by Rosgidromet) who examined the air contamination of the atmospheric in the towns of Russia for 1993 and 1998. These data contain information on concentrations of 75 various chemicals (groups of substances) in the atmosphere of 291 populated areas, in which their monitoring was carried out. Among the controlled substances, we selected the data of

ten carcinogens, namely, formaldehyde, lead, hexavalent chromium, benzpyrene, benzene, cadmium, nickel, arsenic, acetyldehyde, and carbon tetrachloride It should be noted that the data of the Russian Weather Service for 1993 involve the most complete set of controlled chemical substances, and therefore they are most suitable for a comparative analysis and integral evaluations. In the present work, no risk assessment was made for suspended substances and soot, since substantiated assessments require data not only on the concentrations of suspended substances and their size distribution, but also on the chemical composition of particles. The use of universal procedures to evaluate the risk of death from exposure to dust and soot irrespective of their chemical compositions (see, e.g., US EPA, 1989; US EPA,1999) is, in our opinion, incorrect.

In the present work no risk assessments were made for exposure to asbestos whose concentrations are presented by the Russian Weather Service in mg/m^3 rather than in the number of fibers per unit volume (as required by US-EPA's procedures), which made it difficult to use these data for risk assessment. Some of the controlled substances, such as soot, also, as a rule, involve carcinogenic substances. However, their complete identification and, more so, the determination of concentrations does not seem possible. A sampling analysis of the accessible data on the contamination of the atmosphere of Russian towns (Reshetin, Kazazyan, 2004; State Report, 1998) allows a conclusion that though a considerable group of carcinogens are being controlled at the present time, there are carcinogens in the air of towns that are not controlled by the Russian Weather Service. Among them are: benzoanthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, 1,3-butadiene, 1,2-dichloroethane, tetrachloromethane, tetrachloroethylene, chloroform, and some others. The particularity of the data on monitoring of chemicals in the atmosphere of Russian towns is the fact that a set of controlled substances varies across different towns. Hence, it is difficult to assess the total risk of carcinogenesis caused by all the carcinogens in the atmosphere.

With this work the fuzzy set methodology is used for assessment of risk of carcinogenesis in the ten biggest industrial centers of Russia with a total population above 21.7 million, which approximately corresponds to 20% of the total urban population of the country. Concentration of the carcinogen is presented in the form of a triangle number. In those towns where there were the data of daily monitoring we selected the annual average concentration as the most probable value for exposure assessment. The assessments were performed separately for the exposure levels of 1993 and 1998. For 'optimistic' and 'pessimistic' scenarios of the input data, the maximum and minimal annual values among the data collected on various observation stations were chosen. In towns where there were no data of Rosgidromet on a certain chemical, expected values of concentrations corresponding to a 'normal' exposure scenario were calculated in accordance with the formula

$$\overline{\mathrm{CCA}}_{\mathrm{i}} = \mathrm{CCA}_{\mathrm{av},\mathrm{i}} \times \Psi_{\mathrm{i}}, \qquad (7)$$

Where, $\mathrm{CCA}_{\mathrm{av},}$ is average concentration calculated on the basis of inventory data and a stochastic trajectory model of impurity propagation in the atmosphere[5], Ψ_{i} is a correction factor, representing the ratio of measured and calculated annual average concentrations averaged across Russian towns where Rosgidroment carried out daily monitoring. Analogous assessments were performed for 'optimistic' and 'pessimistic' values of concentration:

$$CCA_{min,i} = \overline{CCA}_i \times \Psi_i^{min}; \quad CCA_{max,i} = \overline{CCA}_i \times \Psi_i^{max}, \qquad (8)$$

For the calculation of the correcting factor Ψ_i^{min}, the ratio of minimal among the observation stations annual concentration to annual concentration averaged over the observation stations were calculated for all the cities. As a correcting factor Ψ_i^{min}, the minimal value of this ratio was chosen. A correcting factor Ψ_i^{max} was defined analogously. In addition to the data enumerated above, the data of the case studies (Surrounding medium, 1999) on the following five carcinogens: 1,2- dichloroethane, tetrachloromethane, etrachloroethylene, chloroform, 1,3-butadiene which concentrations were measured by other organizations were used for assessments.

To evaluate a mean individual exposure, four universal exposure scenarios have been developed that allow one to take into account different physical activity of urban residents. In evaluation of mean individual exposure averaging was made over the four scenarios; this made it possible to take into account their contribution to the town-average activity of the population. The weights in the scenario convolution were assessed on the basis of existing data on age, sex and activity of population (Reshetin et al., 2000). In the current paper for assessment of impact of small doses the US-EPA approach was applied. In particular for assessment of carcinogenesis risk the no-threshold hypothesis was taken and the values of unit risks from well-known informational system IRIS created by US-EPA's specialists were used (US EPA, 1999). In such a way init risks were assigned in the form of exact numbers. For fuzzy coefficients $\underline{\beta}$ (see eq 1) we use interval symmetric assessment ±20% from expected value $\overline{\beta}$. In our opinion such a value represents sufficiently weighted assessment of uncertainties connected with assignment of weights in the exposure scenario convolution.

In the case of estimation of attributable deaths caused by cancer, the number of people who fell ill with cancer was multiplied by the factor 0.6, which corresponds to the average for Russia's survival rate of cancer patients. It should be noted that according to the Russian Federation report (State Report, 1998), of 50 people who developed cancer of upper respiratory tracts in Russia 47 die. However, taking into account the fact that formaldehyde, just as other carcinogens present in the atmosphere of towns, can induce cancer of different localizations, the survival rate of cancer patients is on average higher than the value 3/50, which is typical of the cancer of upper respiratory tracts.

Attributable cases are commonly interpreted as the preventable fraction, which is meant to be taken as prevented had exposure been removed. Caution, however, is warranted with such an interpretation. First, for long-term effects – the benefit of lower air pollution levels – would take years to be fully realized. Second, the attributable risk estimate does not take competing risks into account. Removing one risk factor – e.g., air pollution – will increase the relative importance and contribution of other risk factors and causes of morbidity and mortality. Accordingly, it is well-known in multicausal diseases that the sum of attributable cases across several risk factors will not add up to 100% but may be larger (Smith et al.,1999). So, for reduction of the risk of premature death, measures should be undertaken to cut off all the competing risks.

The contribution of each carcinogen in total mortality caused by all the carcinogens is shown in Figure 3.

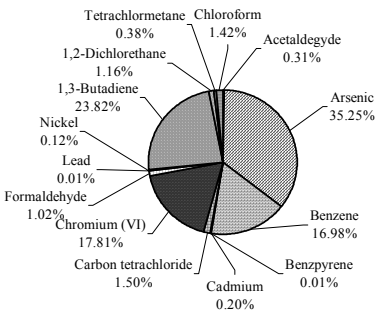

Figure 3. The fraction of various carcinogens in the total cancer incidences from exposure to 'expected' (or 'normal') scenario.

For all the scenarios, exposure to hexavalent chromium, benzene, 1,3-butadiene makes a large contribution to carcinogenesis risk. Taking into account that the cancer rate in Russia is equal to 238 and 168 incidences per 100000 people correspondingly for men and women (data for 1998) (State Report, 1998), the contribution of 15 carcinogens presented in the atmosphere, to the cancer rate are approximately equal to.1%, 6% and 16% of the number of incidences recorded every year in selected towns or 450, 2860 and 7540 cancer incidences per year corresponding to 'optimistic', 'normal' and 'pessimistic' scenarios. At the cities examined by this work the total number of recorded cases of cancer was 45.4 thousands during 1998.
The confidence function CONF plotted against the value of carcinogenesis risk is shown at Figure 4. As is seen from this figure in the framework of selected fuzzy set model, in mentioned towns carcinogenesis risk for life does not exceed 0.013 with probability of 80% and the same probability has the event that risk is lower than 0.008. Note that the contribution of four known human carcinogens, namely, benzene, hexavalent chromium, arsenic and nickel into the total cancer rate caused by all the carcinogens from which the other 11 belong to the group of probable human carcinogens is equal to 85%, 70% and 71% correspondingly for 'optimistic', 'normal' and 'pessimistic'.

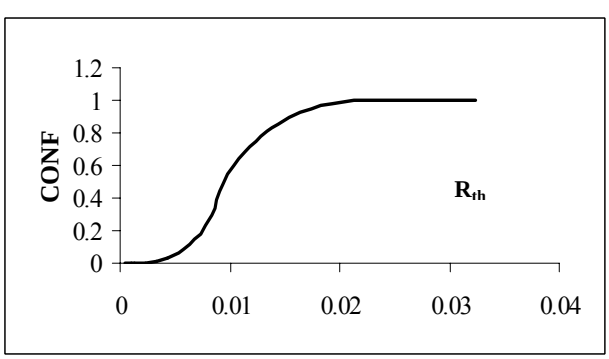

Figure 4**.** CONF as a function of carcinogenesis risk for ten Russian towns.

On the whole, assessments for the data of monitoring in 1998 coincide with presented results. However, the fuzziness of assessments increases still more by taking into account that the data in 1998 are considerably less representative in comparison to those of 1993.

5. CONCLUSIONS

The methodology of fuzzy sets allows the modeling of uncertainties of data needed for exposure assessment when data of low representativeness and of relatively low quality are available. With this method all the exposure scenarios for individual factors were reduced into one combined scenario in the form of a triangle number where three points can be marked out; the minimum possible, the usually expected and the maximum possible values. In this case, the weights of scenarios were presented in the form of triangular function of exposure level and risk to the fuzzy set of 'approximately equal average value'.

Assessments presented in this work testify that in the ten of the largest industrial centers of Russia with total population of 21.7 million, the contamination of the atmosphere with carcinogens might cause 450, 2860 and 7540 annual cancer incidences under an 'optimistic', a 'normal' and a 'pessimistic' scenarios. These correspond respectively to approximately 1%, 6% and 16% of the cancer incidents recorded every year in the towns examined by this work.

The methodology of fuzzy sets allows also the estimation of the degree of confidence that the risk does not exceed the given level. Particularly in the framework of the selected model, one can assert with confidence of 80% that carcinogenesis risk for life in ten towns is not higher than 0.013.

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AirPolTool: A WEB-BASED TOOL FOR ISTANBUL AIR POLLUTION FORECASTING AND CONTROL

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ABSTRACT

A web-based tool AirPolTool for air pollution prediction and control in Istanbul is developed. It models the relationship between local meteorological data and air pollution indicators concentrations like SO_2, PM_{10} and CO by using neural networks. AirPolTool presents on the user-friendly website airpol.fatih.edu.tr three-days predictions of air pollution indicators and supports appropriate episode warning signals and the relevant actions to be taken by the government or the public to reduce that particular pollutant to non-harmful level.

Key Words: Air Pollutants, Prediction, Meteorology, Web Page Modeling

1. INTRODUCTION

Air pollution is one of the most important environmental problems in metropolitan cities like Istanbul. The spatial and temporal variations in emissions of air pollutants and the accompanying variability in meteorological conditions can lead to occurrences of pollutant levels, which can cause adverse short-term and chronic human health impacts (Künzli et al., 2005). Urban air quality management and information systems are required to predict of next day's air pollution levels and for providing proper actions and controlling strategies. Air quality warning systems are therefore needed in order to obtain accurate advance notice that ambient air concentration levels might exceed air quality guideline or limit values. Warnings can be utilized to alert health care as well as traffic and environmental management so that the adverse effects can be minimized. Such warning systems must be sufficiently reliable and understandable by the majority of people.

Currently the municipality of Istanbul has been monitoring nine permanent air pollutants at stations from from Istanbul parts Yenibosna to Kartal. A web based information system www.ibb.gov.tr/index.htm presents information about the current and the earlier periods of air pollution conditions in Istanbul. However there are not future predictions of air pollution situation of the city. This is not only a Turkish national gap but also a worldwide one including many developed countries which

have not such a system. There are few very limited examples in this area (cf. http://turkish.wunderground.com/US/NY/New_York.html).

In recent years, neural network models have been developed and applied to atmospheric pollution modeling in general (Gardner and Dorling, 1998) and air quality problems in particular (Gardner and Dorling, 1999a; Gardner and Dorling, 1999b).

In this study a web-based system *AirPolTool* implementing the neural networks-based air pollution prediction model NN-AirPol (Karaca et al., 2005) is developed.

The objectives of this tool can be summarized as follows:

1) Three-days prediction of air quality .

2) Creating of a user-friendly website which provides access to air quality forecasting information.

3) Supporting of episode warning and actions.

4) Supporting the best possible emission reduction scenario.

5) Reducing the cost of measuring air pollutants by modeling techniques

2. DESCRIPTION OF AirPolTooL

AirPolTooL has the following steps (cf. Figure 1). At the first step, for the air pollution data gathered, the best fitting backpropagation algorithm (BPNN) minimizing the error between neural network output and target value is selected. At step two, by for the concentration of air pollution indicators SO_2, PM_{10} and CO, the air pollution data for the next 3 days according to weather forecasting are determined. The prognoses of these concentration indicators present the outputs of the neural network (NN). For more details about air pollutants prediction see Karaca et al 2005. If the concentrations are higher than the threshold values (cf. Figure 1) relevant episode measures and strategic action plans are proposed. If the concentrations are dangerous for human health (> 300 mg/m^3 for SO_2 and PM_{10}, and >3000 $\mu g^{-3}$for CO) red ecowarnings and ecoactions are proposed. If the concentrations are higher than national air quality standards for certain areas (> 150 mg/m^3 for SO_2 and PM_{10}, and >1500 $\mu g^{-3}$for CO), yellow episode and strategic action plans are proposed. If the concentrations are lower, green episode and strategic action plans are proposed. A two-layer neural network with tan-sigmoid transfer function, a hidden layer and a linear transfer function at the output layer were used (cf. Figure 2). This NN has 7 input parameters and 3 output parameters (SO_2, PM_{10} and CO), which are essential for accurate modelling of the air pollution.

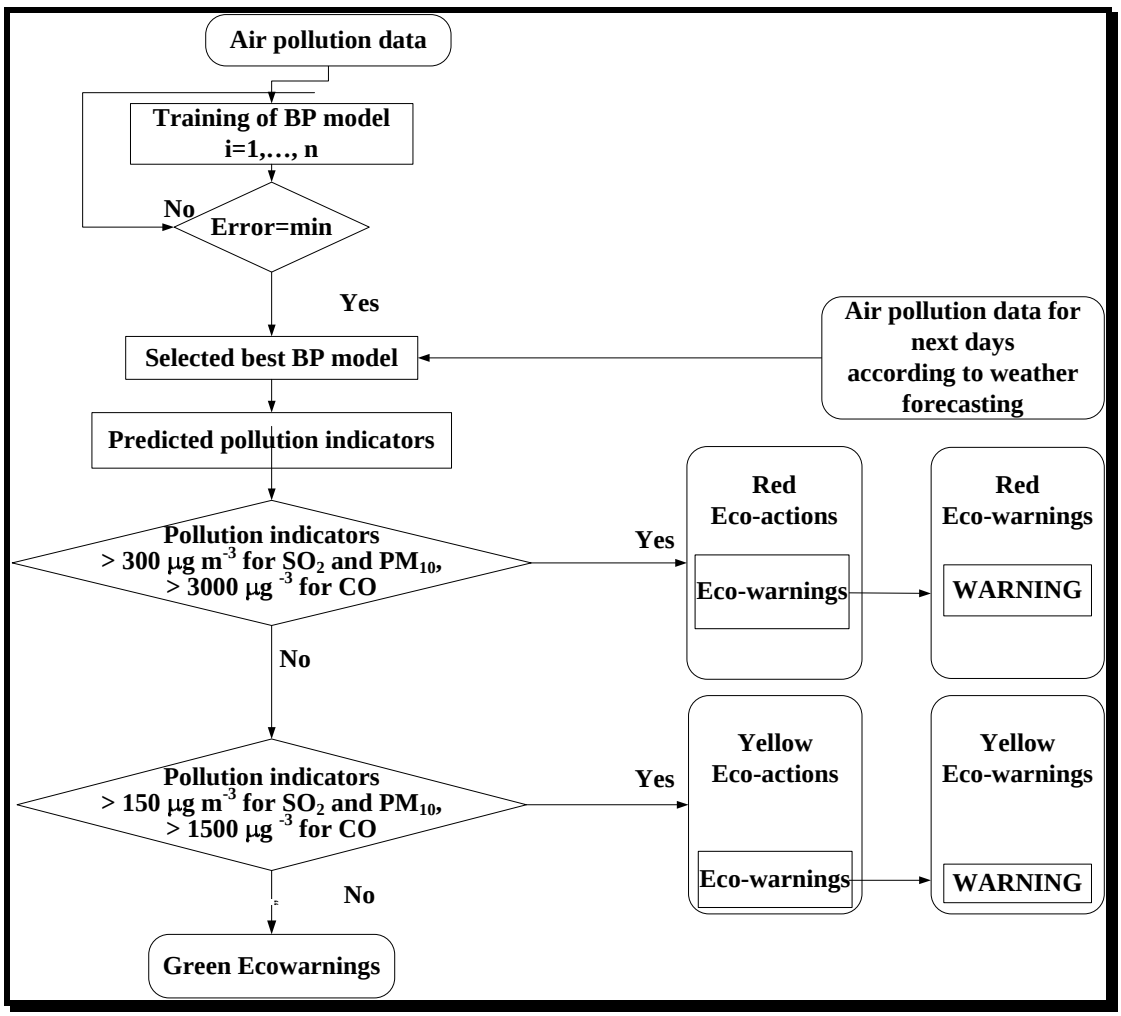

Figure 1. AirPolTool sequence of steps

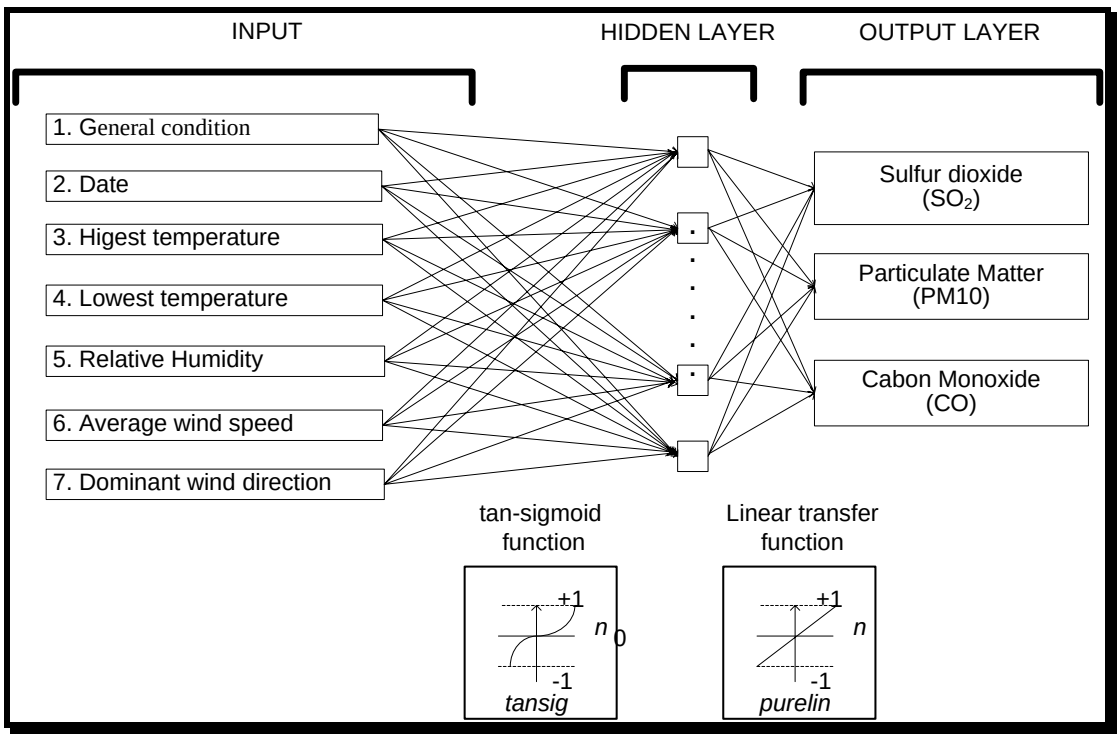

Figure 2. The neural network structure of AirPolTool

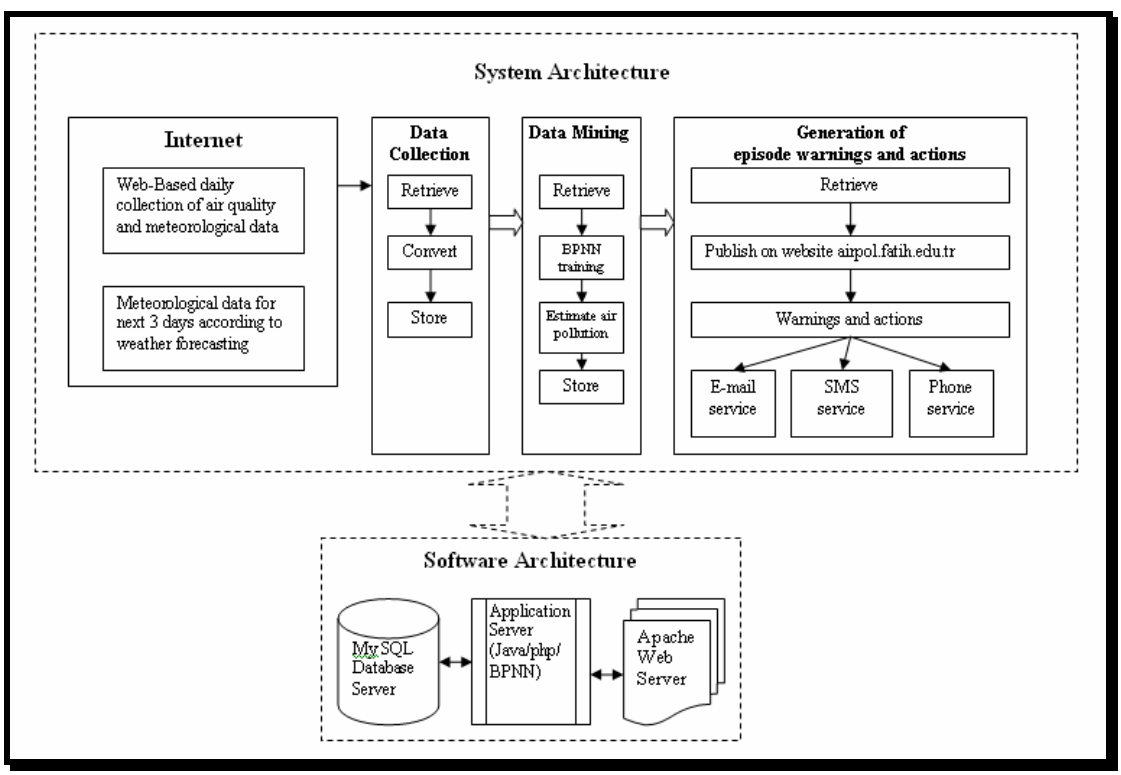

Figure 3. AirPolTool architecture

In the following the AirPolTool architecture shown on Figure 2 is explained.

2.1. Data Collection Module

The data collection module retrieves data from Internet, converts the data in html or xml (see EML, 2005) format to strings and stores the data in a MySQL database.

This module collects daily weather forecasting and air pollution data. Air pollution data are collected from www.ibb.gov.tr in html format. It is parsed by Java program and placed in a MYSQL database. Currently there are 7 weather forecast parameters (cg. Figure 3). These parameters are currently retrieved from www.bbc.co.uk/5day.shtml. Weather forecast parameters are retrieved by a program written in Java and placed in the database.

2.2. Data Mining Module

Data mining is performed on the collected data to predict air pollution levels for the next 3 days. This is done training a feed forward backpropagation neural network applying MATLAB script. Both data collection and data mining is performed daily with new day's forecast and pollution levels using a windows script that invokes application programs.

2.3. Data Presentation Module

The data presentation module consists of a dynamic web page created by application programs hosted in a web server. A screenshot of the main page is given in Figure 4. The page contains a map of Istanbul, today's weather forecast data and estimated pollutant levels in the form of a drawing. The web page currently provides air quality estimation for Istanbul part Yenibosna only, indicated by a bright spot on the map. However we will include other stations/locations in Istanbul in the future. The page displays pollutant levels as a graph. The warning and danger levels are indicated with yellow and red lines on the drawing.

2.4. Software Architecture

The software used in the AirPolTool consists of a database server (MySQL version 4 see MySQL, 2005), a web server (Apache version 2. see Apache, 2005), and application software written in Java (see Java, 2005), Php (see Php, 2005) and Matlab (see Matlab, 2005) scripting language.

The database consists of 2 tables: *DailyMeasurements, Estimates*. *DailyMeasurements* table stores daily weather forecast data and 3 pollutant levels. *Estimates* table holds 3-day estimated values of pollutant levels for each day in the *DailyMeasurements* table.

The web server is used for publishing the results as a web page. It invokes application programs (collectively called application server) that perform various tasks such as conversion, visualization, data mining, etc.

The application server consists of a set of programs for performing the tasks mentioned above. These programs retrieve data from the database server, perform the required tasks and store the result in the database.

3. DESCRIPTION OF AirPolTooL WEB SITE

On AirPolTooL website aitpol.fatih.edu.tr, Istanbul air pollution forecasts for today, tomorrow, the day after tomorrow are displayed (cf. **Figure 4**). A menu bar (see section 1 on **Figure 4**) gives information and support to users. By clicking over an area located on the map section (see section 3) small yellow circles, it is possible to view the forecasts (see section 5) for the selected area and at the same time it is possible to get current meteorological data for selected area (see section 2). When an area is selected, as default, forecasted SO_2 values appear on the screen. Alternatively, in order to see the forecasts of other pollutants (CO and PM_{10}); the pollutant should be selected from pull down menu (see section 4) at the middle right side.

On Figure 5 are shown examples of simulated air pollution forecasts within red zone (3000 $\mu g/m^3$) for March 6, yellow zone (2000 $\mu g/m^3$) for March 5, and green zone (855 $\mu g/m^3$) for March 4.

A sample demonstration of the forecast results is shown on **Figure 6**. These results are from 03.03.2005 till 06.03.2005. The current day is 03.03.2005 and the simulated value is a measured value. The values of the following days (04.03., 05.03. and 06.03.) are predicted values.

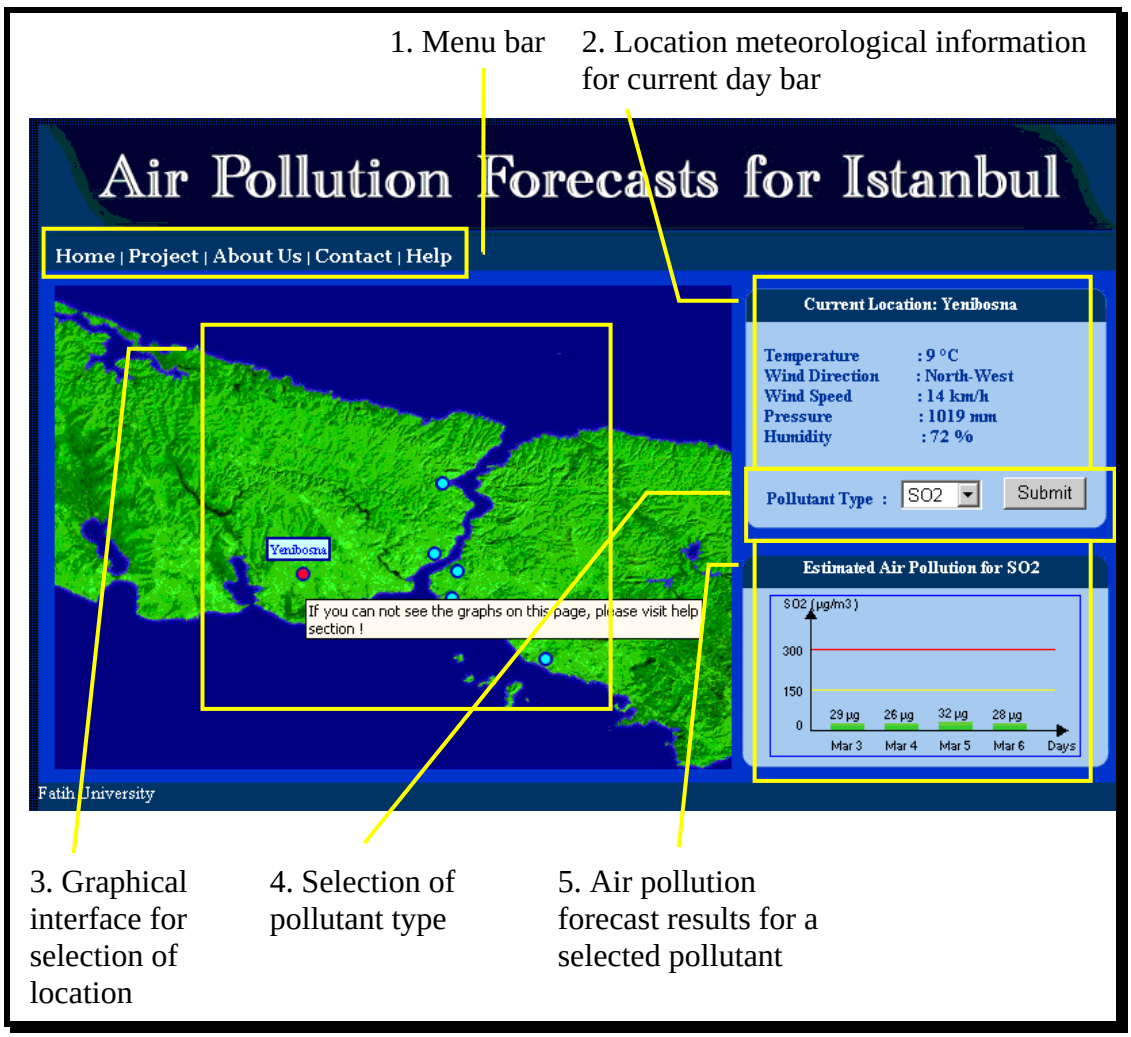

Figure 4. User interface of the web site

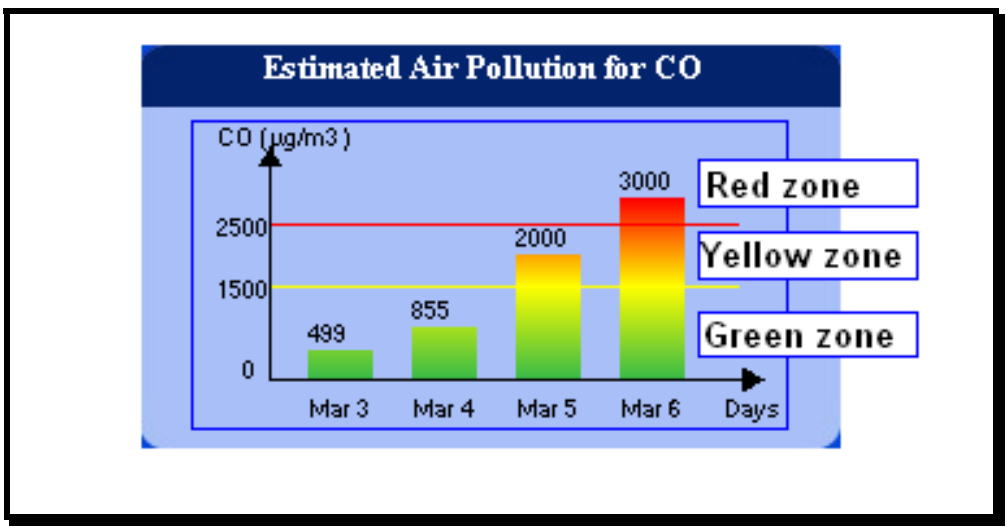

Figure 5. Presentation of pollution levels

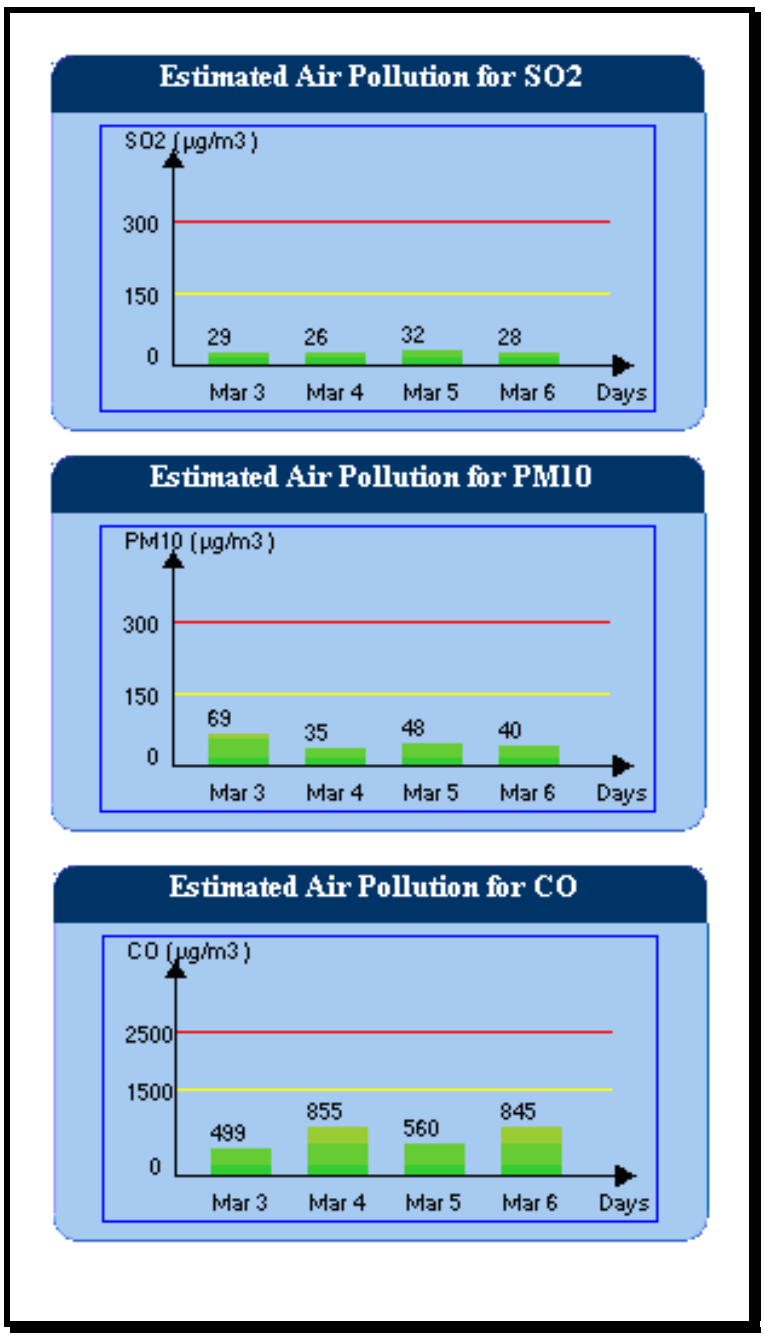

Figure 6. Forecasted results for SO_2, PM_{10} and CO on March 4-5-6

4. CONCLUSION

A web-based tool AirPolTool for air pollution evaluation and control in Istanbul is developed. The most popular neural networks, the backpropagation algorithms, were used to model the relationship between local meteorological data and air pollution indicators concentrations SO_2, PM_{10} and CO. AirPolTool is a user-friendly website for prediction of air pollutants in a metropolitan city like Istanbul. It offers appropriate episode warning signals and the relevant actions to be taken by the government or the public to reduce that particular pollutant to non-harmful level.

The application-oriented outcomes of this study are:

1. Website for Istanbul air pollution forecasting http://airpol.fatih.edu.tr;

2. Map presentation and visualization of air pollution predicted data;

3. Supporting of proper actions and warnings; like fuel curtailment or old people and children warning.

Further developments:

- A more detailed (up to 11 parameters) weather data can be retrieved from www.weather.com which provides a web service (see Web Services, 2005) to retrieve data in XML format. In the next version of the program we plan to this web service to provide a better estimate of air quality.
- For providing a web service to concerned parties that can estimate air quality for Istanbul. Web service applications such as early warning and control systems can be developed.
- The website will also provide a query form for past data by choosing a past date. The estimated and real values along with error rates will be shown.

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QUALITY ASSURANCE OF AUTOMATED MEASURING SYSTEMS BY STATIONARY SOURCE EMISSIONS DIN EN 14181

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ABSTRACT

Presentation of European Standard DIN EN 14181:2004 of the quality assurance of automated measuring Systems on stationary source emissions and the operational experience by the implementation in Germany.

The standard describes the quality assurance procedures needed to assure that an automated measuring system installed to measure emissions to air are capable of meeting the uncertainly requirements on measured values.
Three different quality assurance levels are defined to achieve this objective. These quality assurance levels cover the suitability of an automatic measuring system for its measuring tasks, the validation of the system following its installation, and the control of the automatic measuring system during its ongoing operation on an industrial plant. An annual surveillance test is also defined. The surveillance test specifies the evaluation of the correct function, the calibration function and the variability as previously determined.

The DIN EN 14281 manage extensive the quality assurance of automated measuring systems. It concerns the manufacturer, the system designer, the validation service and the operator of the automated measuring system.

Keywords: DIN EN 14181, automated measuring systems, stationary source emissions, quality assurance

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PRELIMINARY ASSESSMENT OF AMBIENT AIR QUALITY IN THE CITIES OF ANKARA AND KÜTAHYA

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ABSTRACT

Preliminary assessment studies were conducted for the cities of Ankara and Kütahya for the seven air pollutants regulated by the European Union directives. Passive sampling campaigns were conducted for sulfur dioxide, nitrogen dioxide, ozone, and benzene in winter and summer seasons. Based on the results of the preliminary assessments it was concluded that both cities were exceeding the European Union standards for all the pollutants. Coal combustion was found to be a significant source of pollution in whole of Kütahya and some parts of Ankara. Furthermore, traffic was observed to be the major source of pollution in Ankara, and a growing concern in certain parts of Kütahya.

Key Words: Air Quality Management, Preliminary Assessment, Air Quality Monitoring, Passive Sampling, Turkey

1. INTRODUCTION

According to Article 5 of the European Union (EU) ambient air quality framework directive, 96/62/EC, member states that do not have representative measurements of the levels of pollutants for all zones and agglomerations shall undertake series of representative measurements, surveys, or assessments. This assessment, referred to as "preliminary assessment", can be considered as the first step in developing an air quality management policy for a region. It provides an overview of ambient air quality levels, air pollution sources and emissions, and other secondary information necessary for interpretation of the air pollution levels.

Turkey is a candidate country for the EU membership and will be required to align its environmental policies with those of the EU during the accession process. There are already on-going legislative activities to align the Turkish air quality regulations with the EU air quality directives. However, there have not been many technical assessments on air quality in the past to support implementation of the EU directives.

The current study was conducted under the Matra Pre-accession Program of the Dutch Government during the two-year period between 2003 and 2005. It provides the first preliminary assessments for Turkey for the cities of Ankara and Kütahya.
Ankara is the capital city of Turkey with a population approaching the 4 million mark. Major activities in the city are administrative and service related. Although some industry is found in and around Ankara, these are not deemed significant sources in terms of air quality. Ankara harbors traffic of roughly 900,000 vehicles, making traffic one of the chief sources of air pollution in the city. Most parts of the city made the switch from coal to natural gas heating in the early 1990's, and therefore, the role of heating in air pollution has decreased over the last 20 years. Ankara is located in a basin surrounded by hills where dispersion of pollutants is problematic at times. It was chosen for the first preliminary assessment study due to its large population and its importance as the capital city.

Kütahya is a small city with a population close to 200,000. With respect to its size, it has some significant industry in the power and mineral sectors. Owing to the abundance and proximity of lignite reserves in Kütahya, residential and industrial sources mostly utilize coal for their power and heating requirements. High sulfur and ash content of the local lignite, together with inefficient combustion techniques place Kütahya among the top cities with serious air pollution problems. It was chosen for the second preliminary assessment study due to its high air pollution levels.

The preliminary assessments were conducted for seven pollutants (i.e. sulfur dioxide (SO_2), nitrogen dioxides (NO_2), ozone (O_3), benzene, carbon monoxide (CO), particulate matter (PM), and lead (Pb)) that are regulated under three EU daughter directives, 1999/30/EC, 2000/69/EC, and 2002/3/EC. Initially, existing information on the ambient levels, sources, and emissions of the seven pollutants were compiled. It was observed that while there was information on SO_2 and PM to some extent, information regarding NO_2, O_3, Pb, CO, and benzene was either non-existent or inadequate.

In order to reduce the gap in the knowledge, several passive sampling campaigns were conducted in both cities for SO_2, NO_2, O_3, and benzene. Passive samplers are inexpensive yet efficient means to establish the pollutant levels over large areas, providing indicative results accurate to approximately ± 30%. In the assessment of PM, Pb, and CO, secondary information and limited existing data were utilized.

The focus of this paper will be on the results of the passive sampling campaigns in Ankara and Kütahya for the four aforementioned gaseous pollutants.

2. SULFUR DIOXIDE

The SO_2 passive sampling measurements were conducted in winter and summer to observe the seasonal effects. Approximately, 360 SO_2 passive samplers were used over 4 months (i.e. two months in winter and two in summer) in the city of Ankara, which has a geographical spread of 40 km x 30 km. For the city of Kütahya, 70 SO_2

passive samplers were employed over 2 months over an area of 15 km x 5 km. In each month, the passive samplers were exposed to ambient conditions for four weeks in Ankara. Two weeks of sampler exposure time was used in Kütahya.
A grid-based approach was employed for selecting sites for passive sampling since sources for both pollutants are ubiquitous within the urban environment. In this approach, the city was divided into grids and samplers with varying density were placed into each grid based on the population density and urban structure. With a balanced distribution of samplers, both background and specific conditions (e.g. traffic hotspots, industrial and commercial areas) were represented in the assessment.

The distribution of SO_2 levels over Ankara for the winter season is given in Figure 1. The average winter levels over Ankara varied between 20 and 110 μg/m^3. It was observed that pollution due to coal usage is still significant in some neighborhoods of Ankara. Levels as low as 20 μg/m^3 were observed in southeastern neighborhoods such as Çankaya, where natural gas is predominantly used, whereas levels 4 to 5 times higher were observed in the western neighborhoods such as Etimesgut, and in the east-northeastern neighborhoods such as Mamak and Altındağ. Although, natural gas is used in the central parts of the city, relatively high ambient SO_2 levels were observed due to high traffic emissions and transport of pollutants from the neighboring areas.

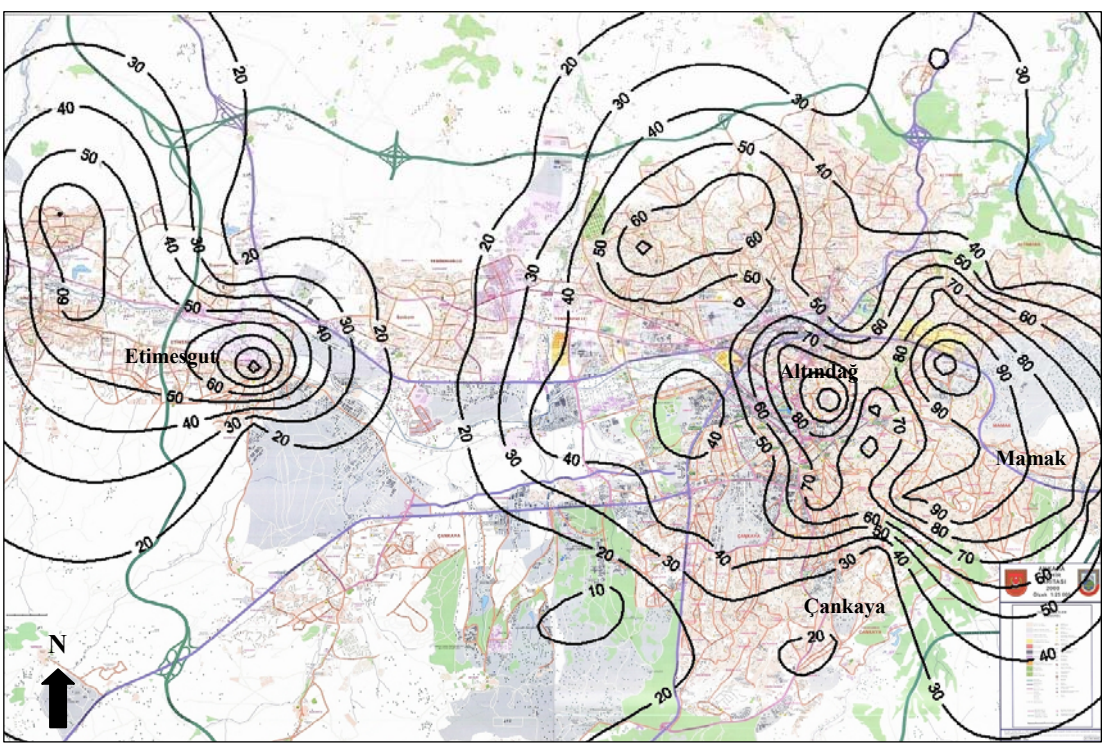

Figure 1. Winter SO_2 Levels (μg/m^3) in Ankara (Ref: Arpacıoğlu et al. 2004a)

The summer concentration distribution over Ankara was uniform as compared to winter, and average levels varied between 15 and 40 μg/m^3. This high difference

between the summer and winter levels indicates that residential heating by means of coal is still an important source of air pollution in Ankara.

It should be noted that the traffic hotspots were removed in Figure 1 to have better representation of the background conditions. Maximum SO_2 levels as high as 80 $\mu g/m^3$ in summer and 130 $\mu g/m^3$ in winter were observed at locations close to traffic hotspots. On the average, traffic locations had SO_2 levels 1.3 and 1.6 times higher than the urban background locations for summer and winter, respectively.

The distribution of SO_2 levels in Kütahya for the winter season is given in Figure 2. The average winter levels over Kütahya varied between 60 and 290 $\mu g/m^3$. The maximum SO_2 concentration was observed in the city center, where daily activity (e.g. business, schools etc.) is higher and dispersion conditions are poor due to dense buildings. The effect of coal usage for heating is highly evident in the city. The southeastern parts of the city had relatively lower SO_2 levels. These parts of the city have newer buildings with better coal combustion efficiency and better dispersion conditions due to better urban planning.

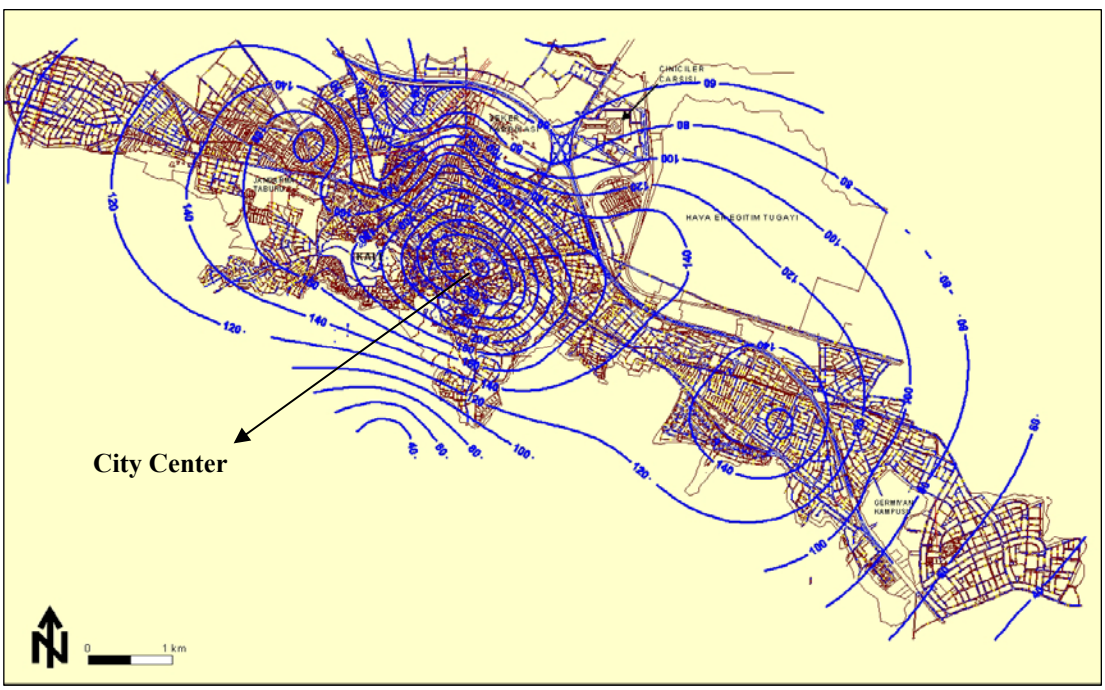

Figure 2. Winter SO_2 Levels ($\mu g/m^3$) in Kütahya (Ref: Arpacıoğlu et al. 2004b)

Average summer SO_2 levels over Kütahya varied between 35 and 100 $\mu g/m^3$. These rather high SO_2 levels indicate the use of low quality coal for heating (during relatively colder summer nights) even in the summer season, as well as for cooking and water heating. The summer SO_2 levels in Kütahya are comparable to the levels observed in winter in eastern parts of Ankara.

3. NITROGEN DIOXIDE

The NO_2 samplers were collocated with the SO_2 samplers following the same grid-based logic. Duration and quantity of NO_2 sampling were the same as SO_2 sampling. The distribution of NO_2 levels for the winter season over Ankara is given in Figure 3. The average winter levels over Ankara varied between 30 and 60 $\mu g/m^3$. High NO_2 concentrations were observed in different parts of the city (e.g. Keçiören, Kızılay, Sincan, and Mamak) where busy traffic or congestions are known to be frequent. These locations exhibited NO_2 levels higher than EU annual standard of 40 $\mu g/m^3$.

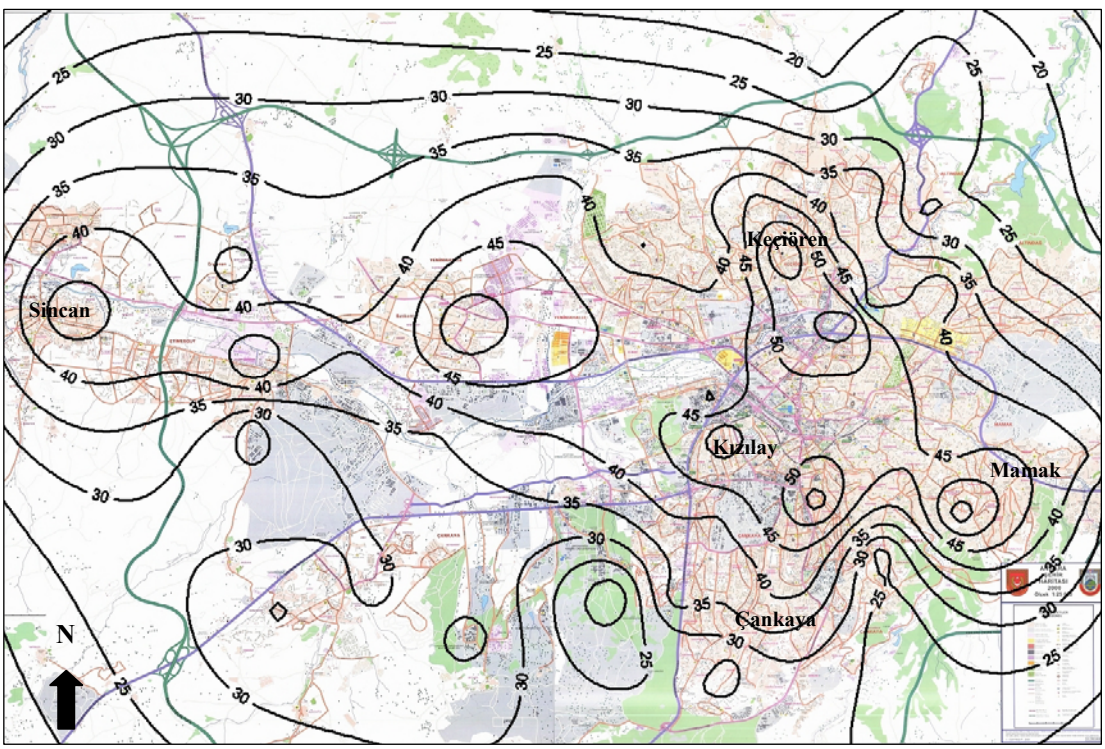

Figure 3. Winter NO_2 Levels ($\mu g/m^3$) in Ankara

The average summer NO_2 levels over Ankara varied between 10 and 70 $\mu g/m^3$. Although the maximum level observed in the summer (70 $\mu g/m^3$) was higher than that observed in winter (60 $\mu g/m^3$), the overall winter levels were generally 10 – 20 $\mu g/m^3$ higher than the overall summer levels. The winter NO_2 levels at the periphery of the city were approximately 30 $\mu g/m^3$, and 3 times higher than the summer levels at the same locations. This fact can be attributed to higher volumes of traffic observed in winter (due to schools opening, people returning from vacation etc.), and unfavorable winter meteorological conditions.

It should be noted that the traffic hotspots were removed from Figure 3 to have better representation of the background conditions of the city. The average NO_2 levels at traffic locations are about 20 $\mu g/m^3$ higher than those levels at the background locations. The effect of different traffic volumes (i.e. road types) in Ankara is shown in Table 1. As one would expect, the NO_2 levels increase with higher traffic

volumes. On the average, annual levels near highways were almost twice high than back roads.

The distribution of NO_2 levels over Kütahya for the winter season is given in Figure 4. The winter levels in Kütahya varied between 20 and 48 $\mu g/m^3$. Highest NO_2 level was observed in the city center. At the city periphery, NO_2 levels decreased to 20 $\mu g/m^3$ level. The summer NO_2 levels in Kütahya varied between 10 and 46 $\mu g/m^3$. Highest NO_2 levels were observed at the city center (41 $\mu g/m^3$) and Afyon Highway Intersection (46 $\mu g/m^3$), where traffic intensities are higher than other parts of the city. Both the winter and summer levels indicate that traffic related NO_2 pollution is becoming important in the central parts of the city, if not all of Kütahya.

Table 1. Average NO_2 Levels with respect to Road Type

Road Type	Average Level ($\mu g/m^3$)	
	Summer	Winter
Highway	61 ± 29	58 ± 17
Boulevard	51 ± 12	56 ± 1
Street	34 ± 21	43 ± 12
Back Roads	22 ± 10	38 ± 10

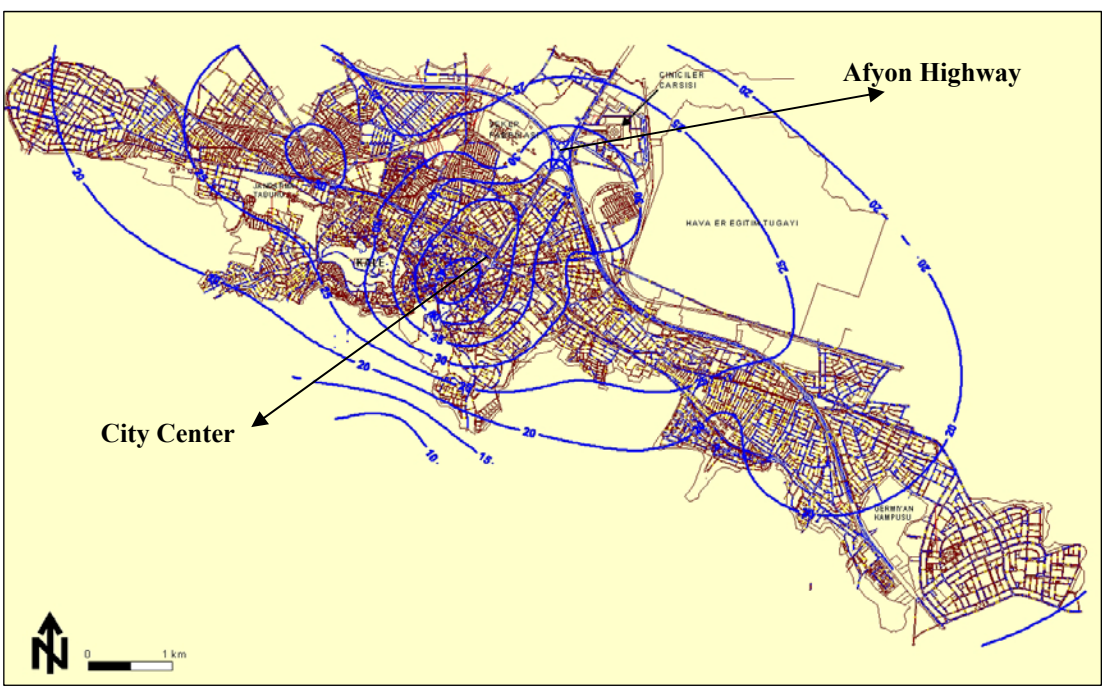

Figure 4. Winter NO_2 Levels ($\mu g/m^3$) in Kütahya

4. OZONE

Ozone passive sampling measurements were conducted in winter and summer to observe the seasonal effects. Approximately, 140 O_3 passive samplers were used

over 4 months (two months in winter and two in summer) in the city of Ankara. For the city of Kütahya, 45 O_3 passive samplers were employed over 2 months. In each month, the passive samplers were exposed to ambient conditions for four weeks in Ankara. Shorter exposure times (two weeks) were employed in Kütahya.

A traverse-based system was employed for selecting passive sampling sites. In this approach, the city was crosscut along two axes. The samplers were placed at approximately every 2 km along the axis to obtain a profile of ozone through the city. This was done considering the fact that ozone is a secondary pollutant and certain time in the dominant wind direction is required before it could form.

Summer O_3 levels over Ankara are shown in Figure 5. As can be seen from this figure, O_3 levels were lower in the center of the city (around 70 $\mu g/m^3$), and higher at the city borders or outside the city (around 110 $\mu g/m^3$). There was roughly a factor of 1.5 difference in O_3 levels between the city periphery and the center. Similar trend was also visible in the winter O_3 levels; however, it was not as pronounced as in the summer. In the winter, O_3 levels were 10 $\mu g/m^3$ in the city center and 50 $\mu g/m^3$ in the south of the city. Due to the reduction in solar radiation intensity and duration in winter months, the photochemical reactions necessary for formation of ozone were not happening as much as in the summer months.

Summer O_3 levels observed over Kütahya are shown in Figure 6. The O_3 levels showed similar patterns to those in Ankara. Levels in the city center were observed around 70 $\mu g/m^3$ and in the city periphery around 120 $\mu g/m^3$. In the winter, the O_3 levels dropped dramatically to 20 – 25% of the summer levels.

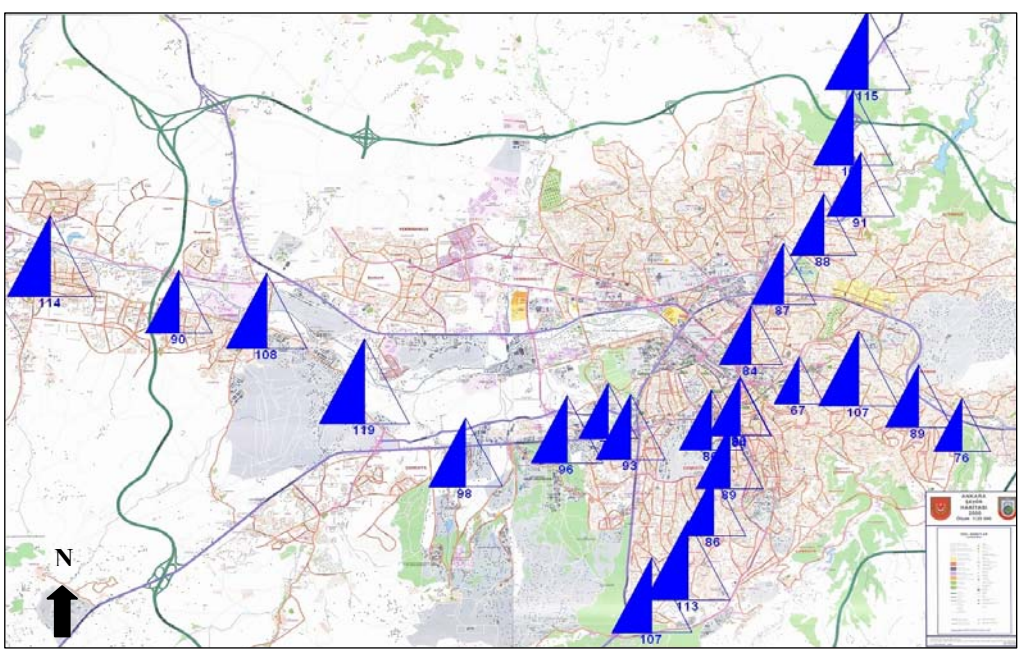

Figure 5. Summer O_3 Levels ($\mu g/m^3$) in Ankara (triangle heights proportional to O_3 levels)

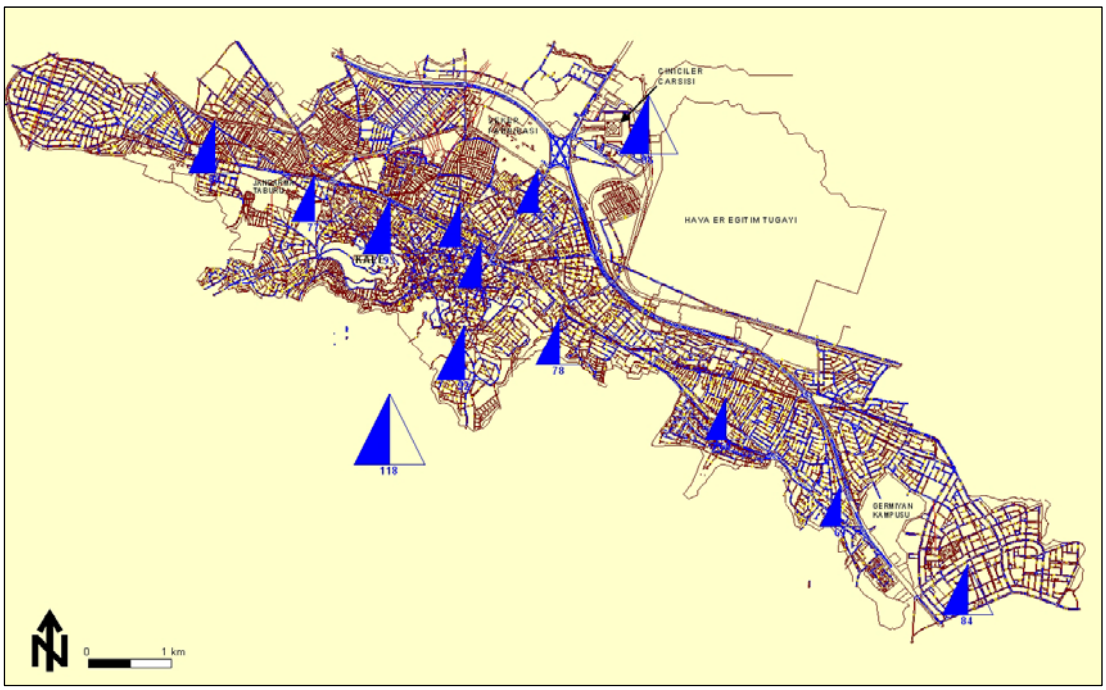

Figure 6. Summer O_3 Levels ($\mu g/m^3$) in Kütahya (triangle heights proportional to O_3 levels)

5. BENZENE

Benzene passive sampling campaigns were conducted for one month in the winter and one month in the summer for both cities. In selecting locations for the benzene samplers, a different approach was followed as compared to SO_2, NO_2, and O_3. In this approach, unique locations where measured benzene levels would represent certain typical conditions were selected. Thus, samplers were located at gasoline stations, shopping and hospital parking lots, traffic intersections, where hotspots and high human exposure were expected. In addition, locations such as schoolyards, residential neighborhoods were also sampled to determine the background conditions. These measurements provided a valuable initial insight into range of benzene levels to be expected in the Turkish cities.

Eight sampling locations were selected in Ankara. The description of locations and measured benzene levels in Ankara are given in Table 2. As observed in this table, all the measured benzene levels were higher than the EU annual standard of 5 $\mu g/m^3$. The residential areas had levels twice as high as the EU standard. As expected highest benzene levels were observed at the petrol station, where no vapor control mechanism was available. The winter benzene levels were generally higher than the summer levels. This was probably due to two factors:

- Less vehicular activity (hence less emissions) in summer time due to schools closing, people going out of town for vacation etc., and
- Unfavorable meteorological conditions (frequent inversions, low mixing heights etc.) that limit vertical and horizontal dispersion in wintertime.

Three sampling locations were chosen for Kütahya. The description of locations and measured benzene levels in Kütahya are given in Table 3. Highest benzene levels were observed in the petrol station as expected. Winter levels were higher than the EU annual standard of 5 $\mu g/m^3$, and 3 – 5 times higher than the summer levels, as also experienced in Ankara.

Table 2. Benzene Sampling Results for Ankara

Site Name	Description	Level ($\mu g/m^3$)	
		Summer	Winter
Hacettepe Hospital	Parking Lot	13	14
Kızılay Square	Curb-side	14	21
Petrol Station, Beşevler	Station Canopy	29	52
7th Road, Beşevler	Residential	10	18
Real Shopping Center	Parking Lot	12	-
Kurtuluş Primary School	School Yard	25	14
Bus Terminal (AŞTİ)	Bus Park	10	11
Koza Road, G.O.P.	Residential	12	8

Table 3. Benzene Sampling Results for Kütahya

Name	Description	Level ($\mu g/m^3$)	
		Summer	Winter
Governorship	Parking/Pedestrian Area	3	15
Çinigar	Intercity Bus Terminal	3	11
Petrol Station	Petrol Station	6	18

As observed in many other European cities, a decrease in benzene levels will be observed from the hotspots in the city centers to the city perimeters. It is expected that, in both Ankara and Kütahya, outer parts of the city will observe less benzene levels than the ones presented in these tables.

6. CONCLUSION

By means of passive sampling and some other basic information and methods, it was possible to obtain indicative results about ambient levels of pollutants to optimize and base further air quality monitoring and control strategies for Ankara and Kütahya.

By comparison of the passive sampling results and other relevant data with the standards, it is determined that for all pollutants regulated by the three EU daughter directives ambient air quality standards are being exceeded in both cities.

Inefficient combustion of low quality coal is a significant source of SO_2 pollution in Kütahya. The parts of Ankara that has not made the switch to natural gas are still observing high SO_2 levels, although not as high as Kütahya. Diesel traffic in both cities is also a major contributor to SO_2 levels at traffic hotspots due to high sulfur content of the fuels.

Traffic has become a major source of air pollution for Ankara, and is becoming a significant source for Kütahya as well. This could be clearly seen from high NO_2 and benzene levels observed in the cities, especially during winter season when activity rates are higher and meteorological conditions are conducive to adequate pollutant dispersion.

Ozone levels for the summer season are high in both Ankara and Kütahya. The role of high summer solar radiation intensity and duration is evident by comparing the winter and summer ozone levels. However, ozone levels should be further studied to understand better the mechanism of formation of this pollutant through its precursors in the Turkish cities.

Both cities were found to be in Regime-1 (non-compliance with the limit values) monitoring requirement under the EU air quality assessment scheme. Therefore, both cities are required to conduct mandatory high quality air quality monitoring. Both short and long-term exceedances of limit values were observed in the cities of Ankara and Kütahya.

7. ACKNOWLEDGEMENTS

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APPLICATION OF THE STEAM JET AEROSOL COLLECTOR (SJAC) FOR DIFFERENTIAL MEASUREMENTS OF ORGANIC COMPOUNDS IN THE GAS VERSUS PARTICLE PHASE.

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ABSTRACT

A new approach of using the Steam Jet Aerosol Collector (SJAC) for the determination of semivolatile organic compounds has been investigated. Gas phase and particle phase were investigated separately. The SJAC, an alternative for filter based sampling method, is one of condensational growth sampling systems which uses water as a condensational liquid. In our setup for the determination of the gas phase compounds an extra XAD adsorbent cartridge was applied. Collection of gas phase fraction takes place after particle phase collection; therefore no denuder technique is used. Collection efficiency for particles was examined with hydrophobic soot and octacosane particles. In order to estimate the amount of bias caused by the transfer of components from gas phase to the particle fraction, streams of individual organic compounds with different polarity in synthetic air were examined. Laboratory tests showed negligible amounts of gas phase material measured in the particle fraction and high collection efficiency for hydrophobic particles.

Key Words: Semi Volatile Organic Compounds, Aerosol Sampling, Gas-/Particle Portioning

1. INTRODUCTION

One of the most important issues of an analytical procedure is a representative sample. Both health and ecological impacts of semivolatile organic compounds (SVOC) depend on their chemical species and physical form of appearance. Therefore it is very important to be able to determine their concentration in the gas phase (Gp) and particulate phase (PM).

Theoretical predictions were developed to describe SVOC gas/particle partitioning. They are based either on the adsorption model using subcooled liquid vapour pressure (Pankow 1994), the absorption model using octanol-air partition coefficient K_{OA} (Finizio et al., 1997; Harner and Bildeman 1998), or combine black carbon adsorption and organic matter absorption (Dachs and Eisenreich 2000). Lohmann and Lammel (2004) showed that theoretical values of gas-particle partition coefficient K_p calculated according to different models disagree with each other and developed another model which combines diesel soot adsorption and organic matter absorption. Thus, finding a really unified method to predict SVOC partitioning seems to be rather difficult.

Aerosol collection of SVOC on the other hand, carried out most often by means of (denuder)/filter/adsorber techniques, is subjected to significant biases. Major physical sampling artefacts are caused by evaporation of components from PM (collected on the filter and inside denuder, blow off) and adsorption of Gp (to the filter and PM collected on the filter, blow on). Even 100 % overestimation of PM because of blow on or 20 % underestimation - from blow off can occur (Mader et al., 2003). Another source of error is chemical degradation. Because PMs exposed to high amount of air containing reactive gases (e.g. O_3, NO_x,) which pass through the collected material, can undergo chemical reactions, hence the determined amounts of target analytes can be inaccurate (e.g. for PAH Schauer et al., 2003).

Corrections for SVOC measurements developed so far still suffer from their underlying yet unrealistic assumptions (equilibrium condition for backup filter, 100% denuder efficiency) or do not take into account all possible biases during sampling (evaporation of SVOC from PM inside denuder). Recent comparison of filter/adsorber, filter/filter/adsorber , denuder/filter/adsorber and electrostatic precipitator/adsorber methods used for diesel exhaust measurements showed that none of these methods can be applied for accurate determination of K_p (Volckens and Leith 2003).

Aerosol growth technique is widely used in Condensation Particle Counters with butanol as a condensing liquid, and recently also with water. The Steam Jet Aerosol Collector (SJAC, Khlystov et al., 1995) and Gas and Aerosol Monitoring System (GAMS, Simon and Dasgupta 1995) were the first approaches using water condensation onto PM for chemical measurements of aerosol. This technique was later applied to other methods with different technical setups: Versatile aerosol concentration enrichment system (VACES, Kim et al., 2001), Particle-into-Liquid Collector (PILC, Weber et al. 2001), a condensation-growth and impaction system, (C-GIS, Sierau et al. 2003). All those approaches were specifically interested in water soluble fraction of PM.
SJAC was originally designed for online determination of inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-, Cl^-) in the particle phase. In this concept the aerosol passes through a wet denuder (Keuken et al. 1989) in order to remove gas phase components (NH_3, HNO_3, HCl, SO_2). Rapid mixing the aerosol (cold stream) with the injected water steam (hot stream) creates supersaturation conditions. This causes condensational growth of particles to droplets sizes of several micron. Those are removed by means

of the cyclone with the cut point aerodynamic diameter of about 2 μm and are subsequently analysed online for inorganic compounds by ion chromatography.
In our work we adapted the original concept of the SJAC for sampling water soluble as well as insoluble organic compounds both in particle and gas phase.

2. EXPERIMENTAL PART

2.1. Technical setup

SJAC modification is based on the reverse to original sampling order concept. In this setup no denuder technique is used therefore collection of gas phase components follows particle phase collection (Figure 1). Ideally Gp and PM go through inlet to the mixing chamber, where steam is injected. Then water vapour starts to condense onto PM because of supersaturated conditions. Grown particles are removed by cyclone like in the original setup (aqueous solution of particle phase sample P). Gp compounds either absorb in water steam condensed inside the cooler (aqueous solution of gas phase sample G_1) or are adsorbed in the adsorbent cartridge containing XAD4 (gas phase sample G_2). The addition of the cooler prior to XAD4 adsorber was necessary in order to get rid of the high amount of water from the cyclone exhaust, which would cause increase of the pressure drop (XAD4 swelling) and lower sorption efficiency of the adsorbent.

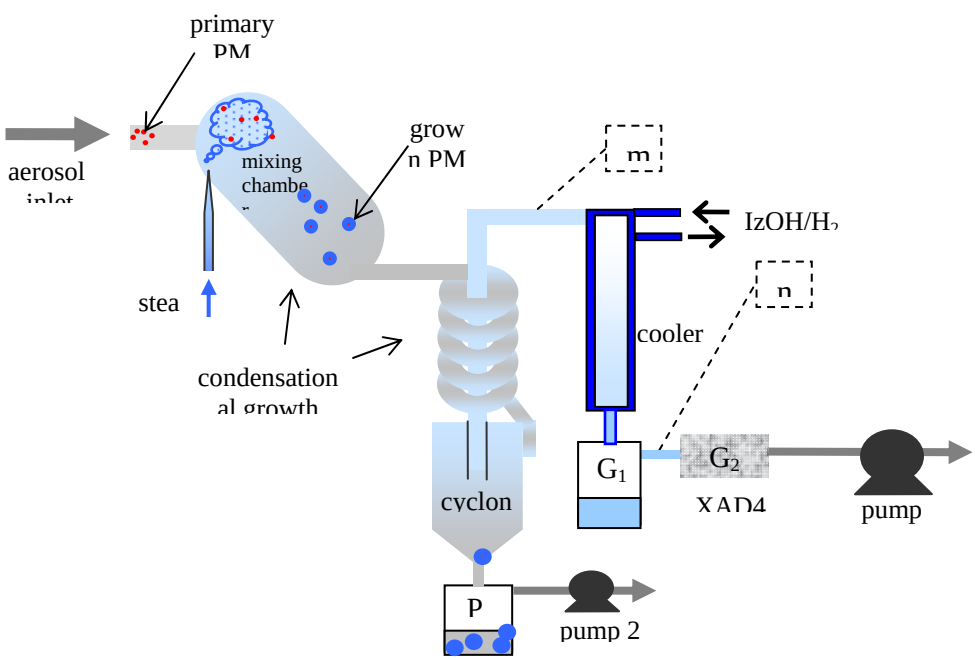


Figure 1. Setup of the modified SJAC for differential measurements of organic compounds in the gas and particle phase; P – particle sample, G_1, G_2 – gas phase samples; m, n – location of the SMPS sampling lines.

SJAC working conditions were as follows: flow rate of main air pump 1: 1m^3/h; flow rate of pump 2 (cyclone): ca. 200 ml/min, cooler temperature: 1°C. Steam was supplied by an electrically heated boiling pot (Figure 2a). Power optimum of boiling pot was found to be – 1.05 A, 200V. It corresponds to ca. 2.7 ml/min steam flow and is slightly higher then optimum steam flow rate used for inorganic compounds measurements (2.5 ml/min; Slanina et al., 2001).
Additionally a resistive heated capillary (Figure 2b) was tested for steam generation A stainless steel capillary (1 m length, 0.2 mm ID, 0.5 mm OD) was connected to the mixing chamber of the SJAC by means of a Teflon adapter and on the other side to a HPLC pump operating at flow rates 1.5 – 4 ml/min. In order to generate steam a direct electric current (2.5 A) was applied to the capillary.

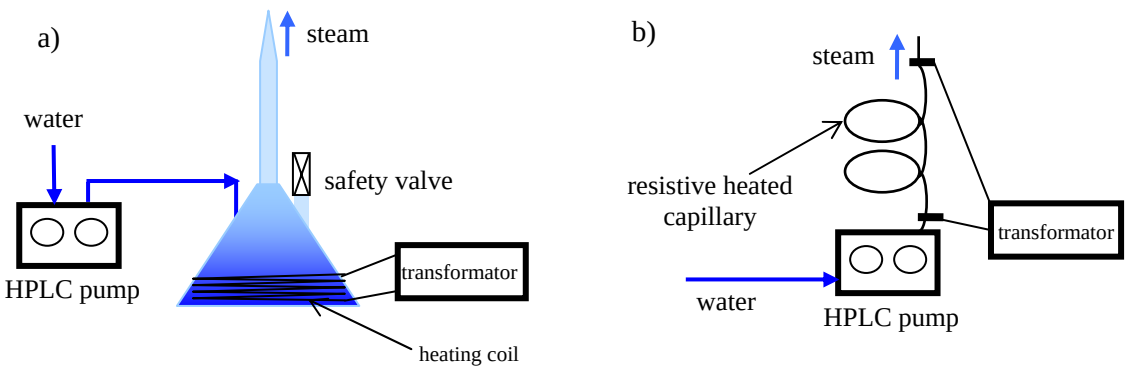


Figure 2. Different steam generators used with SJAC – original steamer – boiling pot (a) and resistive heated steal capillary (b)

2.2. Particle collection efficiency

Particle measurements were made by means of Scanning Mobility Particle Sizer (SMPS, Model 3936, TSI, USA) in the size range of 14.1 – 737 nm. PM measurements with different steam parameters were carried out and compared to measurements without steam application.
Particle collection efficiency was examined with two types of non volatile hydrophobic particles – soot and octacosane PM.

Soot particles were delivered from spark generator (GFG 1000, Palas, Germany). The smallest particles (with mean diameter of ca. 35 nm) were obtained with minimum spark frequency of about 3 Hz and were immediately diluted by means of synthetic air. 170 nm particles were generated by 800 Hz spark frequency and diluted like previously. 250 nm particles were generated by 300 Hz spark frequency and using a 20 L glass vessel for coagulation growth of primary soot particles.
SMPS sampling line was placed upstream the cooler (location “m” – Figure 1). In this case, in order to remove excess water, which would disturb the SMPS measurements, an additional heater and dryer in the sampling line of the SMPS were applied.

Octacosane condensation particles were generated by purging constant flow (ca. 150 ml/min) of nitrogen through a heated impinger vial containing octacosane. Subsequent cooling of the octacosane vapour led to homogeneous nucleation. A monodisperese aerosol with median diameter of 70 nm was obtained.
Because of the large active surface of the dryer, used in the experiments with the carbon particles, octacosane adsorption to drying material took place. Therefore SMPS sampling line had to be moved downstream the cooler (location "n" – Figure 1). In this case water concentration was much lower than in position "m" allowing for omission of heater and dryer. SMPS measurements in location "n" are subject to overestimation of SJAC efficiency because of additional supersaturation caused by the cooler. Yet negligible differences in SJAC collection efficiency of soot particles obtained from sampling location "m" and "n" proved validity of SMPS measurements of octacosane particles in position "n".

2.3. Transfer of gas phase to particle fraction

Pure vapours of individual SVOC (heptadecane, undecanol, naphthalene and metoxyacetophenol) with dilution air were applied in order to estimate the amount of bias caused by the transfer of components from gas phase to the particle fraction. Vapour generation took place simply by purging constant flow of particle free nitrogen (20 - 100 ml/ min, depending on the compound) through a thermostated impinger vial containing analysed compound (Figure 3).

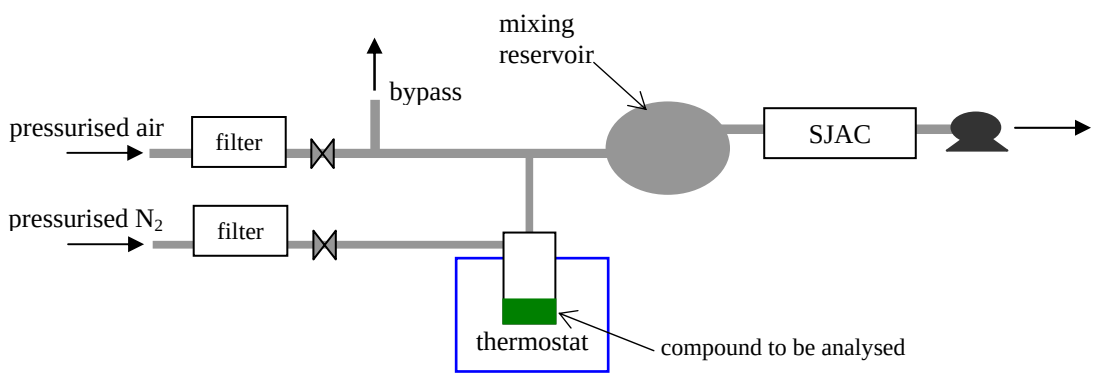


Figure 3. Gas phase measurements setup

2.4. Sample preparation

For aqueous samples – P and G_1 a liquid-liquid ultrasonic-assisted extraction with dichloromethane (3 x 30ml) was applied. XAD4 samples – G_2 were extracted by means of Accelerated Solvent Extraction (ASE® 200, Dionex, USA) based on modified Dionex Application Note 347 (Dionex Extraction Applications) – acetone/hexane 30/70 (v/v); 3 cycles; 100 °C, 100 bar. In order to minimise the blank concentration of XAD4 samples ASE extraction cells were used as an adsorbent container during sampling. Both extraction methods were followed by drying the extracts with sodium sulphate and reduction of solvent. For quantitative analysis GC-MS analysis (HP 6890) based on internal standard addition method was applied.

3. RESULTS AND DISCUSSION

3.1. Particle collection efficiency

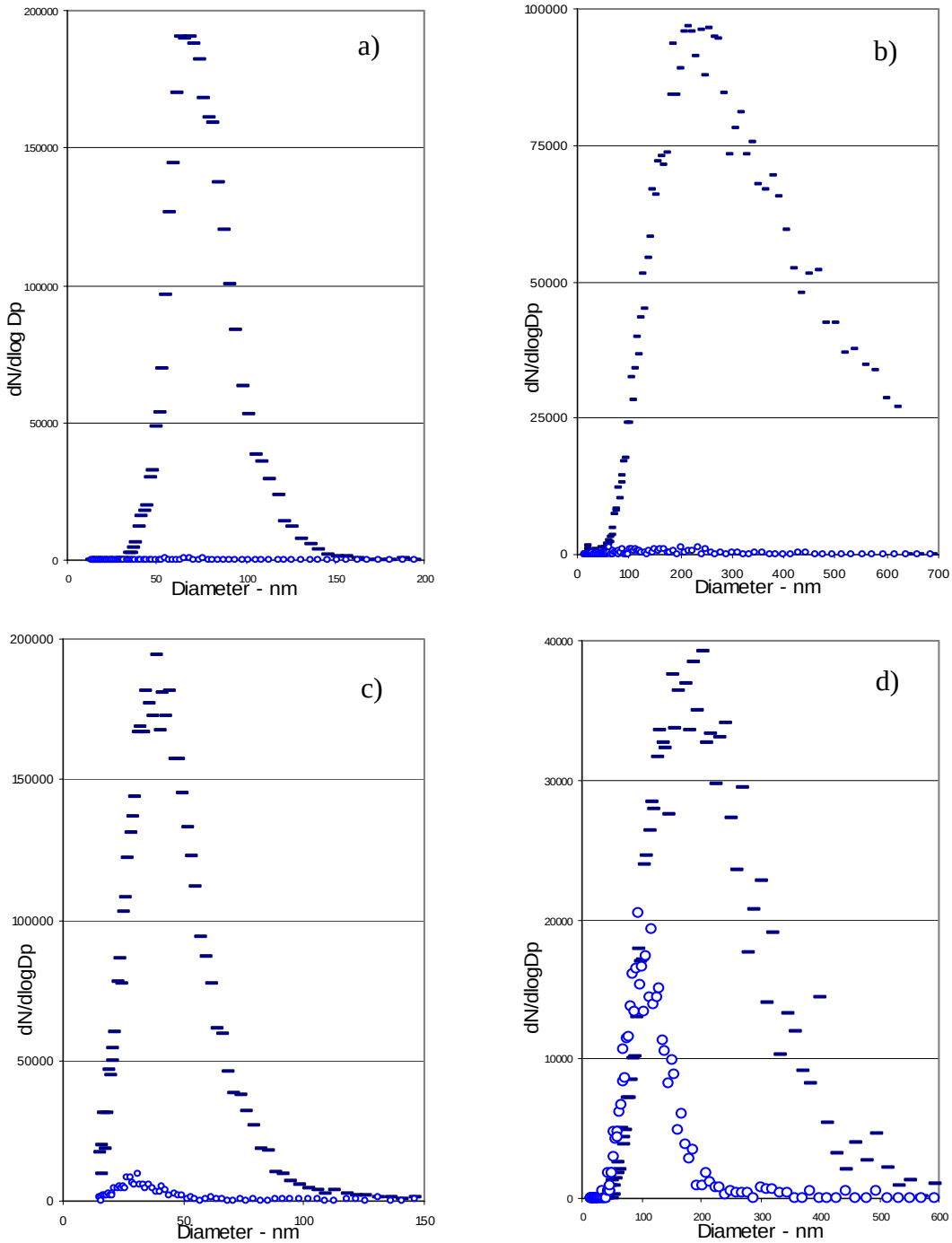


Figure 4. SJAC particle collection efficiency; primary size distribution ----- , size distribution after SJAC ooooo ; a – octacosane, mean diameter 70 nm, b – soot, mean diameter 250 nm, c – soot, mean diameter 35 nm, d – soot, mean diameter 170 nm with heated capillary as a steamer.

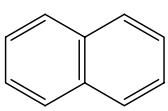
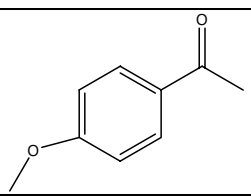
Hygroscopic growth of organic particles is weaker as for inorganic compounds (Weingartner et al., 1996). Therefore there was concern that the particle collection efficiency especially for small non polar particles will be low. The applied cyclone together with preceding mixing chamber working under supersaturation conditions was found to remove over 99% (number of particles) of soot particles as well as octacosane particles in general (Figure 4 a, b). Only for the smallest soot particles, with the mean diameter of ca. 35 nm, efficiency was slightly lower – 95% (Figure 4 c).

Applying a different steam generation technique (restitive heated steal capillary, Figure 2 b) with optimum steam flow rate of 2ml/min did not increase the collection efficiency – on the contrary – it was clearly lower (ca. 66% of particles number) than in case of original SJAC's boiling pot (Figure 4 d).

3.2. Transfer of gas phase to particle fraction

Wide ranges of water solubility and polarity of four individual test compounds were applied for gas phase bias measurements in order to cover a broad range of compounds in the ambient aerosol and to check those two properties impacting on behaviour of Gp in SJAC sampler (Table 1).

Table 1. Properties* of test compounds and concentration ranges applied in the experiments.

component	heptadecane	undecanol	naphthalene	metoxyacetophenol
water solubility [mg/l]	0.00029	19.1	31	2030
vapor pressure at 25 ^{o}C [mm Hg]	0.00023	0.003	0.085	0.08
log P (octanol-water)	8.7	4.3	3.3	1.8
chemical formula	$CH_3(CH_2)_{15}CH_3$	$CH_3(CH_2)_{10}OH$		
concentration range; [µg/m^3]	20 – 400	20 – 400	10 – 400	20 – 300

* SRC PhysProp Database - http://www.syrres.com/esc/physdemo.htm

"The worst scenario" assumes that polar, water soluble compounds will partly dissolve in the droplets and be removed by the cyclone and cause overestimation of particle sample P. Therefore for undecanol, naphthalene and methoxyacetophenone amount of the bias was expected to be higher than for the water insoluble heptadecane which supposes to have the smallest gas to particle fraction transfer and what follows the smallest percentage concentration of the particle fraction P during gas phase experiments.

Table 2. Average fractionation of gaseous test compounds between three samples of the modified SJAC during gas phase measurements; in percent with standard deviations, n=5-8.

sample:	gas phase sample G_1 (cooler)	gas phase sample G_2 (XAD–4)	particle phase sample P (cyclone)
heptadecane	0.0 ± 0.0	100.0 ± 0.0	0.0 ± 0.0
undecanol	9.5 ± 3.1	88.7 ± 1.7	0.0 ± 0.0
naphthalene	1.2 ± 0.2	98.6 ± 0.4	0.0 ± 0.0
metoxyacetophenol	73.5 ± 1.3	24.0 ± 1.1	2.4 ± 0.7

Percentage concentrations of each given fraction were calculated dividing the concentration of the fraction by the concentration of the sum of all fractions and multiply by 100%.

The bias caused by transfer from gas to particle fraction for haptadecane, undecanol and naphthalene was found to be negligible – average percentage concentrations in the particle sample P during gas phase experiments was found to be 0.0 (Table 2). Only in case of metoxyacetophenol, which has the highest water solubility, SJAC measurements showed bias caused by transfer from gas to particle fraction. Maximal percentage share of the sample P for this compound was 3 %. Hence it confirms that for much less water soluble compounds than metoxyacetophenol (e.g. alkanes and PAHs) correction for SJAC measurements is not necessary.

Distribution between gas phase samples G_1 and G_2 illustrates differences not only in water solubility but also volatility of examined compounds. G_1 fraction of naphthalene is lower than for undecanol but water solubility of naphthalene is higher then that of undecanol. This distribution pattern can be useful as a kind of “online pre-separation” of measured compounds according to water solubility and volatility of SVOC in complex matrices of organic aerosols.
The distribution pattern shown in table 2 has proved to be concentration independent for the used range of concentrations (Table 1) of test compounds.

Evaluation of the modified SJAC yielded negligible bias caused by transfer from gas to particle phase and high collection efficiency for ultrafine hydrophobic particles. Therefore SJAC is a potential method free from physical artefacts for SVOC aerosol measurements. Furthermore chemical degradation of particle phase material is likely to be lower than that for filter based methods – lack of PM contact with reactive air compounds. Hence the future examinations aim for field comparison of the modified SJAC with standard sampling methods.

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QUALITY ASSURANCE PROGRAM FOR AMBIENTAIR QUALITY MONITORING AT REFIK SAYDAM CENTER OF HYGIENE, MINISTRY OF HEALTH

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ABSTRACT

Within the framework of the Matra Pre-accession Project Program managed and financed by the Dutch Agency for International Business and Cooperation (EVD), an institutional strengthening project on ambient air quality assessment and management was carried out in the period 2003 – 2004 in Turkey. One of the objectives of the project was to introduce a laboratory quality assurance system in accordance with the international ISO 17025 standard at the Air Quality Control and Research Laboratory (AQCRL) of Refik Saydam Center of Hygiene (RSCH). The paper describes the methodology of introduction of a QA/QC system, the results, the experiences gained, and recommendations.

Keywords*:* air quality monitoring, quality assurance, quality control

1. INTRODUCTION

The Air Quality Control and Research Laboratory is one of the environmental laboratories of the Turkish National Institute of Hygiene (Refik Saydam). The AQCRL has several major responsibilities with respect to ambient air quality monitoring in Turkey. AQCRL operates the largest urban ambient air quality monitoring network in Turkey for the city of Ankara. The current network consists of five automatic and several seasonal semi-automatic monitoring stations. In 2006, the monitoring system will be renewed with nine fully-automatic monitoring stations with telemetric and central control network functions. Besides the regular urban air quality monitoring activities, the laboratory operates the only regional background continuous air quality monitoring station in Turkey. The monitoring station operates within the framework of EMEP program to monitor the long-range transmission of air pollutants in Europe. Furthermore, the laboratory is responsible for the overall technical coordination of semi-automatic ambient air quality measurements conducted nationwide on behalf of the Ministry of Health, and the AQCRL provides training for new technical staff in this field. Recently, the laboratory has been selected as the National Reference Center (NRC) on ambient air quality within the European Environment Information and Observation Network (EIONET).

The laboratory has been conducting its activities along the lines of certain scientifically accepted laboratory quality assurance principles, and has shown in international ringtests, such as organized within the EMEP-framework, to be able to produce high quality results.

However, there has not been any systematic formal laboratory quality assurance program within the laboratory. Both for internal purposes as well external relationships, like exchange of air quality data with the European Union Environmental Agency, it is important that a laboratory is able to show and prove the quality of its results. With the Matra project, a formal laboratory quality assurance system was introduced to the AQCRL in accordance with the international standard ISO 17025 – General Requirements for the Competence of Calibration and Testing Laboratories. The project involved introduction of the system to the laboratory through institutional strengthening activities over a two year period.

2. QUALITY ASSURANCE AND CONTROL ACCORDING ISO 17025

A quality system according to ISO 17025 contains all the requirements that testing and calibration laboratories have to meet if they wish to demonstrate that they operate a quality system, are technically competent and are able to generate technically valid results. All requirements of ISO 9001 and ISO 9002 that are relevant to the scope of testing and calibration laboratories are covered also by this quality system. The laboratories that comply with ISO 17025 will therefore also operate in accordance with ISO 9001 or 9002.

When projected on analytical work, quality can be defined as “delivery of reliable information within an agreed span of time under agreed conditions, at agreed costs and with necessary aftercare”. Through Quality Assurance (QA) laboratories should undertake all actions to provide adequate confidence that a product, process, or service will satisfy given quality requirements. A major part of the quality assurance is the quality control (QC), which is primarily aimed at the prevention of errors. Secondly, if errors have been discovered, proper actions should be taken in order to avoid the same errors in future (corrective actions).

In order to achieve a structural improvement of the quality, a cyclic approach is followed. This cyclic process is often summarized as “PLAN-DO-CHECK-ACT” in the so called Deming Cycle:

1. PLAN: Determine the quality objectives;
2. DO: Develop the necessary procedures and documents and start working according these procedures;
3. CHECK: Perform quality control, organize internal audits and have periodical quality management evaluation sessions;
4. ACT: Take where necessary the appropriate corrective actions and update the quality system. Start the cycle again.

This process should be a continuous process of improving the quality performance and consequently the reliability of the information produced by the laboratory.

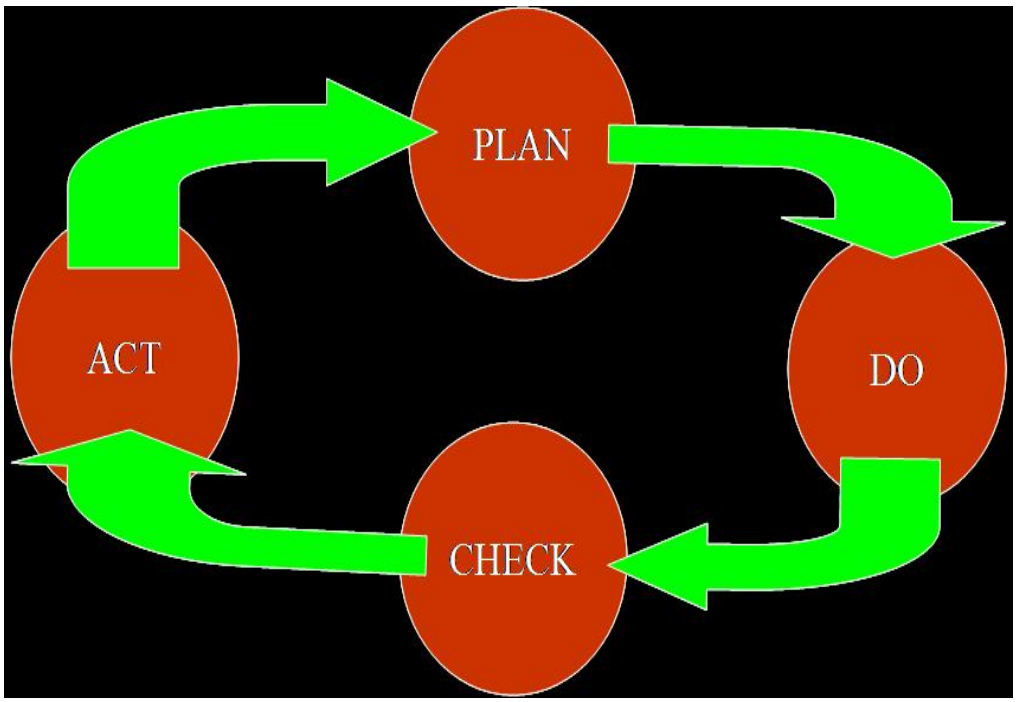

Figure 1: The Deming cycle.

In a quality system laboratories should describe their quality system in a quality handbook. In this quality handbook also the quality policy of the laboratory is described. Furthermore the laboratory should work according unambiguous Standard Operating Procedures (SOPs) in which all the internal processes and all analytical methods are described. The Quality Triangle visualizes the hierarchy of the QA/QC system.

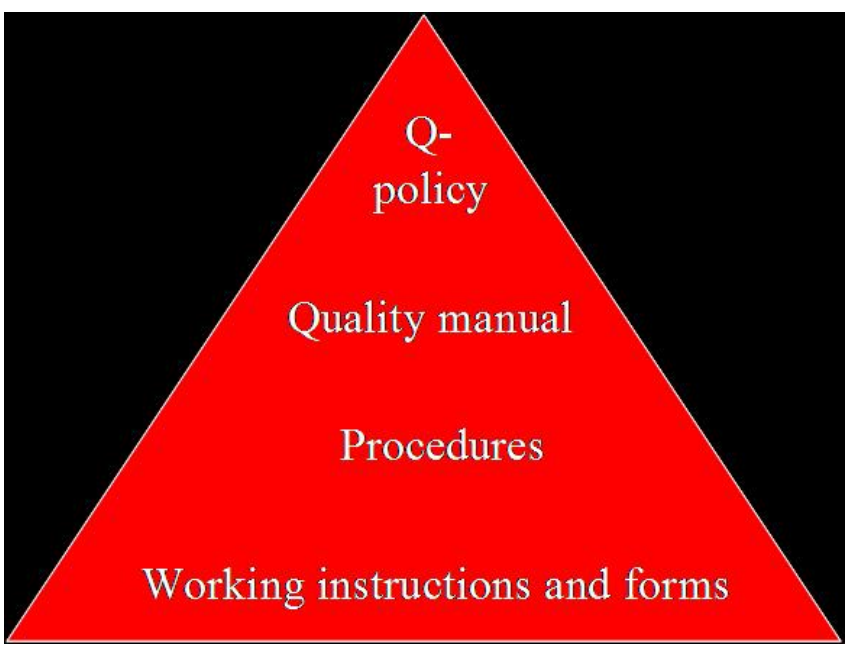

Figure 2: The Quality Triangle

The shortest summary of a quality system can be expressed as ”write what you do, and do what you write”.

3. METHODOLOGICAL APPROACH

The development and implementation of the QA/QC system was performed in a two-years period by a small team of international experts in close cooperation with the AQCRL staff. The approach was as following:

- A combination of theory and learning on the job. The project started with introduction-seminars on the theoretical concepts and organization of quality assurance and control, and especially the ISO17025. During the two-years period, repeatedly seminars on quality were organized, both for the AQCRL staff as well as colleagues from other environmental laboratories and management within the Refik Saydam Centre. However, after introduction of the theoretical concepts and structure of a quality system, in an early stage most technical staff of the AQCRL was involved in preparing Standard Operating Procedures (SOP’s) for their own working activities. This increased the incorporation of the system by the laboratory staff, which is essential for effective implementation of the QA/QC system in a later stage.

- In 2003 a lot of attention was paid to the Quality Assurance system within the Laboratory. First Technical SOP’s were prepared. Earlier experiences of the consultant with introduction of QA/QC system, showed that, in general, workers initially have some doubts about the usefulness of a QA/QC system. Most frequent occurring resistances against a QA/QC system are:
  * laboratory workers consider that they are already doing their jobs in a proper way, so why a starting a QA/QC-system?
  * the large amount of work in the development stage of the quality system and the expected “daily bureaucracy” during the implementation.
  In order to stress the importance and benefits from a quality system, the consultant involved an air quality monitoring expert from the Dutch National Air Quality Monitoring network (RIVM, Netherlands National Institute of Public Health and Environment). Based on his experiences it became more clear to the AQCRL laboratory staff what working according a quality system means for a routine air quality monitoring network. In September 2003 a start was made with the preparation of the managerial SOP’s and the QA-handbook. The way of working according to this Laboratory Management System was new for the Staff. Regular attention during the missions and the arranged Study Tour (October 2003) changed the mindset and increased the motivation of the staff about a QA/QC system.

- The works were conducted in two parallel paths: Management and technical. The management part of the project involved establishing the necessary management processes among the laboratory staff, the relationship between the laboratory staff and RSCH management, and establishment of a structure for internal audits and management reviews. The technical part of the project focused on establishing structured Standard Operating Procedures (SOPs),

quality control mechanisms, and data and procedure validation methods. Furthermore, information from a parallel study (preliminary air quality assessment in Ankara) was used to promote effective urban ambient air quality monitoring, demonstrating the relationships of the quality system with the aim and strategy of the monitoring activities.

- External audits during the process of development and implementation of the QA/QC system. In the beginning of the project, in February 2003, a zero-audit was performed by an experienced, external auditor, to determine the status in QA/QC in AQCRL and to define the needs for assistance and for training. In 2004 the QA-Handbook and the Standard Operational Procedures according to ISO 17025 were further prepared and step by step implemented in the laboratory. In April 2004 an intermediate audit was performed to determine the progress of the implementation of the QA-system. The main finding was still a lack of implementation especially of the managerial and system procedures. In September 2004 a pre-accreditation audit was performed. This audit showed that the quality system is in place and is in conformity with the ISO-standard. In the field of the management requirements the documentation was developed during 2004 and the implementation was arranged on most aspects by the end of 2004.

- Use of the Training of Trainers concept: within the MATRA project the laboratory staff of AQCRL in Ankara started a Training of Trainers (TOT) program for their colleagues in the Province of Kütahya. The Ankara staff introduced a basic quality system to the laboratory performing air quality analyses in Kütahya. During this TOT program technical staff members of AQCRL and the local staff of the Kütahya Public Health Laboratory from the MoH worked closely together. Presentations about QA/QC in air quality monitoring were provided and documentation (SOP's) was presented and explained to the local Laboratory staff by the Ankara staff.

4. RESULTS

In the 2 years period much has been achieved. In the beginning of the project there was almost no procedure at all in the laboratory. The laboratory was hesitating about afraid not be able to face all the administrative work of preparing the SOP's and other documents and records. During implementation, the Laboratory became more and more aware of the concept and the structure of the QA-system. The AQCRL has produced many required documents, but more important they have implemented the procedures in the laboratories. The mindset of the laboratory workers was changed. Usually the whole process takes about 2 years to achieve the level of accreditation.

All for the Quality System required documents, like Quality Handbook and Standard Operational Procedures have been produced. Table 1 gives an overview of the structure, according the quality triangle, and the corresponding documents.

Table 1. Overview of the QA/QC system at the Refik Saydam Air Quality Control and Research Laboratory.

Organization Level (according Quality Triangle)	**Documents**
1. Quality policy	1 Management Quality Statement
2. Quality Manual	1 Quality Handbook
3. Procedures	
- Semi-automatic measurements	6 SOP's
- Wet chemical analyses (EMEP)	16 SOP's
- Automatic measurements	6 SOP's (in preparation)
- General technical	17 SOP's
- Managerial	9 SOP's
4. Working instructions and Forms	Many

Furthermore these procedures also have been implemented.

The project has resulted in a considerable increase of knowledge on the quality system for the staff members and a very high interest and commitment. The auditor was very confident that the laboratory was ready for accreditation according to ISO 17025. This could to be checked by the Turkish Accreditation Body TURKAK. The process of accreditation is scheduled for 2006.

5. STRATEGICAL ASPECTS

The quality system aims to assist in producing measurement results of a known quality. For the interpretation of the meaning of the measurement result to inform environmental policy makers, also additional information about the relevant circumstances of the measurement are important. This additional information concerns a.o. the distance of the monitoring location to nearby air pollution sources and the meteorological conditions during the measurements. Therefor the overall aim of the monitoring activities should be reflected in the quality system, in terms of choice of methods and equipment, measurement frequencies, monitoring locations, necessary quality level etc.
Therefor, quality assurance and control is not only a concern for laboratory staff, but also for the management, and finally for policy makers in the environmental field. Good coordination between policy makers, management and technical staff is necessary to change air quality data into environmental policy information!

6. ROAD AHEAD

The following steps are recommended for the future:

1. Essentially starting the Quality Cycle is most important. By working according this cyclic system, quality improvement of working procedures and products will take place.

2. Accreditation of the quality system by an Accreditation Body (Turkak).
3. Development of air quality monitoring on the assessment level in Turkey is a challenging task. Good cooperation by all stakeholders is necessary to achieve this goal.
4. The experiences and results gained in the field of quality in air quality monitoring in this project, for Ankara and Kütahya, provide a suitable basis for expansion of the quality system to air quality monitoring laboratories in other Turkish provinces.
5. The development of ambient air quality management should be gradual, step by step, and in balance, assuring that all stakeholders have the manpower, knowledge, and tools to play their role in air quality management and solving Turkey's air pollution problems. In order to strengthen the institutional framework in Turkey for ambient air quality, future projects need to pay attention to capacity building, on both technical and managerial level, at the ministries and institutions involved.

7. ACKNOWLEDGEMENTS

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MONITORING OF PARTICULATE MATTER IN A RESIDENTIAL AREA

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ABSTRACT

In this pilot study, a fine dust monitoring network has been installed in the city of Nijmegen. Aim of the pilot study is to determine the contribution of local sources, such as traffic and industry, to ambient particulate matter concentrations. Seven Osiris dust monitors were used measuring hourly mean PM2.5 and PM10, simultaneously. Based on this information, effective local and regional dust reduction measures can be identified. The municipality of Nijmegen will use the results of the pilot study for future air quality monitoring strategy to comply with the European air quality requirements for PM10.

Key Words: Air Quality, Suspended Particulate Matter, Monitoring Network, Contribution of Local Sources

1. INTRODUCTION

In the Netherlands, air quality is determined by a limited number of monitoring stations in the National air quality monitoring network, and additional calculations with air quality models. According to these model calculations, the European air quality requirements for PM10 are exceeded in many locations in urban areas. As a result, spatial planning of new houses or schools near PM10 sources are blocked. However, in some situations, for several reasons, the results of the modeling might not be accurate enough for describing the local conditions. Models in the Netherlands are accepted to be adequate for screening of potential exceedance situations and large scale, time trend monitoring, but are probably not always accurate enough for determination of the occurring local ambient PM10 concentrations. Also the contribution of local sources to local ambient concentrations relative to background concentrations might be different from the modeled situation. Therefore, the municipalities need to get better insight in the contributions of local sources to ambient PM10 concentrations, next to model calculations.

2. EXPERIMENTAL SET-UP

Nijmegen is a city with approximately 160.000 inhabitants, located in the east of the Netherlands, at the border with Germany. Just like most of the country, the area has a

high population density. The city territory is rather flat, with the river Waal (Rhine) in the north and some slight hills in the southeast. The river Waal has a lot of shipping. The industrial area is located in the northwest of the city center, with a wide variety of industrial activities, like a power plant, metal handling, iron foundry, waste handling and incineration, and food industries. During two months, seven Osiris dust monitors were installed at various locations around the industrial area at the western part of the city, and in the city centre near a main traffic artery and in a residential area in the city center (figure 1). Local meteorological information, necessary for interpretation of the monitoring results, were obtained from the nearby meteorological station. The monitoring locations can be characterized according EU-definitions as presented in table 1.

Table 1. Characterisation of monitoring locations according EU-definitions.

Monitoring station	**Area character**	**Sources**	**Sampling height (m)**
1	Urban	Street	2.5
2	Urban	Background	2.5
3	Urban	Industry	3.5
4	Rural	Industry	2
5	Rural	Industry	2.5
6	Urban	Industry/street	3
7	Urban	Background	2.5
M	Rural (meteorological station)	-	

Figure 1. Lay-out of the dust monitoring locations 1 to 7 and Meteorological Station

The most important requirements of a PM monitor to answer the questions of this project are: high time resolution of at least one hour, distinction of the size fractions PM2.5 and PM10 and on-line availability of the dust concentration data. Particle size helps to reveal the character of the dust source: particles < 2.5 µm are mainly emitted by chemical sources (like combustion) whereas particles from 2.5 µm to 10 µm are mainly of a mechanical nature (resuspension by traffic, handling a dry bulk materials, wind erosion).

The Osiris dust sampler fitted our purpose. The Osiris operates on the principal of light diffraction and has a virtually constant response, irrespective of the colour of the particles. This small sampler (0.2 m x 0.2 m x 0.5 m) gives a continuous and simultaneous indication of the PM1, PM2.5, PM10 and TSP mass fractions. Another reason why the Osiris sampler was chosen, is that it has low demands on the receptor site. Due to its small size and little weight, it can be easily installed and only requires a low power supply. The Osiris dust monitor is compared to the European reference method according EN12341. The data were collected at the office by mobile phone connections to the samplers.

The data analysis was focused on the size fractions PM2.5 and PM10, as these are most relevant from the point of view of environmental management. Detailed data analysis was carried out by intercomparison of the results of the monitors, as they were located in different wind directions, including local meteorological data.

3. RESULTS

Concentration trend in time

Figure 2 shows an example of the trend in time of PM2.5 and PM10 at one location.

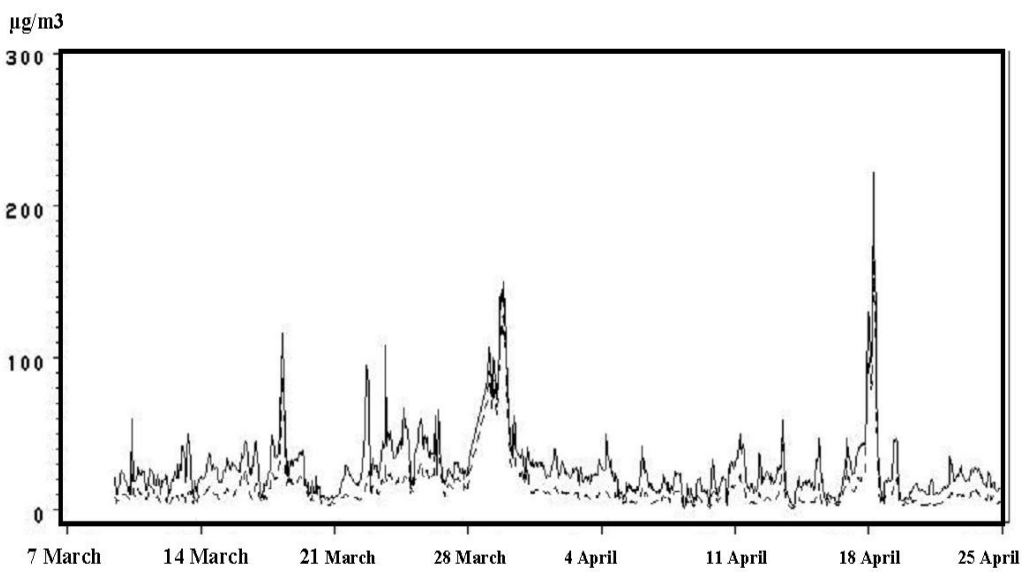

Figure 2. Trend in time of PM2.5 (----) and PM10 (___) at location 4

Highest concentrations were measured on March 29th and April 18th. As PM10 and PM2.5 are almost the same, it shows that it mainly consists of PM2.5. The same peaks occurred at the other 6 monitoring stations. The peak concentrations at March 29th were caused by the traditional Eastern fires in the eastern parts of the Netherlands and in Germany. The reason for the high concentrations on April 18th could not be identified.

Determination of local source contributions

When local sources contribute to the dust measurements, upwind and downwind concentrations will differ. This results in a low correlation between two monitoring sites. Table 2 shows the correlation coefficients between the monitoring locations for PM2.5 and for the coarse fraction of PM10, expressed as PM(2.5-10).

Table 2a. Correlation coefficients between the measuring locations for PM2.5

Location	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	1	0.94	0.83	0.91	0.91	0.90	0.93
2		1	0.95	0.99	0.96	0.99	0.99
3			1	0.93	0.90	0.88	0.91
4				1	0.95	0.97	0.98
5					1	0,95	0.97
6						1	0.98
7							1

Table 2b. Correlation coefficients between the measuring locations for PM(2.5-10).

Location	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	1	0.86	0.64	0.46	0.26	0.46	0.60
2		1	0.75	0.52	0.23	0.63	0.65
3			1	0.53	0.42	0.51	0.56
4				1	0.72	0.75	0.79
5					1	0.79	0.74
6						1	0.83
7							1

The correlation coefficients for PM2.5 are quite high. This indicates, that there is a low contribution from specific local sources and it consists mainly of background dust or general local sources. For PM(2.5-10), the correlation coefficients are much lower. So, the contribution of specific local sources mainly consists of the coarse part of PM10. This reveals, that mostly mechanical processes emit dust, such as windblown dust, resuspension by traffic and handling of dry bulk goods.

More detailed information is obtained, when two locations are compared for different wind directions. The scatterplots in Figure 3a and 3b show the correlation between the industrial monitoring stations north (location 4) and south (location 6) of the industrial area.

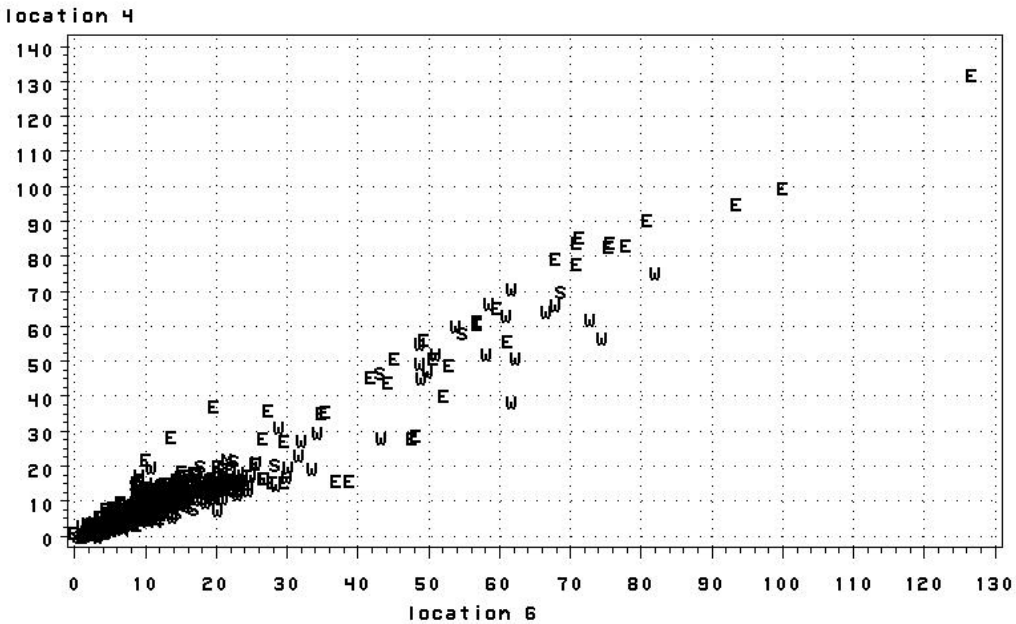

Figure 3a. Comparison of PM2.5 (µg/m³) for locations 4 and 6 for wind directions North (N), East (E), South (S) and West (W).

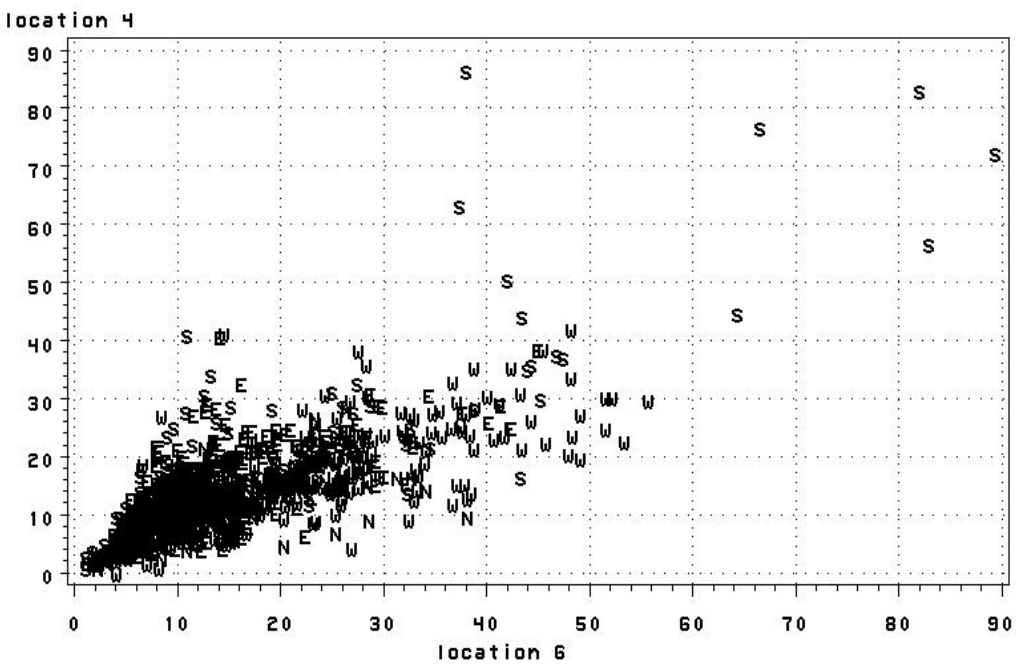

Figure 3b. Comparison of PM(2.5-10) (µg/m³) for locations 4 and 6 for wind directions North (N), East (E), South (S) and West (W).

As was expected, the differences between locations 4 and 6 are small for PM2.5, because ambient PM2.5 levels are mainly determined by large scale background concentrations. For the coarse fraction PM(2.5-10), the concentrations at location 4

are higher with southern winds, whereas location 6 is higher with northern and western winds. This shows a contribution of the industrial area situated in between locations 4 and 6.

Daily concentration pattern

Figure 4 shows the mean daily variation of PM10 and PM2.5 during this two-month monitoring campaign.

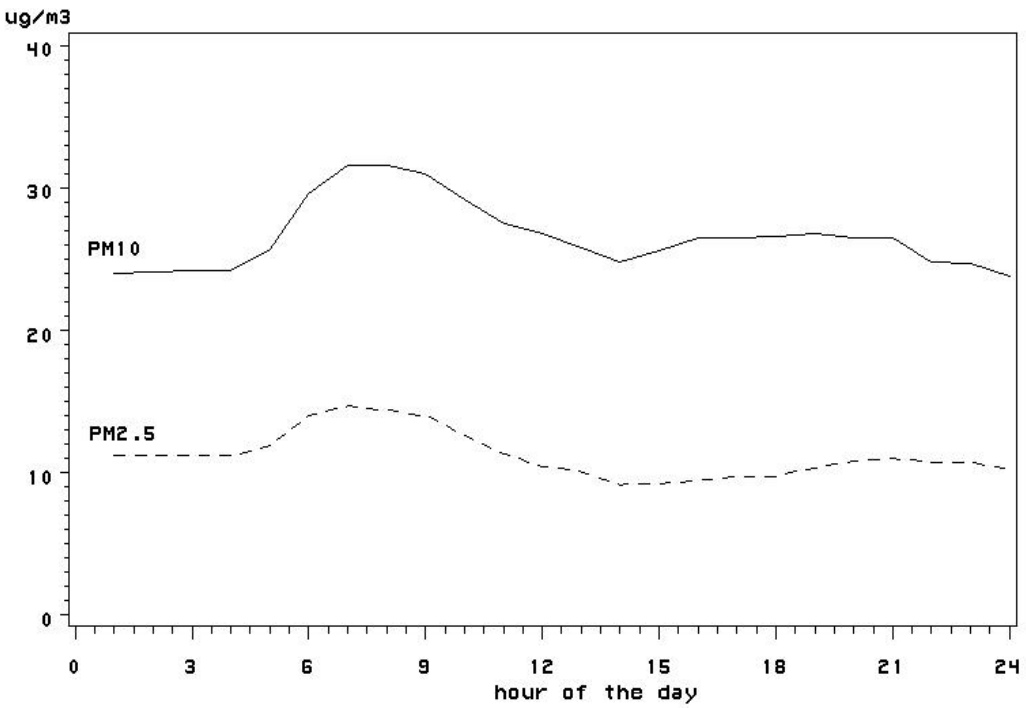

Figure 4. Mean daily variation of PM10 and PM2.5 at location 6.

An increase of PM10 and PM2.5 is observed between 6:00 and 9:00 o'clock. This indicates a contribution of the traffic during rush hours. The same pattern was found at all locations. So, the contribution is probably coming from the whole industrial and residential area.

4. CONCLUSIONS

The dust monitoring network showed a high similarity between the seven measuring locations, especially for PM2.5. For the coarse part of PM10 (PM2.5-10)), local contributions could be detected, caused mainly by mechanical activities at the industrial area. The increase of PM10 and PM2.5 at all locations during rush hours indicates a contribution of traffic from the whole industrial and residential area.
The results of this two-month pilot study show that the contribution of local sources to ambient PM10 concentrations can be determined. This provides a useful tool for ambient air quality management to local environmental authorities.