POSTERS

Third International Symposium
on
AIR QUALITY MANAGEMENT
at Urban, Regional and Global Scales
&
14 th IUAPPA Regional Conference
26-30 September 2005
Istanbul, Turkey

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

AN OVERVIEW OF THE CONTINUOUS EMISSION MONITORING TECHNOLOGIES AND EQUIPMENT INSTALLED BY THE USA ELECTRIC UTILITY INDUSTRY TO COMPLY WITH THE USA ENVIRONMENTAL PROTECTION AGENCY ACID RAIN MONITORING PROGRAM

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ABSTRACT

Since early 1993 more than 3,000 new continuous emission monitoring systems (CEMS) have been installed and certified by the United States of America (USA) electric utility industry to meet the requirements of the USA Environmental Protection Agency (EPA) 40 CFR Part 75's "Acid Rain Rule", and recently the "NO_x Budget Trading Programs." Much experience has been gained during the past ten years by the USA electric utility industry regarding the most reliable air pollution emission monitoring technologies and analyzer manufacturers. Accordingly, this overview of the air pollution emission monitoring technologies and analyzer manufacturers used by the electric utility industry for complying with the CEMS regulations in 40 CFR Part 75 should be helpful to international electric generation and industrial combustion facilities being required to install new CEMS to meet current air pollutant emissions regulations.

This report will present CEMS *Monitoring Plan* information extracted and compiled from the forth quarter 2003's Electronic Data Reporting (EDR) files submitted to the EPA. *Monitoring Plan* data identifies the source, generating units, the emissions monitored, sample acquisition method, analyzer manufacturer, model, etc.

The information compiled and presented in this paper will include, the monitoring technologies, sample acquisition methods, and monitor manufacturers for all the electric utilities submitting EDR's for the forth quarter of 2003. Additionally, this report will present by measurement technology and manufacturer the total number and percent of total of the SO_2, NO_x, CO_2, O_2 analyzers and flue gas flow rate monitors.

Key Words: Continuous Emission Monitoring, Electric Utiltity Industry, SO_2, NO_x, CO_2

1. INTRODUCTION

Since the 1970 Clean Air Act, EPA has proposed and promulgated CEM regulations that currently affect almost all industry sources in the United States of American. During this period, the availability of more reliable CEM instruments including flue gas flow rate and moisture monitors has increased significantly. As a result of these most recent CEM regulations, 40 CFR Part 75 (Part 75) and NO_x SIP Call, the demand for extremely accurate and reliable CEM equipment has also increased to meet the tighter precision and reliability requirements specified by Part 75 and NO_x SIP Call regulations and by many state regulatory agencies. The gas and flow rate monitors are now equipped with improved analytical techniques, enhanced electronics, programmable software capabilities, and troubleshooting diagnostics

One of the EPA's quarterly emissions data reporting requirements is to include monitoring plan information in the quarterly Electronic Data Reporting (EDR). Monitoring plan data identifies the source, generating units, the emissions monitored, sample acquisition method, analyzer manufacturer, model, etc.

This report will present monitoring plan information extracted and compiled from the forth quarter 2003's EDR files submitted to the EPA. The information compiled and presented includes, the monitoring technologies, sample acquisition methods, and monitor manufacturers for all the electric utilities submitting EDR's. Additionally, this report will present the measurement technologies and analyzer manufacturers. The total number and percent of total of the measurement technologies, NO_x, CO_2, O_2 and flue gas flow rate monitors.

2. SAMPLE ACQUISITION TECHNIQUES

CEM systems incorporate one of three sample acquisition techniques: dilution-extractive, extractive (i.e., sampling without dilution of the sample gas), and in-situ. Inherent differences exist among the three sampling techniques, and thus each technique has distinct strengths and weaknesses, which must be carefully evaluated when selecting an appropriate technique for a specific application. The sample acquisition techniques chosen by Part 75 affected utility companies are presented in Table 1. The following sections address the principle of operation for the most widely used and currently available equipment, and technological advancements for each sample acquisition technique.

Table 1 - Sample Acquisition Methods Used By Part 75 CEMS

Sample Acquisition Methods	**% SO_2 CEMS** (1,045 analyzers)	**% NO_x CEMS** (3,193 analyzers)
Dilution (In-Stack & Out-Of-Stack)	87.9	47.2
Extractive (cool/dry & hot/wet)	10.0	51.5
In Situ “Point” Method	1.8	1.2
In Situ “Across-Stack” Method	0.3	0.1

Dilution-Extractive Systems

Approximately 87.9% of the SO_2 and 47.2% of the NO_x CEM sampling systems installed to meet Part 75 monitoring requirements were dilution-extractive systems. The principal reason for selecting a dilution-extractive system is due to its ability to measure flue gas pollutant concentrations on a wet basis. Part 75 requires SO_2 emissions to be reported as a mass emission rate (i.e., lb SO_2/hr). All flue gas flow rate measuring techniques are on a wet basis, consequently, wet basis SO_2 emission data can be used more conveniently to calculate SO_2 mass emission rates. Additionally, the Part 75 requirement to measure CO_2 added to the convenience of using a dilution-extractive system because CO_2 is measured as the diluent gas (instead of O_2) in dilution-extractive systems. Dilution-extractive systems are extractive systems that dilute the sample gas with dry contamination-free dilution air to a level below the dew point of the diluted flue gas to eliminate condensation problems in the CEM system (in lieu of using a moisture condenser). The diluted sample is analyzed by pollutant and CO_2 monitors operating at or near ambient concentration ranges. The most unique component of a dilution-extractive system (relative to other extractive systems) is the dilution-sampling probe. There are two basic types of dilution probes, in-stack where the dilution of the flue gas is performed in the probe and out-of-stack (*ex-situ*).

In-Stack Dilution-Extractive Probe

The in-stack probe design is equipped with coarse and fine filters for removing particulate matter from the stack gas prior to sample dilution, a quartz or glass critical orifice for flow regulation, and an air-driven aspirator and venturi for dilution of the sample gas. Approximately 86.4% and 81.0% of the SO_2 and NO_x, respectively of the dilution-extractive systems used by Part 75 affected sources are the in-stack type.

Out-Of-Stack Dilution-Extractive Probes.

The out-of-stack device uses the same basic dilution-extractive sampling technology as the in-stack dilution-extractive probe, with the following differences. This system is designed to constantly heat the sampling assembly, and all critical parts are mounted out of the stack for quick access and easy maintenance.

The working principle difference is, undiluted stack gas is continuously drawn through the sampling probe tube into the sampling chamber by a by-pass pump at a rate of 1.5 to 15 liters per minute. A vent in the sampling chamber ensures a constant flow of "fresh" stack gas through the chamber. The dilution probe draws a small sample of the gas out of the chamber through a sampling tube at a flow rate determined by the critical orifice of the probe. The operation of the dilution-extractive probe at this point is the same as previously described.

Dilution Air-Cleanup System

Dilution-extractive probe systems require a constant source of contamination free dilution air. The air supply should be dry (-29° to -40°C) and delivered at 6.3 ± 1 kilogram/centimeter^2. Additionally, the dilution air should be free of oils, particulates, CO_2, NO_x, and SO_2. A plant's compressed air system does not generally provide dilution air to the needed specification. Therefore, an additional air-cleanup system is required. In Part 75 dilution-extractive CEMS the air-cleanup system is the critical component of the dilution-extractive system.

Compressed air either from the plant's compressed air supply or from a dedicated air compressor is first filtered for particulates, then liquid and oils condensate by a coalescing filter. Oil removal is necessary to prevent the contamination of silica gel or other drying agents in the heatless air dryer. Additional drying of the dilution air is performed by a heatless dryer that can dry the air to approximately -73°C. The CO_2 extractor utilizes two columns with different adsorbent materials to adsorb any CO_2 in the dilution air. Some air cleaning systems may add a CO to CO_2 converter before the CO_2 extractor if their analyzers respond to interferences from CO. A charcoal filter trap may also be added to remove any hydrocarbons that may be in the dilution air. An additional desiccant dryer may be added to provide additional moisture removal. A submicron filter removes any particulates that may be released from the upstream desiccant traps.

Gas Sample Dilution Ratios

Dilution ratios typically range from 50:1 to 300:1. The dilution ratio most widely used by Part 75 sources is 100:1. The sample gas flow rates from the various dilution probes range from 50 to 300 ml/min. Two criteria are used to determine the desired dilution ratio: (1) the analyzer span range must correspond to the diluted sample gas concentration, and (2) the ratio must be selected to ensure that no condensation occurs in the sample line at the lowest possible ambient temperature.

Sample Umbilical Bundles

The sample umbilical bundles of dilution-extractive systems usually consist of four to six separate lines; one Teflon® line for sampling, a second Teflon® line to deliver calibration and purge gases to the probe, a third line to deliver dilution air to the probe, sometimes a fourth line to monitor vacuum in the probe, and sometimes one or two "spare" Teflon® lines. The spare lines are often used for diagnostic purposes (e.g., resolving or isolating leak problems) or for backup monitoring equipment. The diluted gas sample line should be at least 0.95 centimeter in diameter and, if the overall sample line length exceeds approximately 107 meters, a 1.27centimeter sample line may be needed to reduce the pressure drop between the probe and the monitors. High pressure drops may prevent adequate sample flow to the monitors or cause condensation problems. Using a 1.27centimeter sample line over long distances, however, can significantly impact response times (response times for a 0.95 centimeter line are typically 15 seconds for every 30.5 meters) such that timesharing a CEM system between two locations may be precluded. Heat traced umbilical bundles are required only in very cold ambient conditions or when dilution ratios less than 25 to 1 are used in climates subject to below freezing ambient conditions in the winter.

Extractive Systems (Non-Dilution)

Non-dilution extractive systems are classified as “cold/dry” or “hot/wet” systems.

Cold/Dry Non-Dilution Extractive Systems

Typical cold/dry non-dilution extractive systems have four common subsystems: (1) effluent/CEM system interface, (2) sample transport, (3) moisture removal, and (4) pollutant and diluent analyzers.

Effluent/CEM System Interface

The effluent/CEM system interface typically consists of a corrosion resistive rigid probe, positioned at a representative location in the effluent. A coarse filter made of sintered stainless steel or porous ceramic materials is used to filter out particulate matter greater than 10 to 50 µm. Historically the coarse filter was located at the probe inlet; however, some current designs have the filter positioned out of the stack for ease of maintenance.

Sample Transport System

The sample transport system begins at the junction between the probe and the sample transport line, usually positioned just outside the stack or duct. Sample transport systems consist of heated sample transport lines and a mechanism such as a pump to move the gas sample. The sample tubing is usually a non-reactive material such as Teflon® and the parts of the sample pump exposed to the flue gas are coated or fabricated from non-reactive materials. The sample pump must be designed so no lubricating oil can contact and contaminate the sample gas and no air in-leakage occurs. The most common types of pumps to meet these specifications are diaphragm and ejector pumps.

Sample Moisture Removal System

The third component, the sample moisture removal system, provides a clean, dry, interference-free sample to the analyzers. Two moisture removal methods were primarily used by Part 75 sources in sample moisture removal systems: condensation and condensation/permeation.

Condensation Systems

Condensation systems rapidly cool the sample, thereby condensing sample moisture. The condensed moisture is trapped and periodically removed from the condenser assembly. To avoid absorption of the target gases by the condensed liquid, precautions are usually taken in designing condensers and traps that minimize contact between the condensate and the cooled sample.

Two basic techniques are generally employed to prevent the trapped condensate from contacting the target gases. The first and most common approach uses a standard compressor-type refrigeration unit, and the other is the thermoelectric plate chiller, a solid-state unit with no moving parts.

Refrigeration Condensers

Refrigeration condenser systems for moisture removal typically use a dual condenser system. This method provides secondary moisture removal after the sample pump because flue gas under pressure will condense to a greater degree than the flue gas under vacuum. The limitations of condenser systems are that it generally requires a complex valve and plumbing system (which often requires a high level of maintenance) for adequate moisture removal.

Thermoelectric Chillers

Thermoelectric (TE) chillers work on the “Peltier effect” principle and TE chillers are sometime called Peltier chillers. The most commonly used TE chillers work as flat plate heat exchangers and cool the sample gas to a dew point temperature that causes the moisture in the sample gas to condense on the TE chiller plenum walls and then drain from the system. Some utilities using TE chillers added a permeation dryer after the TE chiller for backup and additional moisture removal

Permeation Dryers

Permeation dryers were used in conjunction with refrigerated condensers for several Part 75 sources to provide additional moisture removal in the event of moisture carry over from the upstream condensers. This technique is based on the selective permeability of water through a membrane. Permeation occurs continuously as moist stack gas flows in one direction through the dryer, while dry purge air flows counter currently on the other side of the membrane.

Hot/Wet Non-Dilution Extractive Systems

For hot/wet systems, the moisture is not removed from the flue gas sample prior to entering the analyzers. Less than 0.6% of the total Part 75 SO_2 and 0.7% of the NO_x CEMS were hot/wet systems.

In-Situ Systems

As the name implies, in-situ gas monitoring systems are designed to measure gas concentrations directly in the stack or duct, without extracting samples for external analysis. Two types of in-situ monitoring systems are currently in use. The first is an across-stack (or path in-situ) system that analyzes the effluent passing by a specific "line of sight" of the monitor, typically ranging from a few feet to the full distance across the interior stack or duct diameter. Approximately 0.3% of the SO_2 CEMS and 0.1% of the NO_x CEMS in the Acid Rain Program are path in-situ type. All of the path in-situ CEMS are OPSIS® systems that measures flue gases by differential optical absorption spectroscopy (DOAS). The OPSIS Model ER 070 emitter and receiver are typically used for stacks less than 4.5 meters in diameter and the Model ER 080 transceiver is typically used for stacks greater than 4.5meters in diameter. EPA distinguishes between path and point analyzers by the percentage of the stack or duct diameter (or equivalent diameter for non-circular ducts) represented by the measurement path. Instruments that measure gas concentrations along a path less than or equal to 10% of the diameter are point analyzers. If the measurement path is greater than 10% of the equivalent diameter, the instrument is considered a path analyzer.

The second is a point in-situ instrument, which analyzes the effluent at one specific point or along a short path in the stack or duct. Approximately 1.8% of the SO_2 CEMS and 1.2% of the NO_x CEMS in the Acid Rain Program are in-situ point type. All point in-situ systems are Teledyne/Monitor Labs®, or Sick Maihak CEMS that measure flue gas by UV (ultraviolet) Second-Derivative Spectroscopy.

3. GASEOUS CONTINUOUS EMISSION MONITORS

The following subsections provide a brief overview of the SO_2, NO_x, CO_2, and O_2 monitors that were most widely used by utility Part 75 sources and their principles of operation.

SO_2 MONITORS

SO_2 monitoring technologies are well established and several of these monitors now incorporate a microprocessor, enabling the operator to check certain monitor operating parameters, perform calibrations automatically, and perform numerous diagnostic functions. A brief overview of these technologies is given.

Fluorescence Monitors

Fluorescence SO_2 analyzers, both pulsed and continuous ultraviolet (UV) light source type, were originally manufactured for ambient air monitoring. Ambient air SO_2 concentrations are in the parts per billion (ppb) range, and these units operate well at that low concentration. Because the fluorescence technology was a proven technology in low concentration ranges and was well-matched for dilution probe applications, it was chosen by approximately 90% of the Part 75 sources with dilution-extractive systems for monitoring SO_2. Two manufacturers supplied 88.4% of all SO_2 analyzers. One manufacturer (Thermo Electron Corporation) with a pulsed-fluorescence analyzer supplied 71.4% of the SO_2 analyzers and another manufacturer (Teledyne/Monitor Labs & Teledyne/API) with a continuous-fluorescence analyzer supplied 15.3%.

UV Spectrophotometric Monitors

Several manufacturers offer UV and two (Teledyne/Monitor Labs & Sick Maihak) offers second-derivative spectroscopic UV SO_2 monitors for in-situ and extractive applications. UV type SO_2 monitors have proven to be reliable instruments, and as with many other monitoring systems, electronic components (e.g., for optical contamination and lamp current compensation) have been improved over the past 5 years. Because the UV spectroscopic type SO_2 monitors were either used in extractive or in-situ CEM systems, less than 15% of the Part 75 SO_2 analyzers are the UV spectroscopic types.

NO_X MONITORS

Typically, only chemiluminescence, UV, or infrared (IR) monitors are used for monitoring NO_x. Recent advances, particularly for chemiluminescence monitors, are noted in the following brief overviews of these long-established monitoring technologies.

Chemiluminescence Monitors

Approximately seven different chemiluminescence monitor vendors are used by Part 75 sources for NO_x monitoring. These monitors have been installed and operated at utility sites for years and have a proven performance record. Approximately 96.6% of the Part 75 NO_x monitors were chemiluminescence monitors. Four analyzer manufacturers supplied 95.7% of all chemiluminescence monitors, Thermo Electron Corporation (64.9%), Teledyne (13.3%), Rosemount (12.4%), and Forney (5.1%).

As with SO_2 monitors, several of these monitors now incorporate a microprocessor, enabling the operator to check certain monitor operating parameters, perform calibrations automatically, and perform numerous diagnostic functions. If ammonia interference is a potential problem, catalytic converters are available that will convert NO_2 to NO without converting ammonia to NO. Essentially all chemiluminescence monitors incorporate a high-vacuum sample chamber to minimize quenching (absorption of the fluorescent light by other molecules).

UV Spectrophotometric Monitors

Several vendors offer UV photometric and second-derivative spectroscopic analyzers for monitoring NO_x. As with the chemiluminescence monitors, UV monitors have been used to monitor NO_x emissions at numerous utility sites prior to the Acid Rain Program, however, less than 3% were used for Part 75 NO_x monitoring. UV photometric analyzers require sample filtering to remove particulate matter and sample conditioning or heated sample cells to maintain the sample gas temperature above the dew point. Various design modifications and improvements to the electronic components (e.g., isolating the electronic and optic components from the sample cell) have been implemented.

CO_2 MONITORS

Essentially all CO_2 monitors use IR-based technologies to detect CO_2. Either non-dispersive infrared (NDIR) or gas filter correlation (GFC) technology is used. California Analytical Inc. and Thermo Electron Corporation supplied approximately 77% of all CO_2 monitors used for Part 75 monitoring. California Analytical Inc. who offers the NDIR technology supplied 38.9% of the CO_2 analyzers. Thermo Environmental Instruments who offers the NDIR GFC technology supplied 34.9% of the CO_2 analyzers.

Before the Acid Rain Program, CO_2 monitors were generally considered to be less reliable and less accurate (for the concentration ranges typically observed in flue gas) than O_2 monitors. When using a dilution-extractive CEM system, however, the relative differences, advantages, and limitations between CO_2 and O_2 monitors are not an issue. A CO_2 monitor must be used to determine diluent concentrations for a dilution-extractive CEM system and CO_2 mass emissions must also be reported.

O_2 MONITORS

Approximately 75% of the Part 75 O_2 monitors are paramagnetic monitors and the remaining Part 75 O_2 monitors are primarily electrocatalytic oxygen analyzers. These monitoring technologies have been used for many years and provide reliable O_2 emissions data. Servomex is the largest supplier of O_2 analyzers with approximately 38% of the market, followed by Siemens (16.2%), Ametek (11.0%), Teledyne (9.0%), and Rosemount (7.7%).

4. FLUE GAS FLOW MONITORING TECHNIQUES

Most commercially available flue gas flow monitors operate using one of five principles for measuring velocity and volumetric flow: ultrasonic pulse detection, differential pressure, thermal detection (convective cooling), audible acoustic detection and optical scintillation. The five varieties of flow monitors are stack or duct mounted and operates as a component (including a microcomputer, pressure transmitters, and temperature transmitters) of a system. Other types of flow monitoring systems are available: fan efficiency, and infrared detection, but these two techniques have yet to be used by Part 75 sources, therefore, sufficient data are not available to evaluate their performances.

Ultrasonic Flow Monitors

Approximately 62% of all flow monitors used in the Acid Rain Program are ultrasonic type monitors. Four manufacturers supplied ultrasonic flow monitors for the Acid Rain Program, with one manufacturers (Teledyne/Monitor Labs.) supplying 86% of the ultrasonic flow monitors.

Principle of Operation

The volumetric flow rate of stack gas is measured by transmitting ultrasonic pulses across the stack in both directions. The tone pulses are accelerated or retarded due to the gas velocity in the stack. The time required to traverse the distance of the stack traveling with and against the flow is a function of the sound velocity and the effluent velocity. Stack flow can be calculated based on the difference in the times required to traverse the stack in both directions. The ultrasonic pulses must traverse the stack or duct at a minimum angle of 10 degrees; however, traverses between angles of 40 and 70 degrees tend to provide the best results, as long as the traverse path length is not so long that the ultrasonic pulses become difficult to detect.

Differential Pressure Flow Monitors

Approximately 30% of all flow monitors used in the Acid Rain program are differential pressure type flow monitors. Three different types of commercially available flow monitoring devices are based on measuring differential pressure: S-type pitot tubes, the Fechheimer dual-manifold pitot probe, and annubars. The principles of operation, which differ somewhat among these three types of flow monitoring devices, are discussed in the following paragraphs.

Principle of Operation

The S-type pitot tube is designed after the Stausscheibe or reverse type pitot tube as described in Method 2 in Appendix A to 40 CFR Part 60. The probe is constructed of two in-line tubes. The sampling point of the probe consists of two opposing open faces perpendicular to the traverse axis. A side view of the probe resembles two stacked tubes with the ends tapered away from one another and the openings planed parallel to the horizontal axis. Approximately 68% of all differential pressure type flow monitors in the Acid Rain Program are the S-type Pitot Tube design and are supplied by one manufacturer Environmental Measurement Research Corporation (EMRC).

The Fechheimer pitot probe consists of flow sensors mounted on two multipoint averaging manifolds. The probe design consists of two manifolds (tubes) welded together with a truss plate. The truss maintains a distance between the manifolds in a plane perpendicular to the flow and the stack wall. One manifold averages multiple points of impact pressure, and the other averages multiple points of wake pressure. The impact and wake pressure averages are registered by the flow transmitter. This technology is used in numerous gas flow monitoring applications other than flue gas. Approximately 19% of all differential pressure type flow monitors in the Acid Rain Program were the Air Monitor Corporation's Fechheimer pitot probe and were supplied by one manufacturer.

The annubar flow monitoring technology is a multipoint, dual-chambered probe. The probe averages multiple in-line (impact and wake pressures) sample points across the stack diameter.

The interior of the probe consists of tubes within a tube. The exterior tube shrouds two averaging changer tubes. The inner tubes consist of the impact differential pressure chamber and the wake differential pressure chamber. Precision pressure points are tapped through the exterior tube into the inner tubes. The pressure registered at the flow transmitter is the average across the stack. Although this technology and its manufacturer (Dieterich Standard) have been around for many years, using this technology for many airflow monitoring applications, only 9.4% of all differential pressure type flow monitors in the Acid Rain Program are annubar type probes.

Thermal Flow Monitors

Currently only 5% of the flow rate monitors installed for Part 75 flow rate monitoring are thermal flow monitors. Two manufacturers (Kurz Instruments and Sierra, Inc.) supplied these monitors.

Principle of Operation

Thermal flow monitors measure the electric power required to maintain a constant temperature of approximately 24 to 38ºC above the exhaust gas temperature in a flow sensor.

The monitors are available for both single-point and multipoint analysis, and non-sensing components of the systems can be constructed from various corrosion-resistant metals.

5. CONCLUSIONS

Much experience has been gained during the past ten years by the USA electric utility industry regarding the most reliable air pollution emission monitoring technologies and analyzer manufacturers. Accordingly, this overview of the air pollution emission monitoring technologies and analyzer manufacturers used by the electric utility industry for complying with the CEMS regulations in 40 CFR Part 75 should be helpful to international electric generation and industrial combustion facilities being required to install new CEMS to meet current air pollutant emissions regulations.

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SIZE DISTRIBUTION OF SUSPENDED PARTICULATE MATTER IN THE URBAN AREAS OF TEHRAN

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ABSTRACT

Statistical size distribution of aerosols is one of the important parameters; since methods of purification of the air depends on the size of the particulate matter which must be separated.

Our objectives were to obtain detailed measurements of aerosol size distribution in Tehran's atmosphere during the 2004 at eight sites. We used Impactor ambient sampler which is comprised of six stages that are held together. In all samples the PM is high for stage 6 (< 0.45 μ). In Enghelab station mean of PM value (< 0.45 μ) is 262 $\mu g/m^3$. The highest PM > 7.5 concentration are found 35.31 $\mu g/m^3$ at the Arjanthin square. The highest $PM_{2.5}$ were found 78 $\mu g/m^3$ at the Bahman square. This paper points out the important role that particle size distribution.

The range of particle size collected on each stage depends on the jet velocity of the stage and cutoff of the previous stage. The average percentage of particulates in the Tehran's areas are respectively 76.5 % for 7.2 μm E.C.D; 64 % for 3 μm E.C.D; 57 % for 1.5 μm E.C.D; 46.5 % for 0.95 μm E.C.D and 35 % for 0.45 μm.

Key Words: Aerosol particle; vehicle emission; PM-10; SPM, Urban pollution

1. INTRODUCTION

The lifetime of finer particles is longer than that of relatively large particles, and they are more likely to be inhaled. The fine particulate matter not only can be found from dirty diesel engine exhausts, but also can b found in petrol engine exhausts (Candle et al. 1999). In terms of the effects of PM on human health, the size of the particles and the number of the particles and their composition are very important. A persistent haze blankets the city, especially during winter the effect of suspended particles on health (statistical center of Iran, 2000).

The particulate emissions from vehicles have a great impact on human health and the environment. The small particles under PM_{10}, which remain suspended in the atmosphere for long periods of time can case changes in rain and cloud pattern. PM_{10} and < PM_{10} denotes the particulate matter with a maximum particle 10 diameter of microns (μm), and PM_{10} was initially taken as a parameter to set the unsafe level for particulate emissions in the emission standards (Gray and Cass, 1998; Bagleg et al. 1996).

As products of the engine combustion, particulate emissions can directly indicate the engine working conditions and the levels of incomplete combustion (Lammel and Novakov, 1995). Therefore the particulate emissions from vehicles are the important issues to the environment protection and the performance of the engines in the on-road vehicles.

The impact of the particulate emissions in the environment and human health , and the relationship between the particulate emissions and engine operation were briefly summarized by Gong and Waring (Gong and Waring, 1998). Airborne particulate matter (PM) originates not only directly from combustion processes, but also from, for instance , wintertime standing of streets , and from wearing of the street surfaces because of studded tyres. Re suspension has a substantial influence on both STP and PM_{10} concentrations (Johansson et al. 1999). PM_{10} denotes the PM with a maximum particle 10 diameter of micron (µm) and PM_{10} was initially taken as a parameter to set the unsafe level for particulate emissions in the emission standards (seinfeld and pandas, 1998).

As in many large cities with limited ventilation, Tehran city experience air pollution problems especially suspended particles.

Much at the northern Alborz range essentially blocks the moist and rain-bearing air from Caspian Sea from reaching the Tehran area and wash out the air pollution. Much attention has been focused on particulate phase components of exhaust fumes due to possible acute and chronic respiratory effects. Exhaust fumes are a complex mixture of particulate (Grifin et al. 2003 ; Mitranda et al. 2002).

The current set of the diesel and petrol vehicles on Tehran roads emites inordinate amounts of particulate mtter (PM). Of highest concern are the fine, respirable particles of sizes 10 and 2.5 µm (PM_{10} and $PM_{2.5}$) which are highly carcinogenic and carry toxic compound with them (Monoli et al. 2002).

The particle from engine exhausts can be much finer than 10 µm as shown by the measurement method discussed in this paper.

2. EXPERIMENTAL

The size distribution of the particulate emissions have been investigated by using impactor instruments, consisting of 5 stages with rectangular jets and a back-up filter. The equivalent aerodynamic cut-off diameters at 50 % collection efficiency for a flow rate of about 18-20 SCFM are given in table 1 (the specific gravity of the particles is assumed to be 1 g/cm^{-3}). As the collection media, whatman glass fiber filters type GF/A are used. The total volume of sampled air passed through a rotameter equipped with a photo relay. Sampling is interrupted when the flow rate decreases more than 5% as would occur in the case of reduced pumping speed due to back-up filter clogging or reduced motor efficiency.

Table 1. Sierra Hi-volume cascade impactor characteristics

stage number	Equivalent aerodynamic cut-out diameters at 50 % efficiency (µm)
1	> 7.2
2	7.2-3.0
3	3.5-1.5
4	1.5-0.95
5	0.95-0.49
6	< 0.49

A major field campaign was carried out in Tehran city through 2004. Measurements during the field program included:

- TSP measurements in 20 sites, inside and suburbs of city (Table 2) .
- Seasonal of PM concentration at 8 locations throughout the city (Figure 1) .
- PM < 7.5, PM < 0.45 (PM size distribution) at 8 sites (Tables 3) .

The Equivalent aerodynamic cut-out diameters at 50 % collection efficiency of the different impactor stages are based on the manufacturers data (Eiguren et al. 2003 ; Hays et al. 2002). Practically , the most useful information is obtained for well determined fractions in the size range below 7 µm , containing the particles penetrating the non ciliated pulmonary region (Wilson and Suh 1997 ; Brook et al. 1997). Distribution patterns have to be described in different manners to allow a valid interpretation.

In this paper, primarily the concentration Vs particle size and cumulative mass distribution representations will be used. Particulate matter (PM) was measured by 47mm fiber filter (< 0.45 µm pore size) were pre-weighed on a microbalance. The sampling pumps calibrated to a flow rate of 510 L/min. Filters were removed after sampling and allowed to equilibrate at the laboratory prior to gravimetric analysis.

3. RESULTS AND DISCUSSIONS

PM measurements in 20 sites

Table 2 shows that the highest PM concentration were observed at "Shahre-Rey" site , whereas the lowest concentrations were recorded at the "Haram-emam" Site .

Table 2. Distribution of total suspended particulate matter ($\mu g/m^3$) .

Number	Station	Mean	Maximum	Minimum
1	Tajreesh	249.44	438.57	133.78
2	Vanak	219.04	323.53	117.43
3	Arjantin	180.46	196.19	159.59
4	Tehran-pars	249.66	387.25	112.0
5	Amir-abad	535.98	820.34	217.4
6	Sadeghieh	391.25	439.02	308.77
7	Karaj-road	126.44	215.77	83.1
8	Azadi	269.71	502.57	62.11
9	Enghelab	397.19	674	96.62
10	Ferdoosi	126.99	175.96	96.62
11	Emam-hossein	195.72	250.0	140.0
12	Bahman	569.97	1127.2	308.2
13	Shoosh	425.51	2186	79.71
14	Rah-ahan	177.57	259	94.6
15	Emam-khomeini	153.99	199.28	106.89
16	Sanat	253.52	391.11	111.34
17	Baseej	233.95	395.73	150.84
18	Afsarieh	274.23	413.19	132.27
19	Shahre-rey	1627.52	2050	93.5
20	Haram-emam	141.97	213.36	69.6

PM concentrations ranged from 69.6 $\mu g/m^3$ at Haram-emam (July) to 2186 $\mu g/m^3$ at Shoosh(September).The highest PM concentration measured during the sampling period was 2186 $\mu g/m^3$ in shoosh in 26 September 2004. The Iranian standard of PM is 250 $\mu g/m^3$ which was exceeded to 9 times .

The distribution of total suspended particulate matter

As shown in table 3 , the geometric mean diameter (d_g) and geometric standard deviation (σ_g) determined. Table 3 shows the size distribution of total suspended particulate matter ($\mu g/m^3$) at 8 locations in Tehran area.

Table 3. Distribution of TSP over the Impactor stages ($\mu g/m^3$)

	Stage number							
Sampling site	1	2	3	4	5	6	d_g	σ_g
Baseej	73.21	87.10	38.74	26.79	18.16	151.68	1.54	0.131
Enghelab	115.12	77.74	35.54	31.84	38.50	260.97	0.694	0.24
Tajreesh	90.35	83.37	40.48	32.28	24.91	167.18	1.412	0.144
Arjantin	25.6	30.38	11.28	8.37	7.77	76.21	0.696	0.23
Karaj Road	15.69	29.65	17.88	11.34	6.54	45.34	1.5	0.228
Azadi	72.12	90.36	54.33	43.97	34.07	207.71	1.06	0.1558
Amir-abad	45.34	41.42	16.57	12.21	6.54	59.29	2.63	0.09
Haram-emam	24.13	20.01	12.36	8.83	11.77	76.52	0.502	0.07

*geometric mean diameter

**geometric standart deviation of PM at 84% to PM at 50%

As shown in table 3, concentration of PM<0.49 µm (fine particle mass) makes up 50-60% of PM-10, from point of view of entering of the particles in respiratory system and their staying in the lungs are more hazardous.

Seasonal measurements

Seasonal variation of PM_{10} concentration at the 8 stations selected in this study have been presented in Figure 1.

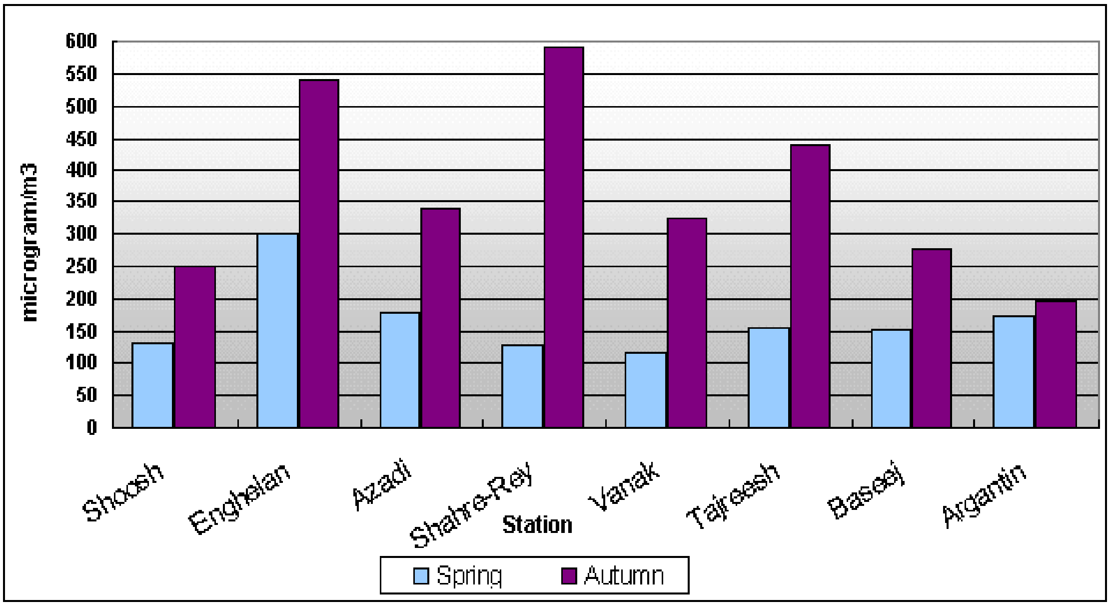

Figure 1. Seasonal concentration of PM

Diurnal variation of PM_{10} concentration at the stations Bazar, Fatemi and Aghdesieh for June month have showed in figure 2.

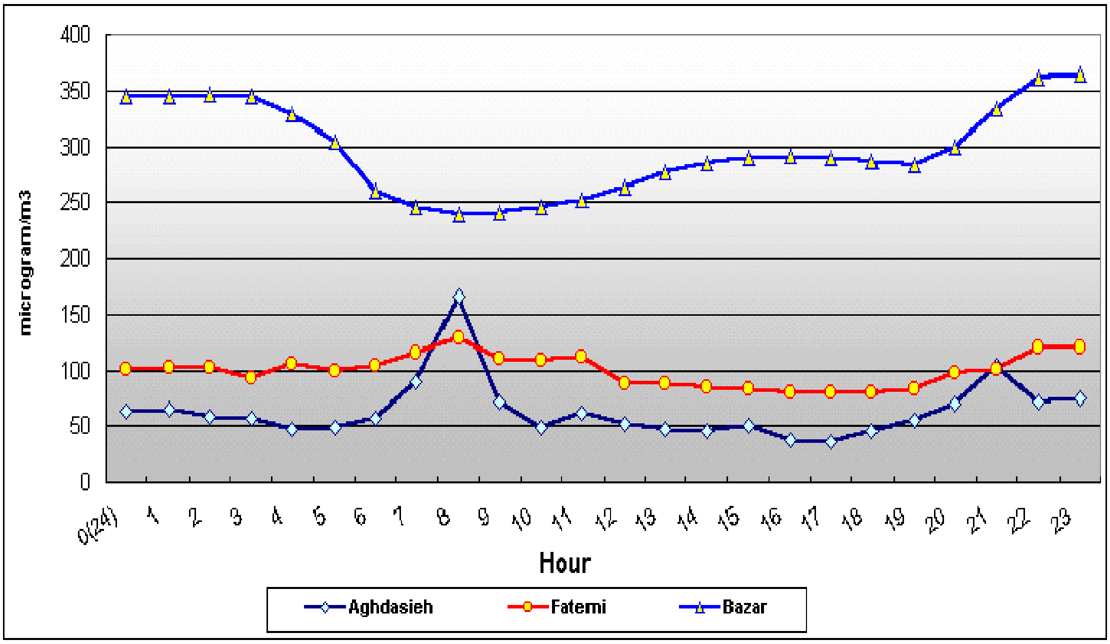

Figure 2. Concentration of PM-10 at the three sampling site (June 2004) *

* Data provided by the Air Quality Control Company (AQCC)

During the June month, the mean of PM-10 concentrations was 298.00 μg/m^3 at the Bazar site. The summer season is occasion for shopping in the Bazar in Tehran (city center).

Motor vehicles are recognized as a major source and primary direct emission of fine and ultra fine particles to the atmosphere in Tehran areas.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

MOTORCYCLES EMISSION AND THE EFFECTS ON TEHRAN AIR QUALITY

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ABSTRACT

The motorcycles in Iran are not equipped with catalytic converters. The Idle emission tests were performed at 1000 rpm (low acceleration) and 3000 rpm (high acceleration), when performance of the engines was stabilized after 5 minutes.

Analysis of the emission were performed by gas analyzer model MGT5, Maha, Germany. Detail analysis of the total hydrocarbon (THC) emission was performed on GC, Perkin - Elmer, Sigma 3B, equipped with AP-L 15%, Chrom M 80/100 column .It is observed that CO and HC emission rates for 2-stroke and 4-stroke were 2-5 times higher than of the standards. It is also noticed that CO and HC pollutants vary in different models. The average HC emission for the 2-stroke motorcycles was approximately 14000 ppm for all brands, but, except for one of the brand of the 4-stroke motorcycles, the emission of hydrocarbons was less than 1000 ppm.

Keywords: Motor emission, Urban pollution, Tehran air pollution, Toxic gases

1. INTRODUCTION

Air pollution knows no boundaries. Local activities can not only lead to local problems, but can also lead to national and international consequences lasting from hours to decades.

Atmospheric pollutants are responsible for both acute and chronic effects on human health (WHO, 2000). Air pollution is a major environmental air problem, affecting developed and developing countries in the world. Increasing amounts of potentially harmful gases and particles are being emitted into the atmosphere at a global scale, damaging the human health and the environment.

Mobile sources are one of the major sources of air pollution worldwide. In many urban areas, mobile sources collectively produce 50 to 90 percent of local air pollution, depending upon the pollutant.(Alexopoulos et al., 1993).

Mobile sources can also produce a significant amount of the toxic or hazardous pollutants found in urban air.

Cars and light trucks continue to be a major source of air pollution all over the world. Emissions from these vehicles come from the tailpipe, as well as from evaporation from fuel tanks, out of the oil reservoir and around engine seals. Refueling is also a significant source of emissions. Considerable progress has been made in reducing emissions from cars and light trucks, especially in the more developed countries. Most cars and light trucks are fueled with gasoline (Kalabokas et al., 1999).

Vehicle ownership is steadily increasing in developing countries, resulting in widespread congestion and increasing air pollution.

According to data compiled by the United Nations , some Asian countries , including Thailand ,Taiwan and republic of China are categorized as some of the most polluted countries in this continent (Sadullah et al., 2003).

However, the fuel consumption in urban centers is approximately 30% higher than in the rural regions, with driving conditions in the former usually poor compared to the latter. The main objective of the new European legislation is seeking to reduce motorcycle emissions over the next four years. By 2006,exhaust emissions from new motorcycles will be the same as for cars (Kassamenos et al., 1995).

The first objective of the new EU-legislation is reducing of 60%the Carbon monoxide (CO) and Hydrocarbons (HC) emissions of new four-stroke bikes. The second one, entering into force on 1st January 2006, will apply a further 50%reduction compared to the 2003 limits. 2-stroke engines will see their emissions output reduce by 30% for CO and 70%for HC. Motorcycles have a quite low level of oxides of nitrogen (NOx) (Tamanouchi, M. 1998) .

2. URBAN AIR QUALITY AND TRAFFIC

Motor vehicle emission has been recognized as one of the major sources of the air pollution, particularly in highly urbanized areas. The main traffic-related pollutants are carbon monoxide, nitrogen oxides, particulate matter (PM) and hydrocarbons (Noor Zaitun 2001).

Almost all present-day mobile sources get their energy from either gasoline or diesel fuel. Most nations are setting standards for both vehicles and their fuels in order to reduce air pollution (Hassan and Crowther ,1998) .

Based on 1997 study by the Japan international cooperation agency (JICA,1997), it was concluded that the air pollution problem in Iran is relatively serious when compared with accepted air quality standards. The annual and daily reading for PM-10 (figure 1) and CO have exceeded the standard.

Unfortunately follow-up studies in 2000 continued to shows serious problem, and motor vehicles were again found to be the air pollution. Studies around the world have indicated that PM is the most abundant pollutant per annum with practically 70 % of all PM produced solely by motor transport vehicles (Walsh, et al., 1997) .

Traffic density and flow condition in Tehran have become progressively worse and consequently, air pollution is getting more serious. As a result of severe traffic problems, motorcycles are coming a popular mode of transportation. The number of motorcycles has grown rapidly in Tehran over the past 3 - 5 years. A report indicates that approximately 1 million motorcycles are assembled from 75 factories in Iran each year, from which 500 of them are registered in Tehran everyday. Approximately 60 % of the motorcycles produced from these factories are 4-stroke and the rest are 2-stroke motorcycles (TTTO, 2000).

2-strock motorcycles are more commonly used than 4-stroke ones; because they are cheaper and also simple manufactured .Almost all of models were tested in this project.

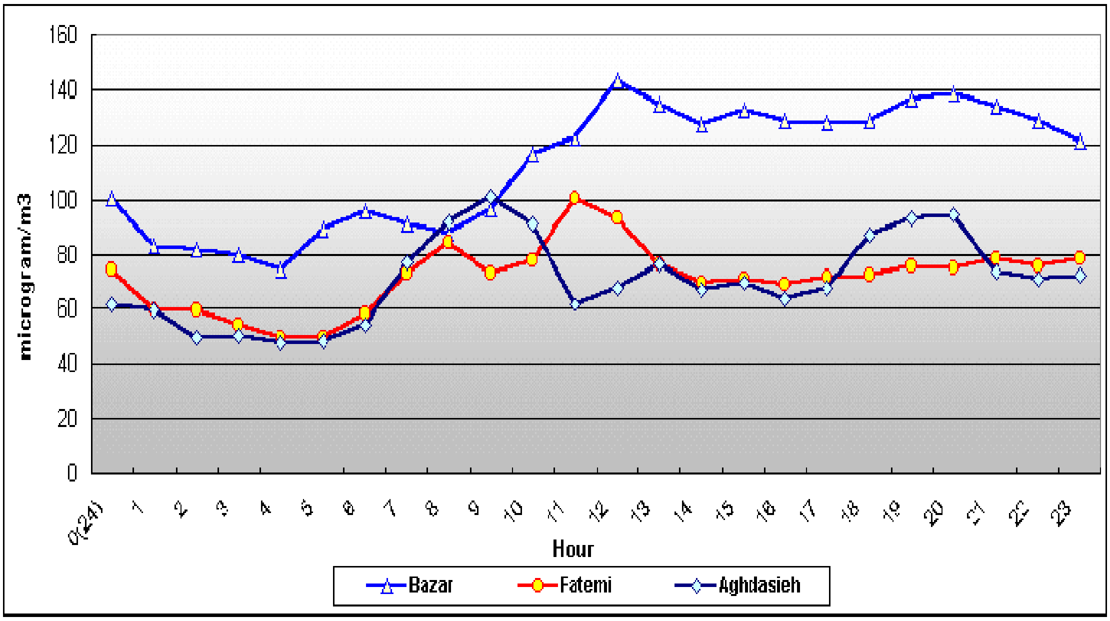

Figure 1. Hourly concentration of PM-10 in the three stations in Tehran (Jan. 2004) - cold season

3. METHODOLOGY

To assess tail-pipe emission of motorcycles in Tehran, some common brands of in-use motorcycles were selected randomly, while running in the city. The tested motorcycles were selected as representative of the Tehran motorcycle fleet in terms of manufacturer, capacity, model, year and mileage.

Analysis of the emission was performed by gas analyzer model MGT_5, Maha, Germany. Detail analysis of the total hydrocarbon (THC) emission was performed on GC , Perkin - Elmer , Sigma 3B ,equipped with AP-L 15% , Chrom M 80/100 column (NIOSH, 1997).

TABLE 1**.** Characteristics of the Test Vehicles

vehicle	year	make and model	engine size	mileage(km)
2-stroke motorcycles	1998	Yamaha 100	50cc	16000
//	1998	Yamaha 125	50cc	19500
//	2002	Vespa(Italian engine)	50cc	3400
4 -stroke motorcycles	1994	Safeer 150	125cc	2540
//	1995	Honda	125cc	20500
//	1998	Bravo	125cc	20000
//	2000	Pishro	125cc	18000
//	2000	Sahra	125cc	14500
//	2000	Kasra	125cc	8500
//	2000	Vespa	125cc	7800
//	2001	Hormoz	125cc	8000
//	2001	Yamaha	125cc	9800
//	2003	Shokooh 125	125cc	10000
//	2004	Safeer 125	125cc	4800

4. RESULTS AND DISCUSSION

Studies shows that factors such as road characteristics, traffic volume, vehicle type, driving conditions and driver behavior affect motorcycle emission levels in real traffic situations. Two-stroke motorcycles have considerably higher HC emissions and quite lower CO emissions than those of four-stroke motorcycles.

When considering gaseous pollutants it is apparent that the nature of the driving used during emissions measurement can have a significant influence on the results obtained. For the purposes of comparison this paper has considered the emission of two pollutants (CO and HC) for different motorcycles.

It is necessary to understand what is meant by environmental performance. Currently, due to the political focus on climate change, low CO2 emissions from transport are seen as a key environmental parameter. More traditionally however the effect of gaseous pollutants on air quality has been the key concern and, particularly in urban areas, this remains the case. This paper therefore considers both CO2 and gaseous pollutants.

4.1. Gaseous Pollutants

The use of two-wheeled transport in areas of high traffic density is seen by many as an effective means to reduce congestion and so speed the traffic flow. Some also argue that motorcycles offer an environmental advantage when compared to the passenger car. The gaseous pollutants for which regulation applies limit values, are carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NOx) and in the case of diesel vehicles, particulate matter (PM). The emission of these pollutants is determined by gas analyzer from the tailpipe.

First consideration of the comparative performance between the two transport categories may be a simple comparison of the regulated limit values that apply.

Whilst passenger car emissions have been regulated for many years, motorcycles only became subject to regulation in 1999.

Although there are only limited data available, it is worth considering the relative performance of motorcycles when tested over different driving cycles and with different interpretations. Figure 2-3 shows average values for CO from low and fast accelerations in two and four stroke motorcycles .

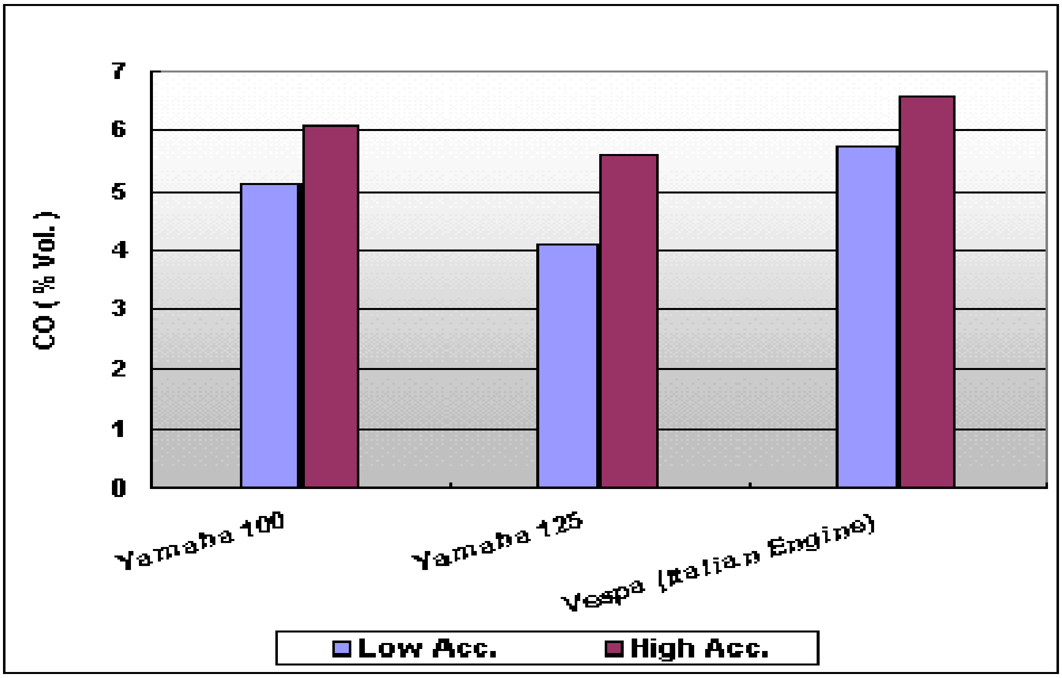

Figure 2. Average CO emission of 2-stroke Motorcycles for low and fast accelerations

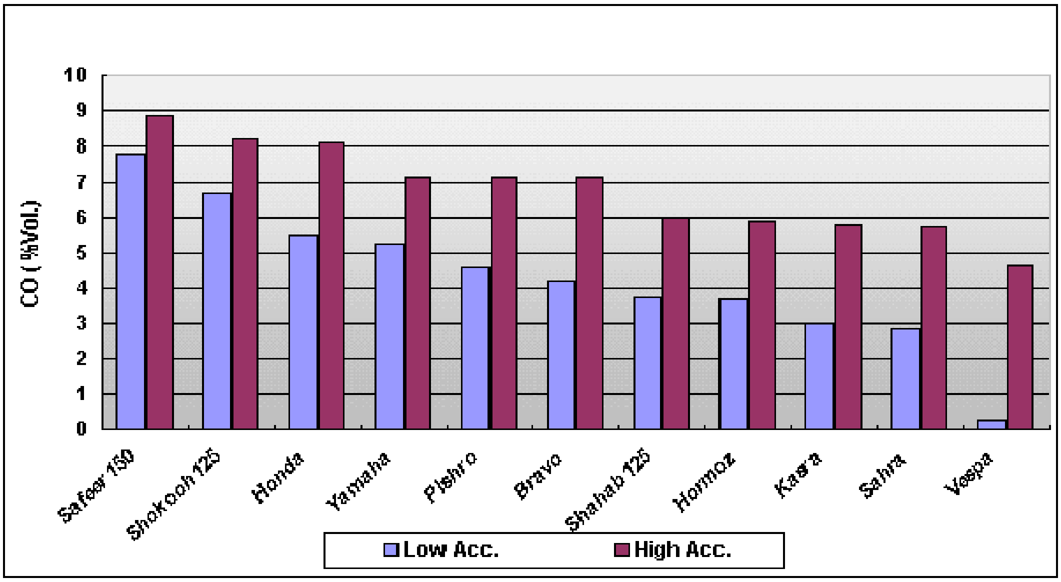

Figure 3. Average CO emission of 4-stroke Motorcycles for low and fast accelerations.

A similar comparison of HC emissions from the same vehicles is shown in Figure 4.

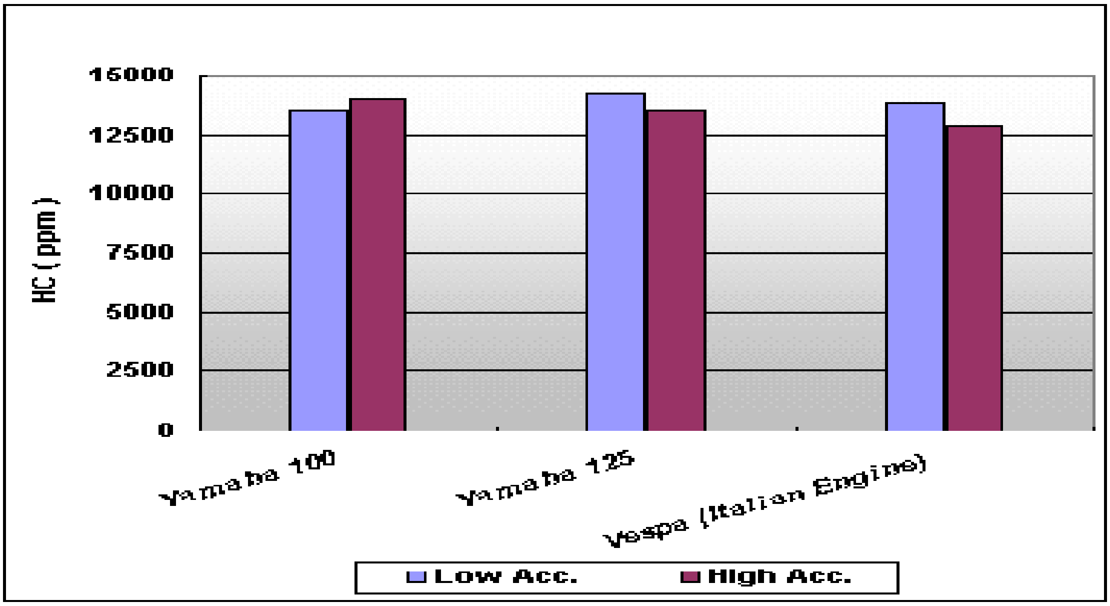

Figure 4. Average HC emission of 2-stroke Motorcycles for low and fast accelerations

This indicates that HC emissions from 2-stroke motorcycles are however worse than of 4-stroke .There is evidence from the test data that much of the HC emission is related to carburetor technology which is still reasonably common on motorcycles .

4.2. Carbon Dioxide

In 1997 the European type-approval procedures for passenger cars was amended to include the measurement of CO2. There is now therefore a considerable database from which to derive the CO2 performance of the fleet. The European Union has also entered into a Voluntary Agreement with motor manufacturers that will see the average emission of CO2 from new vehicles in 2008 reduced by 25% as compared to the emission in 1995. Motorcycle CO2 emission data is therefore limited to that measured in recent programs associated with the development of new type-approval standards.

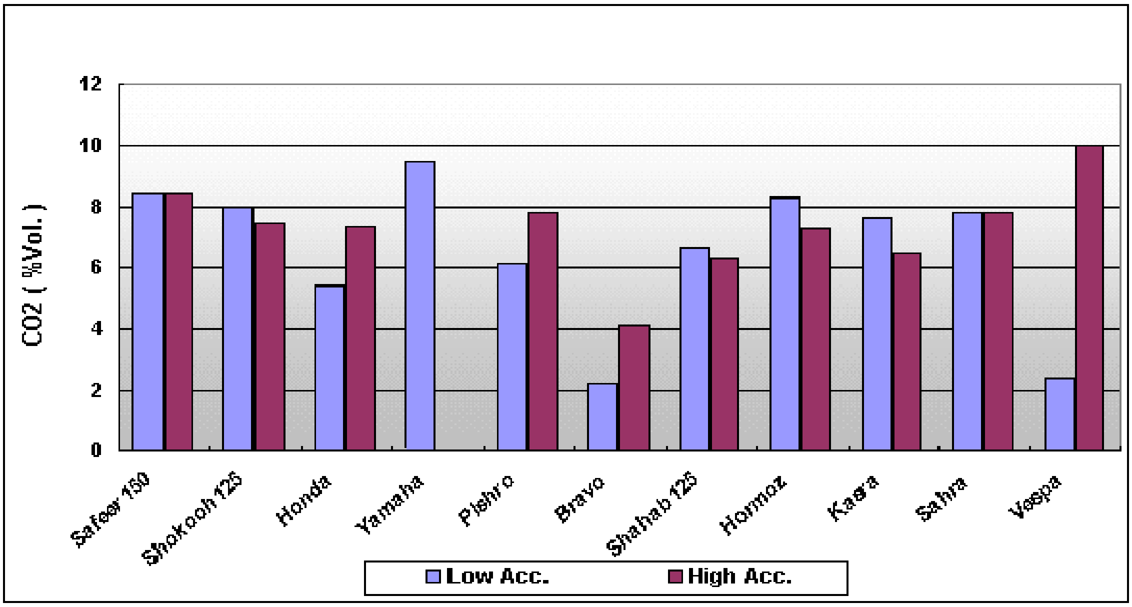

Figure 5. Average CO_2 emission of 4-stroke Motorcycles for low and fast accelerations.

In so far as climate change is a consideration, motorcycles have a clear advantage over passenger cars. The maximum emissions of CO2 from motorcycles recorded in recent tests, fall below the average values recorded from the passenger car fleet.

Average emissions of CO and HC from motorcycles are approximately one Euro standard behind that from petrol fuelled passenger cars. However, the CO performance from motorcycles is generally better than that from diesel fuelled cars that are increasing in popularity because of their fuel efficiency.

5. CONCLUSION

The results also revealed that motorcycles emission, the narrow streets with tall buildings, the meteorological factors such as weak winds and also other vehicles emission dangerously pollute the Tehran atmosphere.

Good traffic management can reduce environmental impact as well as congestion. Inspection and maintenance programs, if undertaken by technologically efficient instruments in a low-corruption context, can have great impacts, as can the replacement of two-stroke motorcycles with four-stroke motorcycles. It is generally recommended to act by providing economic incentives at various group of actors, but in critical situations it may be necessary to reach for prohibitions, e.g. the forced scrap page schemes. Tax structure reform can encourage the use of cleaner fuels and stimulate better vehicle maintenance. This reform, however, requires the design of fiscal measures to handle problems associated with the multi-purpose use of fuels (kerosene and diesel, for example, are both used in several sectors), and to handle the associated conflicting policy objectives, such as road system objectives and redistributive ones associated with the taxation of diesel fuel.

The technical requirements set for new bikes produced from 2006 can be achieved quite easily with current technologies, such as fuel injection systems and catalysers.

Future emission standards have been agreed for motorcycles and these are almost certain to cause the use of carburetors (a major cause of high HC emission) to cease. It is also expected that catalyst technology will be far more widespread in the motorcycle fleet providing further improved emission control. In addition, the complexity of the test cycle over which future motorcycle emissions will be measured should reduce the possibility for disparity between regulated and “real world” emissions.

It is expected that the legislated limits for motorcycles such as other motor vehicles legislative requirements for motorcycles from 2006 will cause this situation will change.

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THE EVALUATION OF THE EFFECT OF AIR POLLUTION ON THE CHILDREN HEALTH STATUS OF ZONGULDAK CITY, TURKEY

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ABSTRACT

Air pollution effects human health particularly some sensitive groups such as children, pregnant, elderly people, asthmatics etc. in many ways, including reduced lung function, increased morbidity, increased use of health care services, and infant mortality. The aim of this study was to assessment of health effects due to particulate matter (PM), sulfur dioxide (SO_2), pollen, and meteorological variables in children in Zonguldak city which is the main mining centre of Turkey. Daily counts of children admission for respiratory diseases to Karaelmas University Hospital were obtained for the period January-December 2002. Some statistical analyses like regression analysis, MSE values and p-values were used to assess the associations between the occurrence of respiratory symptoms and diseases (ORSD) and those parameters: PM, SO_2, pollen and meteorological variables.

Monthly average of ORSD increased significantly with increasing ambient level of PM, SO_2 and pollen. The R-squared statistic of multiple regression models indicates that the model as fitted explains 99.97 % of the variability in total report. In the second case, ORSD episode, higher values than annual mean value, were analyzed to understand the relationship between air pollution, pollen counts. The model indicates that there is a good correlation between ORSD episode and monthly average concentrations of air pollution and pollen in Zonguldak. Current study is the first study of children admissions for respiratory diseases and air pollution in Zonguldak showing that SO_2, PM, pollen and some meteorological parameters are associated with ORSD in children

Key Words: respiratory disease, children, air pollution, Zonguldak.

1 INTRODUCTION

Globally, the main load of anthropogenic air pollution is concentrated in the urban areas, in particular the metropolitan areas. Whereas in some urban areas exhaust gases from industrial process and/or domestic heating are sources of considerable air pollution, in other places it is the automobile traffic which is the main source of air pollution. Atmospheric dispersion and chemical transformation conditions as well as topographic location have an influence on air quality in urban areas (Baumbach, 1997; Karaca et al.,2004). The scientific and social interest in the effects of air pollution on people's health has notably increased in the past decade as a consequence of the growing evidence of its actual relevance to health of the population and concern about related changes in the near future (Ballester et al.,2002).

Many epidemiological studies have demonstrated the association of environmental air pollution and deterioration of respiratory health. Individuals with chronic respiratory diseases such as asthma and chronic obstructive airway disease are particularly susceptible to the adverse effects of air pollution. Experimental studies in humans have also shown that air pollutants including ozone, sulphur dioxide, inhalable particles <10 μm in aerodynamic diameter (PM10), and nitrogen oxides (NOx) all can aggravate airway pathology by including or enhancing airway inflammation (Moshammer and Neuberger, 2003; Martonen and Schroeter, 2003; Helander et al., 1997; Monn, et al., 1999). Many studies have shown that levels of air pollution are associated with reduced pulmonary function, increased respiratory symptoms and, even increased mortality (Monn, et al., 1999; Williams et al., 2000; Alberini and Krupnick, 1998; Wordley et al., 1997; Lipfert and Morris, 2002; Timonen et al., 2002; Nelson and Tony, 2000). In both adults and children, air pollution has also been founded to be associated with increased visits to emergency and admissions to hospitals due to respiratory complaints or asthma exacerbation (Boezen et al., 1999; Duhme et al., 1998; Brunekreef.and Holgate, 2002; Gomzi, 1999; Wong et al., 2001; Qian et al., 2000; Roemer et al., 2000). Zonguldak is the main mining centre of Turkey with many underground coalmines, mainly run by the government. The development of the city is largely based on mining and industry. Underground mining impacts directly on the helath of those working underground, but opencast mining create wider air quality deterioration due to dust and gaseous pollutants in and around the mining complexes (Ghose and Majee, 2001). In Zonguldak, chronic respiratory asthma, chronic bronchitis diseases are prevalent conditions. Epidemiological surveys have shown that children and young adults suffer from asthma (Tomaç et al., 2002).

To clarify the possible role of the air pollution, meteorological conditions and biologic pollen gains on respiratory health of asthmatic children, this has been performed to investigate the temporal relationship between the ambient level of the air pollutants (PM, SO_2), meteorological parameters and pollens- on hospital admission due to asthma and respiratory diseases in children living in Zonguldak.
Aims of this study are to evaluate the effect of air pollution on the health status of Zonguldak City population and to study the relation between exposure to air pollution and the occurrence of respiratory symptoms (ORSD) and diseases.

2 DATA AND METHOD

2.1 The Study Area

Zonguldak is a coastal city located in the western Black Sea region at position 41027′ N, 31046′ E (Figure 1). It has a current population of about 108.000. The city is characterized by “black diamond”, the name which signifies the importance attached to the coal produced in the area. In fact, the local economy has heavily relied on coal mining and coal industry for decades. At present, the decline in the industry has already started to impose its adverse repercussions upon the local economy (Zonguldak Local Agenda 21). The development of the city and rapid rise in the population were associated with the growth of this coal industry after the 19th century. The adverse consequence for the population and industrialization is the increase of environmental degradation, namely air quality in Zonguldak. In the Zonguldak, sulphur dioxide has been emitted into the atmosphere with no controls particularly in hard coal mining region. In addition to SO_2 emission, the hard coal mines emits particulate matter which contains hazard heavy metals, into the city’s atmosphere. Measured monthly average concentrations of SO_2 and PM ($\mu g/m^3$) are shown in Figure 2.

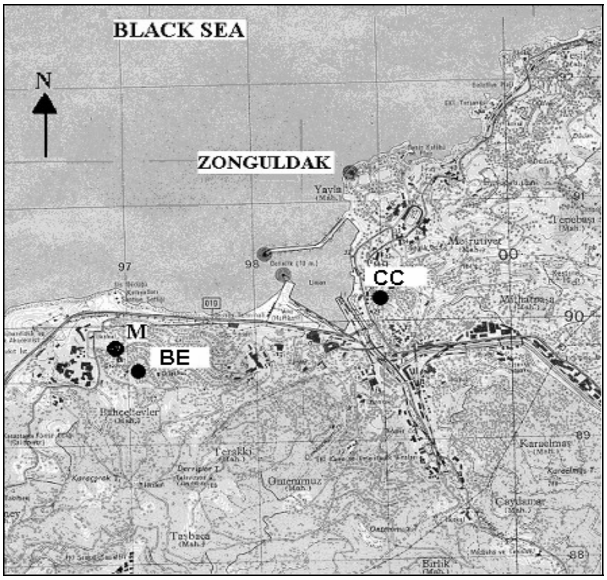

Figure 1. Map of Zonguldak City showing the locations of monitoring stations (M: Meteorological station, BE: Bahçelievler Station and CC: City Center Station)

2.2 The data

The data are provided from the two air quality measurement stations established by Ministry of Health. SO_2 and PM concentrations data for January-December 2002 season are monitored for 24 hour period at two sites. One of the stations is Bahçelievler station, surrounded by the hospital, houses and some social clubs. The other is City Centre station which was placed directly on the city’s main traffic road close to schools and other offices in Zonguldak. The input parameters for the model include the meteorological variables which were provided by the Governmental Meteorology Office. The meteorological station is also very close to Bahçelievler station with a distance of about 100 meters.

The computerized daily number of hospital admission for respiratory diseases in children was collected by researchers form Department of Pediatric Diseases, Faculty of Medicine (University of Karaelmas).

2.3 Statistical Methods

Some statistical analyses like Regression analysis, R-squared values, MSE values and p-values are used to explain the relationships between the ORSD and air pollution data. Regression analysis is a mathematical tool that quantifies the relationship between a dependent variable and one or more independent variables. It is the process of estimating the parameters for a model by optimizing the value for an objective function, and then testing the resulting predictions for statistical significance against an appropriate null hypothesis model. R-squared value is statistic that measures the proportion of the variability in Y that a model accounts for. This value ranges between 0 and 100 percent. MSE is a measure of accuracy computed by squaring the individual error for each item in the set of data, then finding the average or mean value for the sum of those squares. Mallows' Cp statistic is a measure of the bias in a model based on a comparison of total Mean Squared Error to the true error variance. Unbiased models have an expected Cp value of approximately n, where n is the number of coefficients in the fitted model. Cp is based on the assumption that the model that contains all the candidate variables is unbiased; therefore, the full model will always have Cp = n. in order to obtain best result one can look for models that have Cp values close to n. P-value is the probability of observing a value for a test statistic that is at least as inconsistent with the null hypothesis as the value of the test statistic actually observed.

3 RESULTS AND DISCUSSIONS

With the intention of explain the city's health status firstly we compared the percentages of the respiratory symptoms among all the total symptoms reported by the Turkish Health Ministry (2002). This report was prepared based on urgent symptom calls to 112, the Urgent Health Service during 2002. Turkey has 83 cites. The average value of the percentages of the ORSD values among all the total reported symptoms for Turkey is 6,16%. Zonguldak city's value is 8,1% one of the highest percentage of ORSD values among the all cites of Turkey.

Air pollution criteria pollutants, SO_2 and PM have been monitoring in two stations since 1999 in Zonguldak city. Measured monthly average concentrations of SO_2 and PM ($\mu g/m^3$) are shown in Figure 2. Yearly average concentrations of SO_2 and PM have not significant differences, 65,55$\mu g/m^3$, and 72,21$\mu g/m^3$, 70,65$\mu g/m^3$ for SO_2 and 84,35$\mu g/m^3$, 79,68$\mu g/m^3$, 73,09$\mu g/m^3$ for PM from 1999 to 2001. The Turkish Health Ministry, air pollution control regulations annual mean concentration criteria is 60$\mu g/m^3$ for SO_2 and PM and all this records are higher than 60$\mu g/m^3$. In order to understand the relationships between ORSD and this air pollution situation in Zonguldak City, some case studies were carried out.

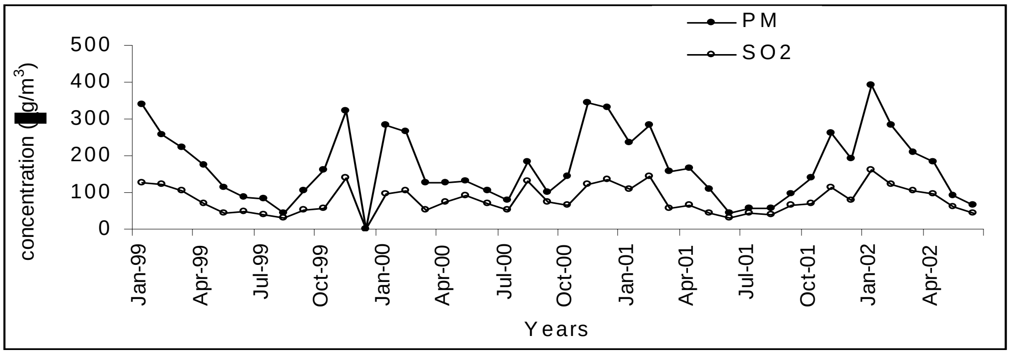

Figure 2. Monthly average concentrations of SO_2 and PM during 1999-2002

3.1 Case 1

Whole year air pollution data, ORSD data and, meteorological parameter were statistically analyzed. No significant relationships were found for the data. In this case we were analyzed monthly averages of whole year data to elucidate the relationship amongst ORSD, air pollution data, and meteorological parameters.

Firstly we used some functions to define the best curve to fit the relationships between ORSD-SO_2 and ORSD-PM. Best fittings were achieved with cubic functions of both pollutants (Figure 3 and Figure 4).

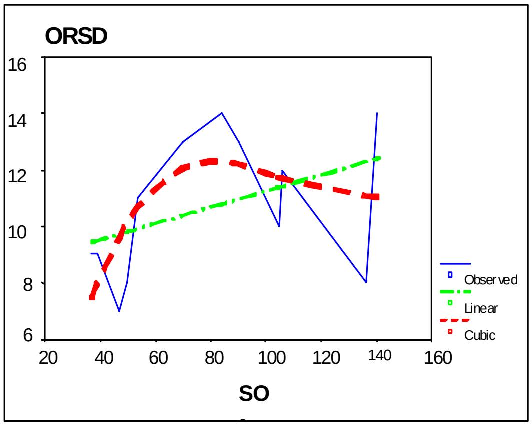

Figure 3. Curve fitting for ORSD-SO_2. ORSD: Monthly average, Person; SO_2: µg/m^3

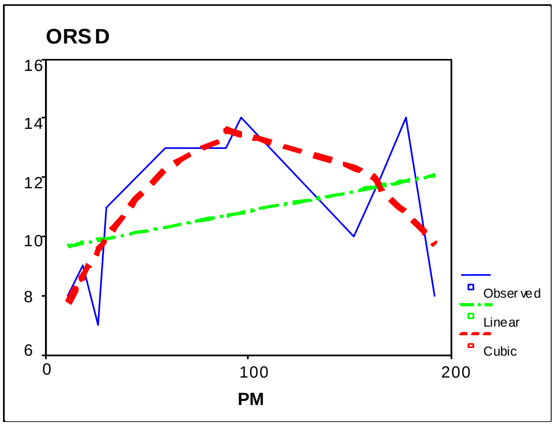

Figure 4. Curve fitting for ORSD-PM. ORSD: Monthly average, Person; PM: µg/m^3

We were used multiple regression models to describe the relationship between ORSD and 10 predictor variables. These are 1/(SO_2^3), 1/(PM^3), pressure, cloudiness, solar intensity, solar radiation, humidity, temperature, precipitation, and pollen. Models have been fit containing all combinations of from 0 to 10 variables. To determine which models are best we compared the mean squared error (MSE), the adjusted and unadjusted R-Squared values, a-nd Mallows' Cp statistic. The adjusted R-Squared statistic measures the proportion of the variability in total report which is explained by the model. Larger values of adjusted R-Squared correspond to smaller values of the mean squared error (MSE). Finally, it was decided that the best model has 9 variables; cubicSO_2, cubicPM, pressure, cloudiness, solar radiation, humidity, temperature, and precipitation. The R-Squared statistic indicates that the model as fitted explains 99,97 % of the variability in total report.

The standard error of the estimate shows the standard deviation of the residuals to be 0,132. This value can be used to construct prediction limits. Since the P-value is greater or equal to 0.10, that term is not statistically significant at the 90% or higher confidence level. All these nine parameters are significant at the 90% confidence level. Obtained statistics for best regression model are summarized in Table 1.

Table 1. Obtained statistics for best regression model

Parameter	Estimate	Standard Error	T- Statistic	P-Value
CONSTANT	1394	121,9	11,4	0,05
x_1= cubicSO_2	412942	47560,9	8,6	0,07
X_2= cubicPM	6460	464,2	13,9	0,04
X_3= pressure	-1,34	0,117	-11,3	0,05
X_4= cloudiness	2,94	0,492	5,9	0,09
X_6= Solar radiation	2,13	0,132	16,0	0,03
X_7= humidity	-0,84	0,026	-31,6	0,02
X_8= temperature	-1,73	0,133	-12,9	0,04
X_9= precipitation	1,44	0,079	18,1	0,03
X_{10}= pollen	0,005	0,000	8,7	0,07

The equation of the fitted model is

$$Y_{\text{Monthly ORSD}} = 1394 + 412942 * x_1 + 6460 * x_2 - 1{,}34 * x_3 + 2{,}94 * x_4$$
$$+ 2{,}13 * x_6 - 0{,}84 * x_7 - 1{,}73 * x_8 + 1{,}44 * x_9 + 0{,}005 * x_{10}$$

3.2 Case 2

In the second case, in order to understand the relationship between air pollution data, pollen counts and ORSD episodes, we analyzed the data according to higher values than annual mean value (episodes) of ORSD.

Of one year PM data 52 days records are over than 24 hour average standards of 150µg/m^3. Annual mean of ORSD is 9 person/day/hospital. 91 episodes of ORSD values were recorded during the period of January 2002 - December 2002 in Zonguldak (Table 2).

Table 2. ORSD episode occurrence numbers and corresponding monthly average concentration s of SO_2 and PM

Month	ORSD episode occurrence	SO_2 average concentration $\mu g/m^3$	PM average concentration $\mu g/m^3$	Pollen count
January	10	136	192	129
February	9	106	165	448
March	9	90	89	62
April	10	84	96	191
May	7	54	30	290
June	5	37	18	18
July	3	50	11	6
August	6	47	26	16
September	3	39	18	8
October	7	70	59	15
November	10	105	152	7
December	12	140	178	5
Total	91			
Average		73,69	79,54	91,92

The Table 3 shows the results of fitting various multiple regression models to describe the relationship between ORSD episode occurrence and 3 predictor variables. Models have been fit containing all combinations of from 0 to 3 variables. The statistics include MSE, the adjusted and unadjusted R-Squared values, and Mallows' Cp statistic. First four model's MSE values are very close to each other, but 4th model's Cp value is the closest one to number of included variables, n=3. 8th model results have optimum R-squared, adjusted R-squared and Cp values. Based on these statistics we selected 8th model as the best model.

Table 3. Model Results of the Selection of Best Regression Model

Number	**MSE**	**R-Squared**	**Adjusted R-Squared**	**Cp**	**Included Variables n=3**
1	8,44697	0	0	30,0716	No Variables
2	1,93197	79,2075	77,1283	0,331886	SO_2
3	2,1793	76,5457	74,2002	1,39854	PM
4	8,44697	9,09091	0	29,1985	Pollen
5	2,13454	79,3247	74,7301	2,28495	SO_2, PM
6	2,0617	80,0302	75,5925	2,00223	SO_2, Pollen
7	2,42041	76,5557	71,3458	3,39453	PM, Pollen
8	2,31876	80,0357	72,5492	4	SO_2, PM, Pollen

The best equation of the fitted model is

$$y_{\text{ORCD episode occurrence}} = 1{,}716 + 0{,}0727x_1 + 0{,}016x_2 + 0{,}002x_{10}$$

ANOVA analysis was performed to check this statistical relationship and P-value was found 0,00002. Since the P-value in the ANOVA analysis is less than 0.01, there is a statistically significant relationship between the variables at the 99% confidence level.

The R-Squared statistic indicates that the model as fitted explains 72,54% of the variability in ORSD episode occurrence. According to this second case study, it is suggested that there is a good correlation between ORSD episodes and monthly average concentrations of air pollution in Zonguldak city (cf. Figure 5).

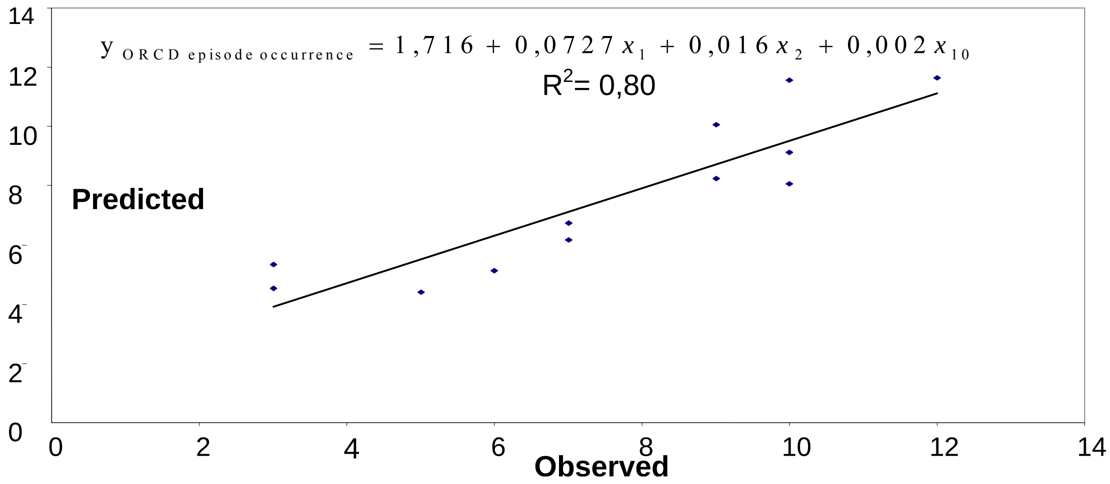

Figure 5. Occurrence of Respiratory Symptoms and Diseases (ORSD), X_1= Observed SO_2, X_2= Observed PM, and X_{10}= Pollen counts.

4 CONCLUSION

Most published studies of health effects of air pollution on respiratory morbidity have been performed in different parts of the word. Turkey has 83 cites. The average value of the percentages of the ORSD values among all the total reported symptoms for Turkey is 6,16%. This value for Zonguldak is 8,1% one of the highest percentage of ORSD values among the all cites of Turkey (Republic of Turkey, Prime Ministry State Institute of Statistics (SIS)). In Zonguldak, chronic respiratory asthma, chronic bronchitis diseases are prevalent conditions. One recent study has been carried out in Zonguldak by Tomaç et al. (2002) related with asthma prevalence, other respiratory symptoms and diseases on children which are 6-17 years old based on questioner method. According to the results of this study the cumulative asthma prevalence, during last year asthma prevalence, wheezing prevalence, bronchitis prevalence were %14.5, %2.1, %27.1 %57, %29.3, respectively. The Turkish Health Ministry, air pollution control regulations, annual mean concentration criteria is 60µg/m^3 for SO_2 and PM and Zonguldak city's air pollution records are higher than 60µg/m^3 during 1999 to 2002.

This study is the first to investigate the relationship between hospital admissions of children due to respiratory symptoms and diseases and air pollutants. Herein, the effect of air pollution on the health status of Zonguldak city population was evaluated and the relation between exposure to air pollution (PM and SO_2) and the occurrence of respiratory symptoms and diseases (ORSD) statistically analyzed. With the purpose of identify with the relationships between ORSD and this air pollution situation in Zonguldak some case studies were carried out.

Statistically in 90% confidence level, no relationships were found among whole year data, so it was necessary to make some detailed analyses. Firstly, monthly averages of whole year data were analyzed to explain the relationship. A regression model was developed by means of parameters; SO_2, PM, pressure, cloudiness, solar radiation, humidity, temperature, precipitation, pollen and Monthly ORSD. There was a positive and significant association between ORSD and two pollutants. In addition, pollen counts were found to be significant associations. The model explains 99,97 % of the variability in total report.

In the second case we analyzed the data according to higher values than annual mean value (episodes) of ORSD and corresponding air pollution data. Annual mean of ORSD is 9 person/day/hospital. 91 episodes of ORSD values were recorded during the period of January 2002-December 2002 in Zonguldak. Another regression model was developed with the parameters; SO_2, PM, Pollen and ORSD episodes. According to this second case study, it is suggested that there is a good correlation between ORSD episodes and monthly average concentrations of air pollution in Zonguldak city. The model explains 72,54% of the variability in ORSD episode occurrence.

Several studies have confirmed the significant associations of the level of air pollutants and visits to emergency department or hospital admissions due to respiratory symptoms (Sunyer et al., 1997; Atkinson et al., 1999; Hajat et al., 2001; Anderson et al., 1998). Given that the majority of studies have demonstrated a positive association, ambient air pollutants probably have a contributory role to respiratory morbidity. In conclusion, current study is the first study of children admissions for respiratory diseases and air pollution in Zonguldak showing that SO_2, PM, pollen and some meteorological parameters are associated with ORSD in children. The results of this study support that the current level of air pollution contributes to respiratory morbidity in children in Zonguldak.

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THE COMPREHENSIVE PROGRAM FOR AIR POLLUTION REDUCTION IN TEHRAN (TRANSPORTATION SECTION)

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ABSTRACT

One of the key elements effecting air pollution today is the increase in the number of motor vehicles. Consequently, the resulting problems arising from new forms of large scale air pollution need to be emphasized. Various measures have been taken to cope with it, but no advanced industrial nation has found a solution to the puzzle of air pollution.

At present, air pollution is one of the most vital environmental issues challenging Tehran. As a result, **The comprehensive program for air pollution reduction in Tehran(transportation section)** was started because of critical situation of Tehran's air pollution at the first half of the 2000's in order to accurately identify the actual magnitude of the problem and present a series of appropriate action plans on specified periods.

Key Words: Comprehensive plan, Emission control, Air pollution reduction, Transportation.

1. INTRODUCTION

One of the key elements effecting air pollution today is the increase in the number of motor vehicles. Consequently, the resulting problems arising from new forms of large scale air pollution need to be emphasized. Thus, the exhaust from these vehicles has brought in its wake distinct, never-before-seen varieties of air pollution. Motor vehicles rapidly increased following the high economic growth period of the 1960s. The growth encompasses both gasoline and diesel vehicles. Various measures have been taken to cope with it, but no advanced industrial nation has found a solution to the puzzle of air pollution. As far as exhaust emissions from motor vehicles is concerned, the influence of lead compounds contained is gasoline, and the carbon monoxide in exhaust emissions, has become ever more hazardous with the increase in the number of motor vehicles. It was following this development that the regime for comprehensive regulation of exhaust emissions from motor vehicles was initiated as a measure to control air pollutants. At present, air pollution is one of the most vital environmental issues challenging Tehran. This has been the case over the last few decades. As a result, integrative studies were undertaken because of critical situation of Tehran's air pollution at the first half of the 1990's in order to accurately identify the actual magnitude of the problem and present a series of appropriate action plans on specified periods.

The main body of these studies has been implemented with the cooperation and support of national and international experts and financial sources that include:

A) The plan for reducing transportation related air pollution in Tehran (The responsible organizations are the Municipality of Tehran and the World Bank (Swedish Consultants)).

B) The Integrative plan for reducing the air pollution of Greater Tehran (The responsible organizations are the Municipality of Tehran and JAICA, Japan)

C) The plan for exhaust emission control from motor vehicles in Tehran (The responsible organizations are the Ministry of Industry and the Academy of Science of the Islamic Republic of Iran)

The Executive Committee of air pollution reduction of Tehran is located in the Department of the Environment (DoE) and has studied on final results and above plans. The necessary action and executive plans must be extracted from the above studies .This committee and its expert members shoulder the grave responsibility for integrating of the final results of this scheme. The above committee has presented executive plans covering seven subjects (New Vehicles, Old Vehicles, Public Transportation, Fuel, Maintenance and Inspection Center for vehicles, Traffic Management and Training) that are approved from the Council of Ministers to be executing from 2000. The Executive Committee of Air Pollution Reduction is convened according to executive directive, Note 82, the act of second five – year plan and concluded the members; High Council of Environmental Protection, Ministry of Industry and Organization of Development and Renovation of Industries, Ministry of Oil, Ministry of Interior, a Province, Ministry Post, Telegraph and Telephone, Municipality of Tehran (Air Quality Control Company, Inspection and Maintenance Center and Exclusive Bus Company), Ministry of Health, Treatment and Medical Training, Disciplinary Force of Islamic Republic of Iran, Islamic Republic of Iran Broadcasting and Department of Environment .

The First Plan Proposition - New Vehicles

One of the most important parameters for designing, manufacturing and selecting vehicles in developed countries is fuel consumption and pollutant level emissions. The electronically controlled fuel injection system is the most widely used technology by manufacturers of petrol/gasoline vehicles worldwide. The balance maintained in the operation, outlet and inlet chambers, the increased number of valves for the continuous augmentation of volumetric efficiency of the engine, has well-proven its relative efficacy for the auto industry. High quality spare parts, material used, dimensions and design are other effective measures bearing on actual engine operation.

Executive Plans:

- Light-duty vehicles

ECE-15.04: Regulation ECE 15-04 was applied to both gasoline and diesel-fueled light-duty vehicles, whereas earlier regulations applied only to gasoline-fueled vehicles. This standard within Cabinet Approval No. 017812/T/79394 dated: May 19th, 1999 (29/2/1378), in execution of Articles 8 and 11 of the Air Pollution Prevention Law approved on April 23rd, 1995 (1374/2/3) by the Islamic Republic of Iran Consultative Assembly, is applied for exhaust gas emission standards for imported and new gasoline-fuel cars and vans. The whole national production vehicles complied with the standard limits.

ECER-83: The ECE did not adopt emission standards requiring three-way catalytic converters until 1988 (ECE regulation 83), and then only for vehicles with engine displacement of 2.0 liters or more. Less stringent standards were specified for smaller vehicles, in order to encourage the use of lean-burn engines. We also required that new standards to implement further reductions in exhaust emissions. Therefore, new vehicles needs to updated limit values for emissions of gaseous pollutants and due to actual emissions limitations in ECE 15.04, did finally upgrade the emission limits. ECE 83 has also approved by Cabinet Approval on February 13th, 1999 (1378/11/24).

In fact, implementations of standard for imported and domestic light vehicles which are equipped to the electronically controlled fuel injection system, new technology and catalysts. Most of the national production vehicles complied with the standard limits.

- Motorcycles (ECE 40.01)

Although the ECE has issued emission standards for motorcycles (ECE regulation 40.01) and now being approved in the Cabinet with approval No. H27433/T/35993 dated: November 3rd, 2002 (12/8/1381). In execution of the Note of Article 6 of the Air Pollution Prevention Law approved on June 26th, 2002 (5/4/1381), it's sufficiently strict to stop producing and transporting of two-stroke engines from 2004 till now and also around 8000 old two-stroke engines replaced with four-stroke engines.

- Heavy-duty engines (Euro 1)

European regulation of heavy-duty vehicle engines has lagged behind U.S. standards for the same reasons as that for light-duty engines. ECE regulation 49.01, for gaseous emissions and ECE regulation 24.03 for black smoke emissions, in effect until July 1992, was comparable in stringency to U.S. regulations from the 1970s, and could be met with little or no effort by diesel-engine manufacturers. The Clean Lorry Directive (91/542/EEC), compulsory throughout the EU, reduces particulate and gaseous emissions for heavy-duty vehicles in two stages. The first-stage standards (Euro 1), which took effect in July 1992, are comparable in stringency to 1988 U.S. standards, while the second-stage standards (Euro 2) are comparable to 1991 U.S. levels. An even more stringent third-stage standard is under discussion, as is a change from the current steady state emissions testing procedure to a transient cycle similar to the one used in the United States. Euro 1 has issued emission standards for heavy-duty engines and approved in the Cabinet with approval No. H20711/T/75660 dated: October 4th, 1999 (12/7/1378). Most of the national production vehicles complied with the standard limits from 2005. On the basis of this standard, it's sufficiently strict to stop numbering the plates of heavy-duty minibuses in Tehran from 2001 and for polluted cities from 2004 as well as heavy-duty buses in Tehran from 2002 and for polluted cities from 2004.

Although, an even more stringent action is implemented for reducing emissions through stop transporting of heavy-duty minibuses in Tehran from 2004 and for polluted cities from 2006 as well as heavy-duty buses in Tehran from 2004 and for polluted cities from 2007.

Effective Plan on Air Cleanliness :

- Increase of total output of engine, reduction of fuel consumption and amount of pollutants like as Co, Hc , Nox , Particles etc. are the most important environmental and economical factors for manufacturing companies,
- Potential environmental benefits influences reduction of undesirable effects on human health ,
- The economic impact of reducing fuel consumption and new vehicles by at least 40% and 80%, respectively, would allow the export of standardized domestic vehicle

Responsible Organizations:

Ministry of Industry and Department of the Environment

The Second Plan Proposition - Old Vehicles

The last scientific research indicates that 71.2 % of Tehran’s air pollution is caused by its vehicle fleet. One of the most important causes for this is related to average age of the vehicle and the level of engine efficiency depreciation in traffic. The average age of vehicles and buses, respectively, was 15.5 and 12.5 years old in 1997. The majority of vehicles operating in the transportation system, whether light or heavy vehicles, were manufactured well before the latest standards of energy consumption and exhaust emissions became primary considerations in vehicle design and production worldwide. In this case, the necessity of compile and implement numerous plans must be widespread regarding old cars (gasoline) and the range of applications is expanding for each type of vehicles .

Executive Plans:

- Use of catalytic conversions

Triple catalytic conversions are used for 25000 public vehicles (less than 10 years old) of private business sections based on paragraph "a" of note 12 for National Budget Act within approval No. 26303/T/3902 dated: April 23rd, 2002 (3/2/1381).

- Repair and maintenance of vehicles

Over than 11 contracts based on paragraph "a" of note 27 for National Budget Act within approval No. 24895/T/20760 in 2001 (1380) and also paragraph "a" of note 12 for National Budget Act within approval No. 26303/T/3902 dated: April 23rd, 2002 (3/2/1381) are being concluded.

- Phase-out plan for old vehicles

It's prepared the plan through DoE and presented to the Cabinet. At last, approved as by-law with Cabinet Approval No. H22175/T/2508 dated: April 13th, 2003 (24/1/1382) in 7 articles. At the first step, we've established of Working Group based on 7th article of by-law to accelerate and supervise the execution procedures. The decrees and implementations of the WG are being:

- Executive directive on Article No.2 of by-law (Definition of old vehicles)
- Executive directive on Article No.4 of by-law (Preferred discount in commercial profits for vehicles importing in lieu old vehicles phase-out as an encouragement mechanism)
- Executive directive on Article No.7 of by-law (To be sufficiently strict to stop and limit using of old vehicles)

- Decree on determining the ages of old vehicles within approval No. H30830/T/25280 based on National Budget Act dated: September 26th, 2004 (4/7/1382)
- Making decision on how to phase-out the old vehicles regarding to Cabinet Approval No. H30589/T/47843 dated: November 17th, 2004 (26/8/1383)
- Legal prohibition for getting annual label of Inspection and Maintenance throughout the last 5 years for the old age of vehicles
- Coordination with vehicle manufacturers in order to public awareness clearly on old vehicle phase-out and presenting the progressing report
- Legal announcement of facilities for qualified vehicles
- Contemplation of the related proposals through private and public sections

Effective Plan on Air Cleanliness:

Emissions reduction of any kinds of pollutants that may cause to reduce 22.5% carbon monoxide(CO) emissions, 20% incomplete combustion of hydrocarbons and NOx (HC+NOx) emissions. Hence, according to the scheme daily petroleum per usage will be reduced by one million liters in Tehran, representing 20% of the total energy consumed by the transportation sector.

Responsible Organizations:

Municipality of Tehran and Ministry of Industry

The Third Plan Proposition-Public Transportation

Tehran is one of the most polluted cities in the world. Globally, for more than 40 years now, experiments in the use of alternative fuels has been most widespread in the public transportation, taxi and bus, sector. Investigations have been shown that taxis and other public transport sectors are the greatest source Tehran's air pollution. A the same time, the use and applications of alternative fuels are growing .The vehicles that consume one type of alternative fuel as well as vehicles that can use a flexible mix of fuels have also been developed and are currently in use. Many modes of vehicular transportation can realize greater efficiency, cost and environmental benefits by supplementing their current fuel with an alternative fuel or by completely switching to an alternative fuel . This switching is implemented in section of public transportation fleet based on Cabinet Approval No. 20711/T/75660 dated: October 4th, 1999 (12/7/1378), and Paragraph 2 of 19th Approved by Environmental Protection Supreme Council - Iran on October 1, 2000 (9/9/1379)

Executive Plans:

- Increasing number, up to 1700, of CNG buses in urban transportation fleet: It's not succeeded completely, because assessed value of bus tickets pro rata real value to be in low rate.
- Improvement of public transportation through railroad transportation systems: It's running the light rail/metro lines, 1 and 2, and increasing other ones especially line 4.

Effective plans on Air cleanliness:

- The efficient use of the reserves of gas and economization of the use of other fuels
- Remarkable reduction of air pollution in Tehran
- Reduction of exhaust emissions especially in taxis
- To accelerate city transportation time to help realize economic benefits

Responsible Organizations:

- Municipality of Tehran (Exclusive Bus Company), Municipality of Tehran, and Ministry of Industry, Ministry of Interior

The Fourth Plan Proposition-Fuel

Fossil fuel consumption includes the different kinds of fuels like as petrol ,diesel, kerosene, mazote, liquid petroleum gas and compressed natural gas .The following measures play a major role in controlling and reducing Tehran's air pollution:

Executive Plans:

1-Quality improvement of current fuels

a- Unleaded gasoline

The lead content of gasoline has been eliminated, whereas the whole fleet of vehicles uses normal petrol from 19th Jan. 2001. This achievement was the result of a collaborative program involving key stakeholders like as Department of the Environment, Ministry of Oil and automobile manufacturers. Unleaded gasoline is being as a successful strategy to reduce vehicular emissions that is obvious to be yielded health benefits to the population in Iran. Unleaded gasoline causes to improve the emission standard level.

b- Super gasoline

Super gasoline is obtained from commingle of imported gasoline, intermediate gasoline, MTBE (Methyl tertiary butyl ether) and green color. It's distributed due to its cost equally to normal gasoline at populated and big cities.

c- Licensed additives

In the long and mid term periods, the lead content of gasoline must be removed completely and the idling of motors compensated by additives like as MTBE and preferably ETBE. MTBE is produced in Petrochemical Refinery of Bandar Imam

d- Reducing Sulfur Content in Diesel and its standardized

The sulfur in diesel fuel is a significant contributor of emissions of sulfur oxides. These oxides consist of about 90% sulfur dioxide (SO_2) and up to 10% particulate sulfates (SO_4). The SO_2 is converted to particle sulfate in the atmosphere, which further worsens PM problems. Under favorable conditions, this conversion can involve a majority of the SO_2. Diesel fuel must be improved from two points of view. The first is to reduce sulfur (from 7,700 PPM to less than 500 PPM) sulfate and particles gases and increase the age of engine life while providing particle filters and catalytic converters. It's been implemented from 2000.

e- Natural Gas Standard

One of the most important factors for CNG plan and quality improvement of fuels is being to have this standard for buses and minibuses.

f- Gas station sites

It's established 107 gas stations for CNG vehicles and will do consider being activated 72 gas stations, be activating 35 gas stations. Also, there are 45 gas stations to be under construction and other 15 gas stations at the initiated phase for utilization.

2- Use of Alternative fuels

- Compressed Natural Gas (CNG)

Typically, natural gas has a high octane rating, and should be used at a high compression ratio in a spark – ignition engine to offset the replacement of air resulting from the gaseous state of this fuel. The use of natural gas in diesel engines requires modifications for proper combustion. The gas must be lacking in water, oil and sulfur compounds that prevents freezing, obstruction and corrosion in cylinders and connector components. The thermal energy of natural gas must be sufficient to maintain and reduce, respectively, engine power and pollutants emission .

In fact, the following measures are performed:

- Producing new CNG buses around 1500
- Use of 200 CNG buses in fleet of Exclusive Bus Company
- Use of 1500 CNG minibuses for urban transportation fleet
- Planning for use of 15000 CNG Taxis in urban transportation fleet

Effective plan on Air Cleanliness:

The use and applications of alternative fuels and vehicle modification, if fuel modification is in conformity with vehicle quality promotion and use of alternative fuels, the Third Five – Year Plan for Socio-Economic and Cultural Development on Pollutant Reduction shall be successfully achieved in Islamic Republic of Iran. According to the plans of the Ministry of Oil in order to promote the quality and production of petrol (80 % of normal petrol with octane rating 92 and 20% of non-leaded gasoline with octane rating 95) there is a need to construct the Ket Craker, isomeration and bensat units in our domestic refineries.

Responsible Organizations:

Ministry of Oil and Department of Environment (DoE)

The Fifth Plan Proposition-Inspection and Maintenance Center for vehicles

Inspection and maintenance centers for vehicles have been in existence for some 50 years in developed countries. The primary objectives of the above plan include improving vehicle safety, traffic congestion and air pollution diminution. Supervision of vehicle safety and quality, accident reduction ,development establishment, regulation and preparation related to vehicle manufacturers quality and allowable vehicle emission will be achieved through standard, public training. Fuel consumption will also be optimized .All of the above plans can be realized by instituting precise and regular inspection and maintenance centers .

Executive Plans:

-Plan for the establishment of mechanized inspection and maintenance centers for vehicles: At present, it's established 6 mechanized inspection and maintenance centers and another one will be establishing. The capacity of the mentioned centers estimated 5000 vehicles per day.

Effective Plan on Air Cleanliness:

If we succeed in fully executing the inspection and maintenance plan for motor vehicles in Tehran, one result would be economization of fuel consumption by 15% of total fuel charge and a reduction of exhaust emission pollutants (CO, HC) by 50 %.

Responsible Organizations:

Department of the Environment, Municipality of Tehran, and Department of Traffic

In order to understand the impact of the random checking for plan of vehicles, the trilateral committee consisting of Department of the Environment, Municipality of Tehran and Department of Traffic has devised a scheme. The guidelines and responsibility distribution among the committee members have been prepared, circulated to other official bodies and made known to the public at large.

The Sixth Plan Proposition-Traffic Management

Traffic regulation including allowing certain types of vehicles in particular zones, restrictions on timing for vehicular traffic, particularly heavy vehicles is effective not only with respect to increasing the efficiency of the traffic signaling system, but also in reduction of pollutants arising from traffic .Modern techniques of traffic control depend on systems of sensitive electronic technologies that collect and process real-time motion data. At last, it allows the easing of traffic congestion. Many factors are effective in reducing pollutants of all varieties (gases and exhaust emission) including: traffic plan areas, traffic systems and regulatory rules inclusive of traffic signs, traffic lights and controls for stopping on the streets, time of day or night, location and age limitations for vehicles, their number and type.

Executive Plans:

Two main factors should been concentrated on as the most important determinants as follows:

-Parking Policies: One of the major deficiencies is being that we have not clear Parking Facility Policy. At present, it is installed 2500 Parco meter and because of not allocation of funds, it's postponed our plans for installation.

- Intelligent Traffic Light: It's installed only 350 Intelligent Traffic Light and because of not allocation of funds, it's postponed our plans for installation.

Effective Plan on Air Cleanliness:

Parking is defined as using the streets for temporary stoppage of vehicles during the day or night. The streets must be free and unimpeded for vehicle operators. Provision of parking services generates income whether in the form of parking meters and / or monthly subscription payments in streets with high residential congestion or parking garages/lots. These facilities help to reduce the time and distances vehicles spend in traffic, cut fuel consumption and emitted pollutants.

In consequence in plan’s execution, through the use of “ Intelligent Traffic Lights “, we can provide the possibility of unimpeded traffic flows through the“ Green Waves“ created by continuity of green traffic lights .

The rate of vehicular stopping and restarting in traffic reduces wear and thus maintenance costs on vehicles. Implementation of the plan anticipates that the installation of any intelligent traffic signal will result in a fuel consumption reduction per day about 5000 liters and the resultant emissions of any type of pollutants.

Responsible Organizations:

Municipality of Tehran and Department of the Environment

The Seventh Plan proposition-Training

Public awareness and training will be one of the most important factors in successful reduction of Tehran’s air pollution. The primary topics of training plans are as follows:

-Training programs at the undergraduate on technical, occupational and applied scientific aspects necessary for the inspection and maintenance of vehicles dedicated centers,

-Training programs at the undergraduate levels of applied scientific for repair shops

-Training programs for traffic officers focusing on monitoring plans of air pollution

-Training programs on the correct manner of driving and general utilization of vehicles and their cumulative effect on air pollution reduction

-Training programs on the correct manner of fueling a vehicle and its cumulative effect on air pollution reduction and fuel waste

-Training programs on proper patterns of fuel consumption and promotion of public awareness on the positive impact proper fuel consumption and the negative consequences of air pollution

-Training and consciousness raising plans for women, men and decision makers in positions of public responsibility

The inspection and maintenance center for vehicles have to be technically proficient and staffed by experts who can accurately assess exhaust emission, if we have highly skilled repairmen in Tehran's repair centers. They can influence on vehicles operation, especially with respect to spare parts with high exhaust emissions rates. The correct manner of driving and fueling are as the most essential aspects of vehicle operation and that must be taught by public training courses dedicated to reducing air pollutants. In such cases, the experiences of other countries highlight the importance of this issue. It's reported that the efficient training programs is responsible for a 20% reduction in air pollutants. The public training and public education activities must be concerned with strengthening, and also alleviating or removing respectively, desirable traffic ethics and undesirable practices. It is necessary to provide efficiently and effectively spending funding in order to make optimal use of media facilities such as the Islamic Republic of Iran Broadcasting, new services ,newspapers, textbooks, posters and other information outlets.

According to the executive directive on prevention of air pollution, traffic officers are the essential component in implementing plans for reduction in traffic jams and the resulting emission of vehicular pollutants that are the major source of smog in the atmosphere. Therefore, traffic officers must be versed in and able to pinpoint, motor vehicles exceeding standard polluting emission levels. They should be able to recognize the tell-tale signs of polluting vehicles and understand the technical aspects of how polluting emissions are created in combustion engines plus the technical and non-technical aspects related to pollutants, emissions and pollutant measurement instruments.

Effective Plan on Air Cleanliness:

The tunes up centers have to be technically proficient and staffed by experts who can accurately assess exhaust emission. If we have highly skilled repairmen in Tehran's repair centers, they can influence on vehicles operation, especially with respect to spare parts with high exhaust emissions rates.

The correct manner of driving and fueling are as the most essential aspects of vehicle operation and that must be taught by public training courses dedicated to reducing air pollutants. In such cases, the experiences of other countries highlight the importance of this issue. It's reported that the efficient training programs is responsible for a 20% reduction in air pollutants.

Responsible Organizations:

High Council of Ministry of Education, Municipality of Tehran, Department of Traffic, Department of the Environment, Mass Media, Ministry of Education, Ministry of Health, Treatment and Medical Training, Municipality of Tehran, Ministry of Industry, and Ministry of Oil

3. CONCLUSIONS

Regarding to activities plan, we have some progressive actions like as:
Observation of ECE15.04 standard for vehicles in 2002, observation of ECE-R83 for new vehicles (injected vehicles) by 2005, completing the phase-out of leaded gasoline throughout the country in 2002, use of catalytic converters, repair and optimization of vehicles uses, phase-out plan for in-use vehicles, expansion and installation of the CNG system on the public transport, improvement of public transportation system especially railroad transport, feasibility of fuel conversion to cleaner fuels, tightening fuel standards, distribution of low-sulfur diesel, development plan for inspection and maintenance centers for vehicles, plans for traffic management and training for public awareness.

The air pollution research bureau has achieved to remarkable results in the past two decades, reducing some pollutants through cooperation by all levels of government and industry. However, air pollution issue is a remaining concern of our country. It calls for the creation of strategic policy to fulfill environmental quality standards, looking into the environmental monitoring of noxious air pollutants, preventative actions and so on.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

APPLICATION OF POLONIUM CONCENTRATION FOR ESTIMATION THE MIXING HEIGHT IN AIR POLLUTION PROBLEMS

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ABSTRACT

The paper presents a new method of evaluation of the mixing layer height (MLH). The data analysis bases on study of variation of chosen meteorological parameters and its comparison with change of the radon Rn-222 concentration in soil gas and polonium Po-218 concentration in the atmospheric air. The Fourier-, Wavelet-, Range Rescaled- and Regression analysis were used for this aim. The obtained results show that the variation of the Po-218 concentration in response to the diurnal changes of mixing state of the lower troposphere may become a good tracer to estimate the atmosphere dynamics and transport of pollution by the turbulent mixing of atmospheric air. The statistically significant relation between the MLH and Po-218 concentration in the air was found and, as a result, the statistical model was developed to define the MLH during the hot season of the year (May-October).

Key Words: Mixing Layer Height (MLH), Air Quality, Natural Radioactivity, Alpha Spectroscopy

1. INTRODUCTION

The air pollution strongly depends on thermodynamic state of the atmosphere. Among meteorological factors, the mixing layer height (MLH) is of the great importance. This parameter influences the form and intensity of diffusion in the atmosphere and, as a consequence, the concentration of primary and secondary pollutants in the lower atmosphere (Garratt, 1992). It shows characteristic diurnal variation but can not be measured immediately. Therefore it is evaluated indirectly by measuring of the others quantities.There is no commonly accepted method of the MLH evaluation due to different genesis of its generation in the boundary layer of the atmosphere taking into account different time of day. The Sodar was used for this aim since 80's of the last century (Reitebuch and Emeis, 1998). Although the obtained outcomes are not satisfactory for every meteorological conditions, this method nevertheless makes it possible to achieve the unmistakable results of so-called equivalent MLH. On the other hand however, the remote sensing monitoring is relatively expensive which limits their application. This work is aimed at presentation of the cheaper method of the MLH evaluation that relies on measurement of natural radioactivity in the atmosphere.

The description of the MLH on base of measurements of the natural radioactivity is one of the methods used in evaluation of the mixing process in the atmosphere (Allegrini et al., 1994, Fujinami and Esaka, 1998, Kataoka et al., 2001, Porstendörfer et al., 1991). According to this, the concentration of the chosen natural occurring radioactive pollutants in air was observed. Up to now, the radon concentration in atmospheric air was taken into account. Radon (strictly, Rn-222), is a member of the uranium series and, under normal conditions, occurs as gas. As a result of turbulence and convection, radon can be transported from soil to considerable heights above the ground and contributes to the ionization of the atmosphere. Such measurements can be however difficult because the natural level of radon concentration in the atmospheric air is rather low. Radon itself decays by alpha emission and its half-life is equal to 3.82 day. The isotopes of polonium, bismuth and lead called the short-lived radon daughters are generated as a result of the radioactive decay of radon (Nazaroff, 1992). The new approach relies on measurements of the polonium concentration (Po-218) in the atmosphere close to the ground. The polonium has considerable shorter half-life (3.05 minutes) than radon, so between these two isotope the equilibrium state will be reached within very short time. On the other hand, the polonium-218 as a free atom, claster or aerosol can be simply collected on a filter and its activity precisely measured by an alpha spectroscopy system. Such method makes it possible to considerably decrease a lower limit of detection in relation to measurement of radon concentration.

The particular emphasis was laid to confirm the assumption about quasi-stable radon concentration in the soil gas. The presented method of evaluation of the MLH, after automatization of the measurement process, can be used for operational modeling of the imission of air pollution.

2. INSTRUMENATION AND MEASUREMENTS

The measurement sites were located in city of Katowice and Cracow (southern part of Poland) and in Ostrava (north part of Czech Republic), close to the meteorological stations of the National Weather Services (NWS). The stations collect meteorological data according to the WMO standards. Additionally, there were conducted gradient measurements of the following meteorological elements: temperature and velocity at 2 and 10 m above ground and the gradient of Richardson's Number (Ri) was calculated basing on these results.

2.1 Barasol

The measurements of the Rn-222 concentration in soil gas were performed on the depth of 1m by means of the Barasol probe. The probe is adjusted to long-term measurements all year round. This device is equipped with a circular silicon detector of the PIPS type with effective area of 450 mm^2 (see Table 1).

The measurements were performed in 1999-2003 in Katowice and Cracow and the results were averaged over a period of 15 minutes.

Table 1. BARASOL probe - basic specification.

Probe length	Diameter	Temperature range	Pressure limit	Background	Measuring range
800 mm	60 mm	-20 to +60 ^{0}C	100 kPa	1 impulse/h	0.1 - 3000 kBq/m^3

2.2 Alpha spectroscopy

Measurements of the Po-218 concentration in air were performed by means of the alpha spectroscopy (Krajny et al., 2005, Osrodka et al., 2003). Immediately after decaying of radon, about 80-82 % of polonium-218 occurs as positive ions that are attached to air gas molecules and water particles within 10^{-7} second (Reineking and Porstendörfer,1986). Free atoms and clasters are called "unattached fraction". Then the clasters, after being bound to the other air-suspended particles, can generate the bigger particles called "attached fraction". During measurements, the air together with all particles is drawn through a filter with adjusted flow rate. A special semiconductor CAM PIPS detector with effective area of 1700 mm^2 was placed above this filter to detect alpha radiation emitted by polonium, that was separated out of the air stream and deposited on the filter (Hindus, 1982). Our detector was a part of an alpha spectroscopy system. Therefore there was possibility to distinguish alpha particle energy and identify isotopes collected on the filter (see Table 2).

Activity of the polonium was measured continuously during air sampling. In years 2001-2004 from May to October anywhere from ten and twenty one-day measurements of Po-218 concentration were performed above the ground under different meteorological conditions. These experiments however were conducted during the well-marked variation of the MLH. The polonium concentrations were then compared with the reference results obtained by the sodar instrumentation.

Table 2. Alpha spectroscopy instrumentation - basic specification.

Nucleopore polycarbonate filter		Flow rate	Sampled time	Lower limit of detection (at 5% significance level)
pore size	effective diameter			
0,8 μm	40 mm	60 dm^3/min	1 hour	0.15 Bq/m^3

2.3 Remote sensing

The remote sensing method was used to collect reference data related to the MLH. The monostatic sodar SAMOS-4C (Katowice) and REMTECH PA2 Doppler sodar (Cracow and Ostrava) were included to perform such measurements. The Doppler sodar was able to evaluate the characteristic of atmospheric boundary layer (vertical wind component, mixing height and inversion level) by means of the Doppler analysis. Physical parameter data of the boundary layer were collected in real time every six seconds by SAMOS and every half-hour by REMTECH. The frequency ranged from 1.6 to 2 kHz The instruments are optimized for long-range detection up to 1200 m above ground. The data have been analyzed automatically.

Data related to the physical parameters of the atmospheric boundary layer were collected in real time as well. However these result were averaged over a period of 1 hour to harmonize it with measurements of the polonium concentration in air.

3. METHODOLOGY

3.1 Radon concentration in the soil gas

The method of evaluation of the MLH relies on assumption that the radon (Rn-222) concentration in the soil gas is quasi-stable. Such statistical methods as Fourier-, Wavelet-, Range Rescaled analysis were applied to analyze the time series of radon concentration and verify this hypothesis.

This analysis was performed after removal of results that had been affected by geological- and geophysical events. On the other hand, the Linear Regression analysis was used to reveal relations between radon concentration in the soil gas and polonium concentration in air and meteorological conditions, especially the MLH

Frequency analysis

The Fourier method was applied to define the global frequencies (annual and seasonal components) in relation to variation of radon concentration. The FFT algorithm (Fast Fourier Transformation) was include to fulfill this task (Cormen et al., 1990).

The Wavelet analysis helped to find the diurnal variation. This analysis is a generalization of the Fourier analysis and makes it possible, for obtained results related to any natural phenomena, where periodicity seems to occur, to reveal the followings:

- for any frequency, further called the scale, local short-term oscillations,
- oscillations with the same scale and time-changeable amplitude,
- oscillations with time-changeable scale.

The wavelet transform relies on conversion of the data series $x_1,........,x_n$ (real or complex numbers) into the Form Table (from values into frequency values to obtain a relation: frequency-measured value):

$$W_k(s)=\sqrt{\frac{1}{s}}\sum_{j=1}^{n} x_j \overline{\Psi(\frac{j-k}{s})} \qquad k=1,...,n,\ s=s_1,...,s_m \qquad (1)$$

where sign „—” means conjugation of the complex number, function Ψ (real or complex function) is called a basic wavelet, $s_1,...,s_m$ correspond to scales (periods) which have been accepted for wavelet analysis. The Morlet wavelet was applied in the analysis (Bialasiewicz, 2000, Farge, 1992, Torrence et al., 1998).

Range Rescaled Analysis - Hurst exponent

The Hurst exponent (Hurst, 1951, Mandelbrot, 1983) is a statistical tool, so all-purpose, that it can be applied for the fractal analysis of the time series. Hurst did a non-dimensional indicator by dividing of the oscillation range related to specific data series by standard deviation related to obtained observations:

$$\underset{c,H\in R}{\vee}\ \underset{n_0\le n\le N/2}{\wedge}\left(\frac{R}{S}\right)_n = c\cdot n^H \tag{2}$$

where $(R/S)_n$ is a rescaled range, $M=d\cdot n$ is a series length, d number of subseries, n number of elements that belong to the subseries, n_0 – minimal length of the subseries, $n\in [10; M/2]$, N – number of observations, c – constant, H – Hurst exponent.

By using a double-logarithmic scale, the curve $n\to(R/S)_n$ can be plotted where its slope is an estimate of the H value. The main point of the analysis is to rescale the range and relies on analyzing of the range R of the time series taking into account different time periods n.The conclusions can be drawn in relation to independence and memory length of the process (even when there are not the Gaussian series) when comparing the series to the similar range in case of the independent random variables. There are three classes of the time series depending on the value of the Hurst exponent: antipersistent or ergodic series ($0 \le H < 0.5$), “white noise” ($H = 0.5$) and persistent series ($0.5 < H \le 1$).

Results of the Analysis

Fourier analysis

According to the Fourier analysis, there was not observed the cyclic variation of the Rn-222 concentration in the soil gas up to depth of 1m (Fig. 1, 2).

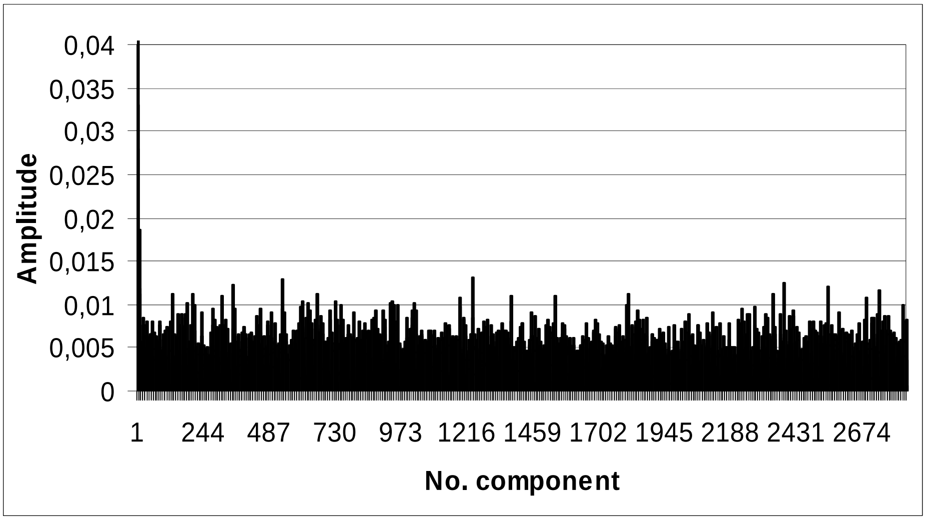

Figure 1. The Fourier spectrum of the radon (Rn-222) concentration in the soil gas during the period 11 July – 7 September 1999 (Katowice).

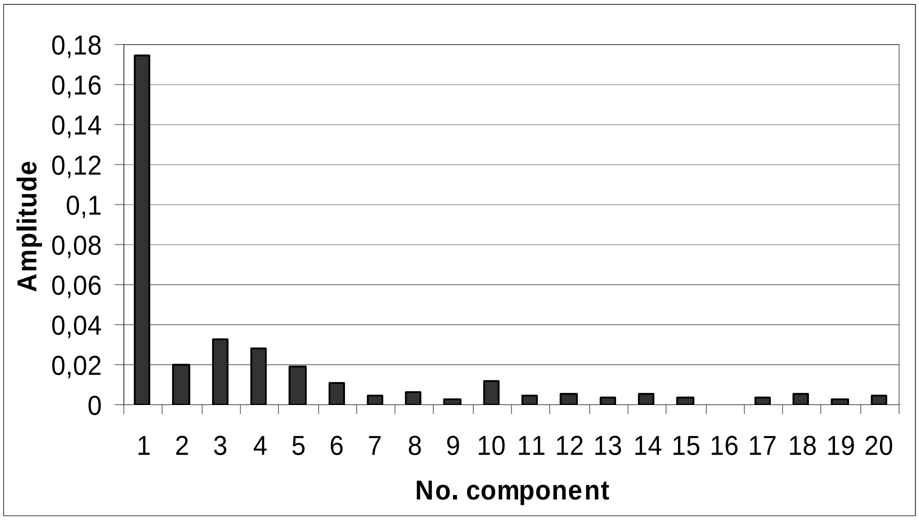

Figure 2. The Fourier spectrum of the radon (Rn-222) concentration in the soil gas taking into account the first 20 components of the FFT analysis, during the period 11 July – 7 September 1999 (Katowice).

Wavelet analysis

The analysis of the amplitude of the wavelet transform gave no reason for separation of any diurnal variation of Rn-222 concentration in the soil gas taking into account diurnal variation of the meteorological conditions. (Fig. 3). So, the short-term changes of the meteorological conditions do not influence the changes of the radon 222 concentrations. On the other hand, the long-term changes of these conditions can affect indirectly the radon concentration in the soil gas.

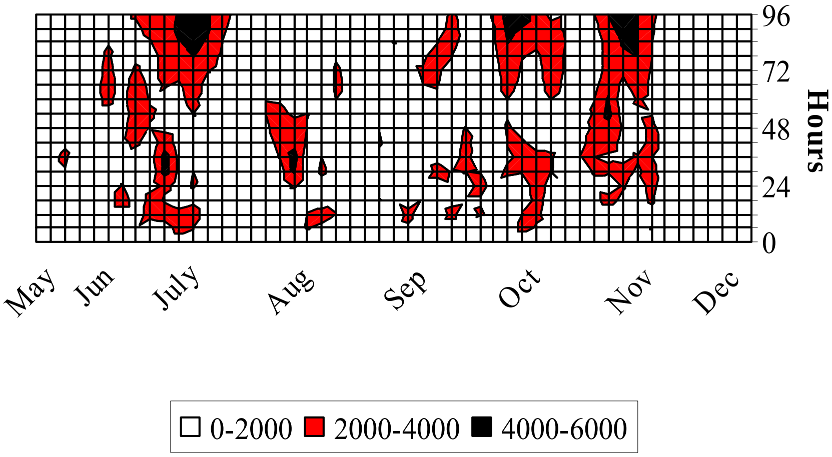

Figure 3. Local amplitude of the Morlet wavelet for the respective one-hour-scales of the radon (Rn-222) concentration in the soil gas in 2000 year (Katowice).

Hurst exponent

According to the Range Rescaled Analysis, the Hurst exponent for the radon concentration in the soil gas ranged from 0.811 up to 0.996 and was greater than 0.9 for the most time. So the changes of Rn-222 concentration in the soil gas are persistent and the phenomena of the radon occurrence in the soil up to 1m have a long-term memory (big positive correlation) or using terms of the chaotic dynamics: there is a subtle sensitivity to the initial conditions (Fig. 4).

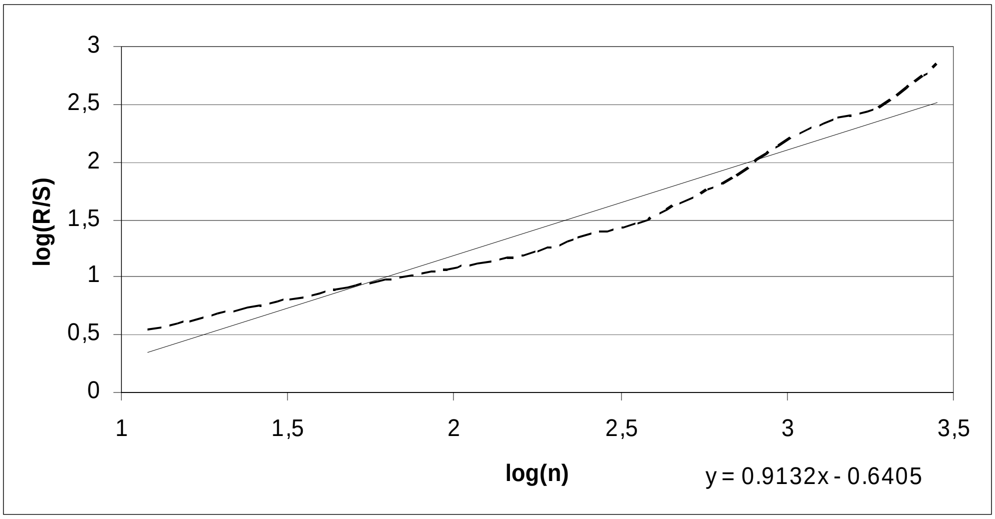

Figure 4. The Hurst exponent (H) for of the radon (Rn-222) concentration in the soil gas during the period 11 July – 7 September 1999 (Katowice).

3.2 Polonium concentration in the atmospheric air

Results of the analysis

The concentration of polonium in atmospheric air shows characteristic diurnal variation with the maximal value in the early morning (3-5 UTC) and minimum value around midday (12-14 UTC) when the shaky thermic dynamical stratification of the atmosphere occurs and as a result the range of the mixing layer is maximal (Fig. 5). The strongest, statistically significant correlation (α=0.05) has been observed between polonium-218 concentration and air temperature (r=-0.759) or wind velocity (r=-0.829). Basing on the comparative analysis for Po-218 concentration and MLH, the following correlation coefficients have been achieved: r = -0.761, -0,575 i -0.580, in Katowice, Cracow and Ostrava respectively, at significance level of α=0.05. The differences were caused by different meteorological conditions that occurred during field experiments. One of the basic parameters influencing directly the Po-218 concentration in air was wind velocity. When the average diurnal air velocity is greater than 4 m/s, the correlation was considerably lower.

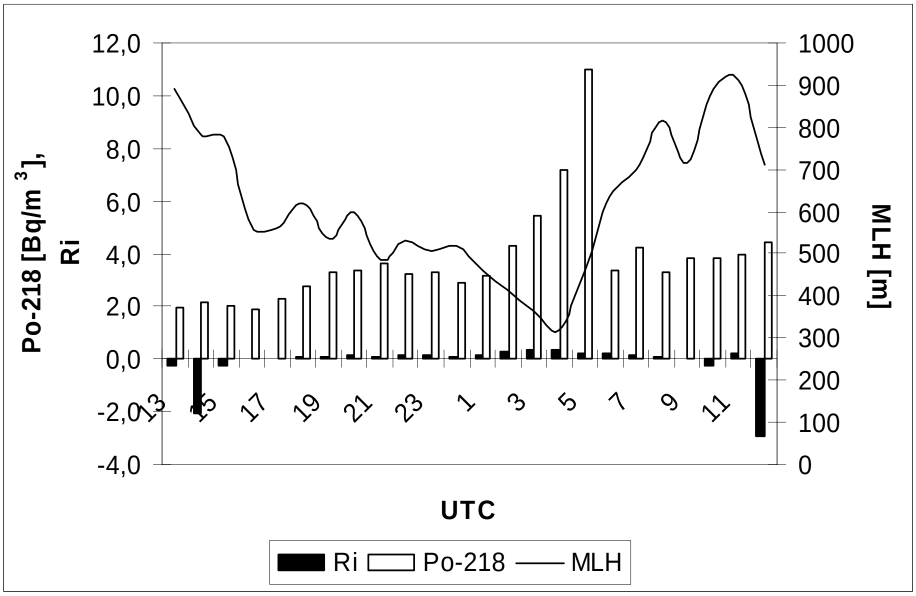

Figure 5. Diurnal changes of the polonium (Po-218) concentration in air and the mixing layer height (MLH) value with the Richardson number (Ri), 6-7 October 2004 year (Ostrava).

4. MODEL FOR ESTIMATION OF THE MLH

The mathematical model was developed taking into account the results of measurements performed in years 2000-2003 in Katowice and Cracow. These experiments made it possible to draw conclusion that between Po-218 concentration in air near to ground (C_{Po}) and equivalent MLH value (h_{eqmix}) occurs a statistically significant relation at significant level of 0.05. This relation can be described by the following mathematical formula:

$$h_{eqmix} = \left(\frac{C_{Po}}{const} \right)^{\beta} \tag{3}$$

where *const* is a local constant that depends on geographical conditions, β=-1.55 - exponent, that does not depend on measurement site. This model was tested during hot season in 2004 in Katowice. The obtained data showed that the model gives satisfactory results when the meteorological conditions are well defined.

5. CONCLUSIONS

1. The frequency and fractal analysis showed that the radon (Rn-222) concentration in the soil gas has a quasi-stable character.
2. The mathematical analysis showed that polonium (Po-218) concentration near to ground has a characteristic diurnal variation and is well correlated with meteorological elements. As a result, this concentration can be a satisfactory indicator of the MLH in the atmosphere.

3. A statistical model for evaluation of the equivalent MLH basing on measurement of the Po-218 concentration in air was developed. It can be presented as a power function. This mathematical model was satisfactory verified for the hot season (months May-October). The mixing conditions seem to be underestimated when the averaged diurnal air velocity is greater than 4 m/s. The examined model can be successfully applied under different geographical conditions.
4. The measuring process should be automatized and present work concentrates on this aim.

6. ACKNOWLEDGEMENTS

The research project was supported in years 2005-2006 by the Polish State Committee for Scientific Research.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

AIRBORNE TOXIC METALS IN INDUSTRIAL COMPLEX AREAS of KOREA USING CCT-ICP-MS TECHNIQUE

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ABSTRACT

The use of collision cell technology-inductively coupled plasma mass spectrometry (CCT-ICP-MS) is one of the strongly recommended choices for the accurate analysis of the toxic trace metals; this is because CCT-ICP-MS technique prevents polyatomic spectral interferences involved in the determination of As and Cr components. Taking advantage of this technique, the measurements of up to 20 metals were undertaken in this study. Based on the analysis of the metal and ionic compositions of PM10 samples, we attempted to explain the distribution characteristics of elements, to identify sources, and to assess their contributions to PM10 (by positive matrix factorization (PMF 2) method).

Key Words: PM10, trace metal, CCT-ICP-MS, source contribution, PMF

1. INTRODUCTION

Airborne particulate matters, especially PM10 (aerodynamic equivalent diameter, AED, less than 10) fraction have been important. This is because of their potential for deposition on to the human respiratory system being accompanied by many harmful trace metals (such as As, Cd, Cr, Cu, Mn, Pb, Se, and Zn) (Dockery and Pope, 1994; Natusch et al., 1974). These trace metals originated from various source processes (soil, vehicle exhaust, combustion of fossil fuel, incinerator, and industrial process) affect the environment not only in locally limited region but also to a wide area (by long range transportation). The first step of figuring out the characteristics of airborne PM10 in the industrial complex area is to make long-term concentration profiles of PM10 and the associated components including toxic metals.

An analytical method aiming to the quantitative determinations of trace elements in airborne particulate samples should be sensitive and precise, while being potent enough to identify the diversity of elements simultaneously. However, studies have rarely been made either domestically or internationally to apply CCT-ICP-MS for the precise analysis of As and Cr components associated with airborne particulate matter. Hence, the use of CCT-ICP-MS is strongly recommended for the accurate analysis of these toxic trace metals, it can prevent polyatomic spectral interferences involved in the determination of As and Cr components (Tomas, 2002; Sakata and Kawabata, 1994). It was reported that more than 90% of the cancer risk from airborne toxic metals can be caused by those human carcinogens (Jang and Lee, 2002). Therefore, it is a very essential task to improve detection methods for those carcinogenic trace metals accurately.

In this study, we undertake the measurements of about 20 metals including 6 carcinogenic ones (using CCT-ICP-MS) and inorganic ion components (using Ion chromatography). Based on our measurement data, we characterize the concentration status of the study area. In addition, we concentrate on an application of receptor modeling for quantitative source apportionment as well as source identification of PM10 in the study area. Positive Matrix Factorization (PMF), new multivariate receptor modeling technique, developed by Paatero and Tapper (1994), is applied in the identification and quantification of air pollution sources. PMF has special features in that it uses realistic error estimates to weight the data values and the imposition of non-negative constraints in the factor computational process. PMF analysis was successfully applied in a number of prior studies to investigate the pollution sources (Hopke, 2003; Liu et al., 2003; Chueinta et al., 2000; Polissar et al., 1998).

2. EXPERIMENTAL

2.1 Site characteristics and sampling

The study area, Siwha and Banwall Industrial Complex, is one of the most polluted areas in Korea. This area is located approximately 70 km southwest of Seoul, the capital of South Korea (Fig. 1). It is a coastal area surrounded by a huge residential area. The characteristics of airborne PM10 in Siwha and Banwall Industrial Complex area are very complicated to figure out, because the pollutants are emitted from various types of stacks (about 2,000 sources). The collection of PM10 samples was made at two sampling stations located in both industrial areas and one residential sampling station. The two industrial stations in Siwha (SW) and Banwall (BW) are located about 2 km north-westerly from coast and the distance between the sites are about 8 km as shown Fig. 1. The residential sampling station Jungwang (JW) is located in the northeast direction of the SW station. This site is mostly affected by road traffic PM10 emissions and also by PM10 sources of industrial process from Siwha and Banwall Industrial Complex area.

For the collection of airborne particulates, a PM10 high-volume air sampler (Kimoto Model-121FT, Japan) was equipped with Whatman 41 air filter (8"×10"). This filter is a fibrous filter made of cellulose with a small pressure drop and good mechanical strength. A total of 86 samples in two industrial stations (SW, BW) and 56 samples in residential station (JW) were collected from September 2003 to January 2005. The fundamental meteorological conditions (including rainfall, temperature, relative humidity (RH), wind direction, horizontal wind velocity, etc.) were recorded at hourly intervals during the study period. Air samples were drawn at a flow rate of 0.85 m^3 min^{-1} for the duration of about 24-hour. The total volume of air passed through a filter was computed using the flow recorder for each sampling period.

Whenever the motor brush of sampler was changed, flow rate was re-adjusted by orifice calibrator (GMW-25). The collected samples were pre-stored for 24-hour in a controlled atmosphere (20□, 50% relative humidity).

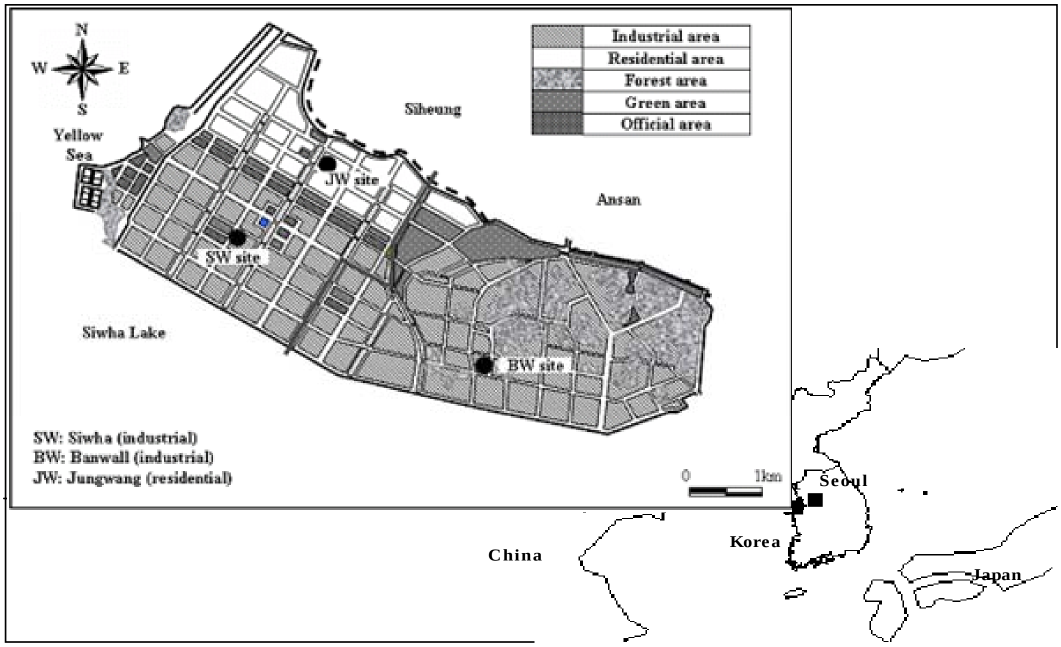


Figure 1. Study area and the sampling sites in Siwha and Banwall Industrial Complex area

2.2 Chemical analysis

The concentration of Al, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Ti, V, and Zn associated with PM10 were determined on a CCT-ICP-MS (X-7 mounting series model with hexapole collision cell, Thermo Elemental), which can remove polyatomic spectral interferences affected by plasma gas (Ar), matrix components, and solvent acid (Tomas, 2002; Tanner, 1995; Sakata and Kawabata, 1994; Jiang et al., 1988). A portion of the sampled filters (1/10) was decomposed by microwave digestion with 5mL nitric acid. All the extracts were pooled and brought in to a final weight of 50 g in polyethylene bottle using 1% pure HNO_3 solution. The instrumental conditions used were basically similar to those reported by the instrument manufacturer. The results obtained by the standard calibration curve method were in general in line with those obtained by the standard addition method (r value above 0.999). The final concentrations were corrected with the combined reagent and filter blanks.

The NIST standard reference material (SRM: NIST, the National Institute of Standards and Technology, U.S.A., SRM 2783, air particulate on filter media) was used for the analytical quality control of CCT-ICP-MS analysis. It was found that relative errors (against SRM values) of Al, As, Cr, Fe, Mg, Mn, Pb, Sb, V, and Zn fell below 20%, while those of Ca, Si, and Ti above 20%.

The filters were also extracted using ultra-pure water using by ultrasonic instrument (Branson 8210, U.S.A.) for 30 minutes. Ion chromatography was also used to determine the concentrations of SO_4^{2-}, NO_3^-, and Cl^-. IC (ΩMetrohm, 761 Compact

IC model) consists of a separation column (IC SI-90 4E, Shodex, Japan), a guard column, and suppressor (SCX Membrane PCR, SeQuent, Sweden) using sulfuric acid. For the IC analysis, the pooled standard deviation for peak area of standard solution was about 4 %, recovery of spiked anions ranged between 97-105 %, and the average precision determined from duplicate analysis ranged between 1.5-7% for three anions. Therefore, the stability and reproducibility of the analytical condition can be considered highly stable.

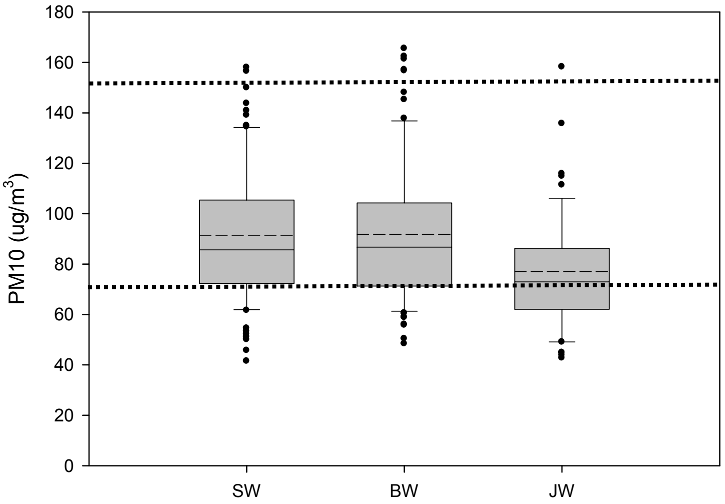
3. RESULTS AND DISCUSSION

3.1 Mass concentration of PM10

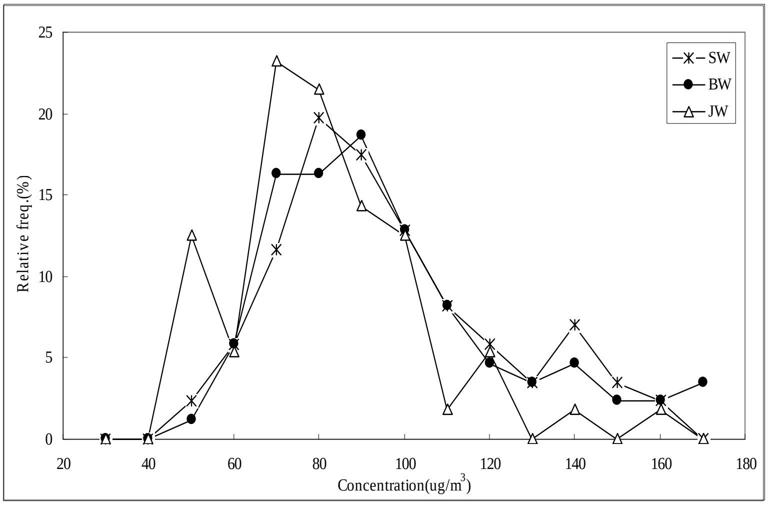
The seasonal values for PM10 measurements are shown in Table 1. The annual average of PM10 was 91.2 □/m^3 (SW) and 91.8 □/m^3 (BW), whereas the counterpart at JW was 77.0 □/m^3. The similar temporal variation of PM10 was observed from three sampling sites, showing the highest concentration in fall while the lowest in summer. The distribution of PM10 concentration is also shown as box-whisker plot and relative frequency patterns in Fig 2. The mean annual concentrations of PM10 at all sites exceeded 70 □/m^3 of Korean annual limit, and also 2 times at SW, 3 times at BW, and 1 times at JW exceeded the daily PM10 limit value, 150 □/m^3. The daily PM10 concentrations between three sites have a strong correlation coefficient, which SW to BW was 0.77, SW to JW was 0.73, and BW to JW was 0.74. This may imply that PM10 concentrations in study area are affected to each other.

Table 1. A statistical summary of PM10 concentration divided in spatial and seasonal base (unit: □/m^3).

		Mean	S.D.	S.E.	Min	Max	N
SW	Spring	95.5	18.7	5.0	61.6	134.9	14
	Summer	63.5	12.5	3.3	45.7	88.5	14
	Fall	100.2	31.8	5.9	41.5	158.0	29
	Winter	93.6	21.0	3.9	61.9	143.7	29
	All period	91.2	26.7	2.9	41.5	158.0	86
BW	Spring	92.0	24.2	6.5	63.2	157.1	14
	Summer	65.5	10.4	2.8	48.3	83.8	14
	Fall	104.4	33.2	6.2	58.9	165.5	29
	Winter	91.9	21.9	4.1	58.8	137.8	29
	All period	91.8	28.2	3.0	48.3	165.5	86
JW	Spring	84.2	24.8	6.6	66.9	158.2	14
	Summer	55.0	10.4	2.8	42.7	73.8	14
	Fall	89.7	20.3	5.4	58.5	135.7	14
	Winter	79.1	16.1	4.3	59.8	111.4	14
	All period	77.0	22.5	3.0	42.7	158.2	56



(a) box-whisker plot



(b) relative frequency patterns

Figure 2. The distribution patterns of PM10 concentrations in Siwha (SW) and Banwall (BW) industrial area; (a) box-whisker plot for inspecting level of PM10 (upper line means daily PM10 limit value, while lower line means annual PM10 limit value of Korea) and (b) relative frequency for shape of distribution of PM10.

3.2 Concentration of metals and ionic species

To constrain uncertainties involved in our measurements, we eliminated some outlying data sets prior to statistical analysis by employing the two independent screening steps (Kim et al., 2002). As a first step, about 7.7 % of data sets were removed on the basis of signal-to-noise (S/N) ratio of less than 2. Following the initial screening, the data sets with the values exceeding ±3 SD from the mean were also excluded to rule out the possibility that the distribution patterns of certain components are distorted by the presence of a few extreme values. Loss of data was about 1.5 % at this secondary stage. The concentration of metals and three ionic species in the study area after this screening procedure was summarized in Table 2.

From the results of the quantitative analysis for airborne PM10 samples by CCT-ICP-MS, it was found that the concentration of metals associated with crustal sources (such as Al, Ca, Fe, K, Mg, and Na) were much higher than that of any other toxic metals. The distribution patterns of different metals were clearly distinguished with their concentrations ranging across five orders of magnitude. Based on a simple comparison of the metal concentrations by their magnitude, the data sets could be grouped into five different categories: 1) < 10^{-1} ng/m^3: Be; 2)< 10^0 ng/m^3: As, Cd, Co, Se, and V; 3) < 10^1 ng/m^3: Ba, Cr, Mn, Ni, Ti, and Sb; 4) < 10^2ng/m^3: Al, Cu, Mg, Na, Pb, Si, and Zn, and 5) > 10^3ng/m^3: Ca, Fe and K.

The mean concentrations of several toxic metals (including As, Mn, Se, V, and Zn) in the SW site were measured as 7.06±3.34, 93.5±49.5, 3.17±1.87, 7.54±5.14, and 451±304 ng/m^3, respectively. In the case of BW site, they were measured to be 5.34±3.26, 79.4±42.5, 4.08±2.86, 6.53±6.33, and 624±394 ng/m^3, respectively. In the JW, they were 5.65±2.92, 39.0±24.1, 3.23±1.69, 8.66±6.10, and 287±194 ng/m^3, respectively.

The mean concentrations of three inorganic ions (Cl^-, NO_3^-, and SO_4^{2-}) were also measured from those three areas as well. In the SW site, the results were 4.91±2.76, 10.5±6.05, and 9.91±6.42 □/m^3, respectively. In the BW site, they were 9.01±6.13, 10.1±6.89, and 10.0±7.53 □/m^3, respectively. In the JW site, they were 2.79±1.92, 9.46±5.64, and 10.4±4.64 □/m^3, respectively. The sum of anionic species in BW was contributed about 29.0 % of total PM10 mass concentration, while sum of those species in SW and JW are about 25 %, respectively.

Comparison of the aerosol compositions in relation with crustal composition can help discriminate the contribution of man-made source processes from other source processes (Senaratne and Shooter, 2004; Gao et al., 2002). The concept of enrichment factor (EF) is based on the fact that some metals originating from well-defined sources (such as Al or Fe) mainly originating from the earth's crust) can be distinguished from other metals derived by different source processes. On the basis of arbitrary EF value criteria of 50, we were able to sort out such metals as As, Cd, Co, Cr, Cu, Ni, Pb, Sb and Se to be enriched in PM10 samples of our study sites. It was noteworthy that most of those metals are the major anthropogenic source components.

3.3 Source contributions

Based on the metal and ionic composition data for PM10 samples, we attempted to identify sources, and to assess their contributions to PM10 by positive matrix factorization (PMF 2) method. Basic equation of PMF model is shown equation (1). The method is to find the unknown matrix, G and F by the solution of a least square method iteratively

$$X = GF + E \qquad (1)$$

Where, X(m×n) is the data matrix consisting of the m chemical components analyzed in n samples, G(n×p) is the source contribution to the each sample. F(p×m)

Table 3. Concentration of metals and three ionic species measured from the two industrial stations (SW and BW) and one residential area (JW) during 2003-2005. The concentration unit of three ions are □/ m^3, while all the rest are in ng/m^3.

	(1)SW			(2)BW			(3)JW		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Al	1090	29	2691	1294	260	6527	1394	43.0	9494
As	7.8	1.6	28.6	6.6	0.9	21.3	7.6	1.4	18.7
Ba	35.3	4.4	218.3	40.3	3.5	207.4	36.6	6.5	103
Be	0.06	0.01	0.21	0.04	0.01	0.09	0.06	0.02	0.19
Ca	995	482	2293	796	52.6	2236	522	38.1	3536
Cd	7.0	0.4	31.7	6.4	0.4	33.1	4.6	0.5	14.4
Co	1.4	0.1	6.4	1.5	0.1	5.9	0.9	0.1	2.7
Cr	78.8	5.5	468	20.9	1.9	83.4	10.9	1.7	37.8
Fe	1331	236	3979	1495	190	5917	1135	103	7422
K	1396	427	13075	1141	90.7	3825	1193	63.6	3736
Mg	348	50.5	1585	398	43.8	1646	376	30.0	2618
Mn	137	5.7	643	111	12.3	421	63.9	5.5	318
Na	578	157	1592	617	38.2	4601	686	112.9	2102
Ni	44.3	4.0	360	29.7	3.5	298	12.0	1.8	39.0
Pb	382	19.7	1672	487	8.2	2891	229	19.2	1662
Sb	8.9	0.9	32.0	8.4	0.6	59.9	6.5	0.5	17.5
Se	3.3	0.5	11.9	4.9	0.6	25.3	2.9	0.7	7.2
Si	520	243	1309	492	146	1430	391	74	967
Ti	22.6	3.4	71.4	30.6	2.5	93.7	28.9	1.6	168
V	6.5	0.4	23.9	5.7	0.7	21.7	6.3	0.5	17.2
Zn	519	38.1	3017	1078	68.7	4756	306	27.1	2685
Cl^-	4.7	0.4	16.8	8.5	0.8	25.9	2.9	0.2	8.1
NO_3^-	9.0	1.4	23.1	9.4	2.1	26.9	8.3	1.6	22.1
SO_4^{2-}	8.3	2.5	30.0	8.8	2.2	29.2	8.8	3.1	20.9

is the matrix of source profile. E presents the residual matrix of calculation, and the main process of the PMF is minimizing the Q-value, which is defined in the equation (2) below as the sum of square of the residuals (e_{ij}) weighted inversely with error estimates (s_{ij}) of the data point (Paatero, 1997; Paatero and Tapper, 1994).

$$Q(E)=\sum_{i=1}^{m}\ \sum_{j=1}^{n}(e_{ij}/s_{ij})^2 \qquad (2)$$

The Q value can be used to determine the optical number of factor. The theoretical Q value should be approximately equal to the degree of freedom of datum in the data set. In the almost all cases, however, calculated Q value is higher than theoretical Q value because of missing and/or below detection limit data points. The more details of PMF are referred to the literatures.

The data set was then used for PMF2 to identify the possible sources of PM10 in the study area. The measured data were used directly, and the expanded uncertainty in 99 % confidence interval of each data value was used as an error estimate. For those data below the detection limit (DL), values were replaced with a half value of DL for each element, and the value of DL was used as an error estimate. For missing data, geometric mean of elemental concentration was used, and four times (of the geometric mean) were used as an error estimate to obtain large standard deviation.

A common nine sources for PM10 in the three sampling sites were found based on Q value, FPEAK, and scaled residual (<±2). Scaled residual values less than ±2 were more than 80% in the three data sets. The results of correlation analysis using observed versus predicted PM10 mass concentrations indicated that the resolved factors effectively accounted for the total mass. Correlation coefficients between reconstructed and measured portions of three data sets were higher than 0.75 in the study area. On average, the extracted eight factors from the data accounted for 97% with respect to the corresponding measured PM10 concentrations.

The natural sources of soil dust and sea salt were enriched by Al, Ca, Fe, K, Mg, and Si and Na, Cl^-, and Mg, respectively. The secondary aerosol source has a high concentration of NO_3^- and SO_4^{2-}, being suspected to be the major sources of air particulate matter. The sources associated with the transportation were divided into road dust and vehicle exhaust. The former was defined as contaminated soil dust on the pave road by vehicle exhaust, particles created through tire, brake, and vehicle wear process as marker of NO_3^-, SO_4^{2-}, Ba, Cr, Sb, Si, and Ti (Abu-Allaban et al., 2003). On the other hand the latter ones were vehicle exhaust directly emitted from tailpipes as marker of Sb, Zn, Cd, Pb, and Cl^-. The incinerator source contains high concentration of Cd, Pb, Sb, and Zn. The elements originating from burning of coal and fuel oils (like As, Se, Mn, V, and Zn) were used for the identification of these combustion source processes (Song et al., 2001; Huang et al., 1994; Ondov et al., 1982).

In the three sites, the number of air pollution sources analyzed by PMF2 is found to consist of nine different ones. The sources included both the natural and anthropogenic ones including soil dust, sea salt, road dust, secondary sulfate, soil dust, secondary nitrate, incinerator, vehicle exhaust, coal combustion, and oil combustion. The average source contributions of each source to the PM10 concentration in each sampling sites were compared in Table 3. The results of PMF2 revealed very well the characteristics of sampling sites as its contribution for the PM10 concentration. It suggested important roles of both industrial and natural source processes, despite the fact that the study site is located at the industrial complex.

4. CONCLUSIONS

The airborne concentrations of PM10 and their components covering 20 metals and 3 anions were investigated from the industrial complex area in Korea. The elemental concentrations in PM10 were determined on a CCT-ICP-MS, It was found that relative errors (against SRM values) of Al, As, Cr, Fe, Mg, Mn, Pb, Sb, V, and Zn fell below 20%, while those of Ca, Si, and Ti above 20%.

Table 3. Average and standard error of source contributions for each factor at each site. (unit: □/ m^3)

Sources	SW	BW	JW
Road dust	20.5±2.54	21.1±2.3	11.2±0.75
Secondary sulfate	15.3±1.65	15.7±1.7	14.5±0.50
Soil dust	10.7±0.68	10.4±1.0	14.0±0.68
Secondary nitrate	9.4±1.14	14.4±2.0	11.5±2.54
Sea-salt	7.2±0.75	4.3±0.6	4.0±0.58
Incinerator	6.5±0.92	7.0±1.0	5.0±1.14
Vehicle exhaust	6.3±1.02	5.9±1.0	3.6±1.02
Coal combustion	6.2±0.58	4.8±0.7	4.3±1.65
Oil combustion	5.8±0.50	6.9±1.2	7.8±0.92
Observed PM10	92.2±3.12	91.8±3.04	77.0±3.0
Predicted PM10	86.2±3.05	89.7±3.44	75.9±4.5

The concentration of metals such as Al, Ca, Fe, K, Mg, and Na associated with crustal sources were much higher than that of any other toxic metal. The distribution patterns of different metals were clearly distinguished with their concentrations ranging across five orders of magnitude. Based on the analysis of the metal and ionic compositions of PM10 samples, we tried to identify sources, and to assess their contributions to PM10 by positive matrix factorization (PMF 2) method. In all three sites, the number of air pollution sources analyzed by PMF2 is found to consist of nine different ones. The sources included both the natural and anthropogenic ones including soil dust, sea salt, road dust, secondary sulfate, soil dust, secondary nitrate, incinerator, vehicle exhaust, coal combustion, and oil combustion. Results of PMF2 modeling also suggested important roles of both industrial and natural source processes, despite the fact that the study site is located at or near at the very active industrial complex.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

AFFORESTATION FOR IMPROVING VALLEY URBAN AIR-QUALITY

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ABSTRACT

Lanzhou is one of the major cities in northwest China and the capital of Gansu Province and located at a narrow (2-8 km width), long (40-km), NW-SE oriented valley basin (elevation: 1,500- 1,600-m) with the Tibetan plateau in the west, Baita mountain (above 1,700-m elevation) in the north, and the Gaolan mountain in the south. Due to topographic and meteorological characteristics, Lanzhou is one of the most polluted cities in China. Meteorological conditions (low winds, stable stratification especially inversion), pollutant sources and sinks affect the air quality. Afforestation changes the mountain-valley local circulation system, destabilizes the atmosphere, and weakens the inversion. Besides, it may absorb some pollutants (sink). Lanzhou local government carried out afforestation and pollutant-source reduction (closing several heavy industrial factories) to improve the air-quality for the past two decades. Numerical model (RAMS-HYPACT) simulates the effect of afforestation on the air pollution control.

1. INTRODUCTION

Lanzhou is located at a narrow (2-8 km width), long (40-km), northwest-southeast oriented valley basin enclosed by 1,600-m elevation with the Tibetan plateau in the west, Baita mountain (above 1,700-m elevation) in the north, and the Gaolan mountain in the south (Figure 1a). The highest elevation in the surroundings is the top of the Gaolan mountain around 2,150-m above the sea level.

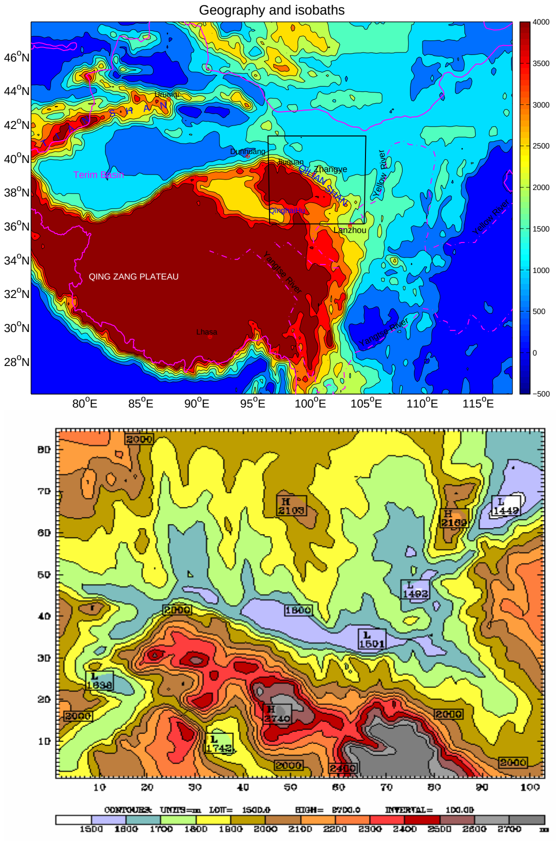

Figure 1. Topography: (a) China, and (b) Great Lanzhou metropolitan area and surroundings.

Meteorological characteristics over the valley (great Lanzhou metropolitan) are semi-arid, weak wind, thick and strong inversion, which makes the low layer atmosphere very stable, low dispersion and causes severe air pollution (Figure 2). Lanzhou is one of the most polluted cities in China. How can air pollution be effectively controlled in valley urban area? Two possible approaches can be adopted: (1) changing meteorological conditions (destabilizing atmosphere) and (2) reducing the pollution sources.

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Figure 2. LANDSAT image.

2. SOME AIR-QUALITY IMPROVEMENT IN PAST DECADE

Since mid 1990s, the local Lanzhou government has conducted afforestation on the mountain slope and shut down several factories that emitted large amount of pollutants. The gaseous pollutants such as SO_2 and NO_x concentrations have been reduced. However, the particulate pollutants such as TSP and PM_{10} still keep high concentrations [Chu et al. 2004]. Figure 2 shows the evolution of annual mean concentration for the three major pollutants (SO_2, NO_x, TSP) measured at the local environmental protection agency (EPA) station (103.631°E, 36.103°N), which is marked as the solid circle in Figure 1b. The annual mean SO_2 has a maximum near 0.12 mg m^{-3} (above the third level standard: 0.10 mg m^{-3}) in 1994, and decreases monotonically to 0.055 mg m^{-3} (below the second level standard: 0.06 mg m^{-3}) in 2000 (Figure 3a). The annual mean NO_x has two maxima (above the third level standard: 0.10 mg m^{-3}) in 1990 and 1995, and decreases monotonically to 0.05 mg m^{-3} (close to the second level standard: 0.05 mg m^{-3}) in 2000 (Figure 3b). Except TSP, the air pollution (SO_2, NO_x) has been greatly improved.

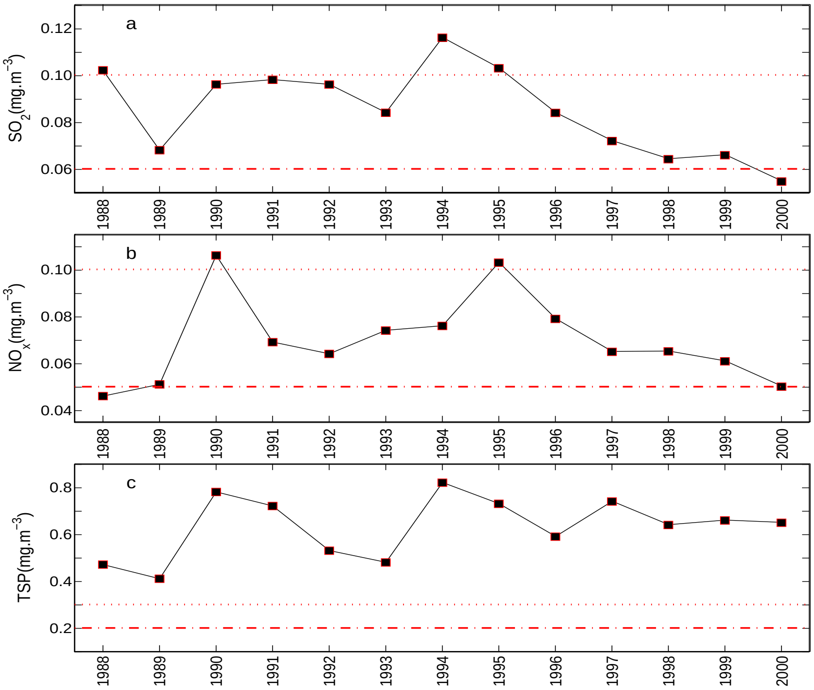

Figure 3. Annual mean concentration (mg m^{-3}): (a) SO_2, (b) NO_x, and (c) TSP measured at the local EPA station (103.631°E, 36.103°N), which is marked as the solid circle in Figure 1b. The second-level standard is represented by the horizontal dash-dotted line and the third-level standard is represented by the horizontal dotted line.

3. MOUNTAIN-VALLEY CIRCULATION

Thermal heterogeneity of land surface can produce local circulations as strong as sea breezes (e.g., Chu 1987, Chu et al., 2005). Differential surface heating on the mountain slope generates local valley winds especially in winter or night (Figure 4).

The downward motion over the valley makes the atmosphere stable, and in turn weakens the diffusion of the pollutants.

Weakening this mountain-valley circulation (strong downward branch over the valley) destabilizes the atmosphere and enhances the diffusion rate. From physical point of view, reduction of surface thermal heterogeneity will weaken this circulation. Afforestation on the mountain slope may reduce the thermal heterogeneity and in turn improve the air-quality by atmospheric destabilization. Furthermore, the forest may also absorb pollutants (as pollutant sink). The Regional Atmospheric Modeling System (RAMS) is used to investigate this mechanism.

4. ATMOSPHERIC MODEL

4.1. Model Implementation

RAMS is a mesoscale modeling system including advanced model physics was developed by The Colorado State University. It is a community regional model widely used for numerical weather prediction, hydrological studies, and air quality studies. The nonhydrostatic RAMS is used in this study. The land surface model is coupled to RAMS to describe the effect of vegetation and interactive soil moisture on the surface-atmosphere exchange of momentum, heat, and moisture. This LSM is able to provide not only reasonable diurnal variations of surface heat fluxes as surface boundary conditions for coupled models, but also correct seasonal evolutions of soil moisture in the context of a long-term data assimilation system. Also, 1-km resolution vegetation and soil texture maps are introduced in the coupled RAMS-LSM system to help identify vegetation/water/soil characteristics at fine scales and capture the feedback of these land surface forcing. A monthly varying climatological $0.15^{\circ} \times 0.15^{\circ}$ green vegetation fraction is utilized to represent the annual control of vegetation on the surface evaporation.

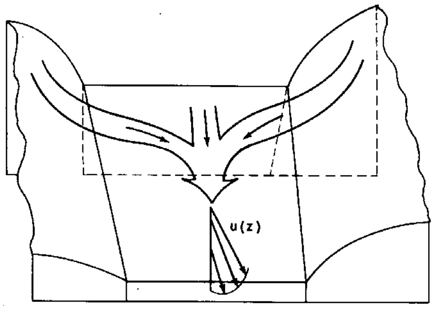

Figure 4. Mountain-valley circulation.

LSM has one canopy layer and the following prognostic variables: soil moisture and temperature in the soil layers, water stored on the canopy, and snow stored on the ground. Four soil layers are used to capture the evolution of soil moisture and to mitigate the possible truncation error in discretization. The thickness of each soil layer from the ground surface to the bottom is 0.1, 0.3, 0.6 and 1.0 m. The precipitation is parameterized by several different schemes. Non-convective precipitation can be represented via an implicit scheme, whereby supersaturated water immediately precipitates, and an explicit scheme including prognostic equations for cloud- water and rainwater. Convective precipitation is parameterized via two cumulus convection schemes. We use the mass flux scheme, which accounts for the effects of penetrative downdrafts (Grell et al. 1994). In the numerical simulation, a flat bottom with elevation of 1460 m is assumed. This indicates that 850 hPa level is nearly at the land surface. Twenty-three vertical levels are used with 10 hPa at the top of the atmosphere. See the RAMS website: **http://www.rams.atmos.colostate.edu** for more information.

4.2. Triple-Nested Grid System

A triple-nested grid systems (Figure 5) with the same center located at (35.1^{o}N, 103.8^{o}E) is used in this study. The first system (large) extends 720 km in the north-south direction and 540 km in the east-west direction with the grid spacing of 9 km. The second system (medium) extends 270 km in the north-south direction and 216 km in the east-west direction with the grid spacing of 3 km. The third system (small) extends 102 km in the north-south direction and 84 km in the east-west direction with the grid spacing of 1 km.

Lanzhou is located in the smallest box. Roy and Avissar (2000) characterize the convective boundary layer (CBL) over domains with meso-gamma-scale (2-20 km) heterogeneity and find two typical length-scales of the processes when the length-scale of the heterogeneity exceeds 5-10 km: (a) 1.5 times the CBL height for turbulent thermals and (b) heterogeneity scale for organized eddies. Only the simulation in the smallest box is used for the analysis.

4.3. Boundary and Initial Conditions

At the surface, we use USGS vegetation 25-catogory with type-1 for urban/built-up land, and type-4 for mixed dry/irrigational plants (afforestation). The NCEP data along the lateral boundary (every 6 hours) of the largest box from December 1 to 31, 2000 are taken as the open boundary conditionOne way nesting is used for the triple-nested grid system. The larger model provides the lateral boundary conditions for the smaller model using a 5 point-buffer zone. The NCEP reanalysis data on December 1, 2000 are taken as the initial condition. The time step is 60 s for the first grid system, 30 s for the second grid system, and 10 s for the third grid system.

4.4. Numerical Experiments

Two numerical experiments are conducted: (1) with mountain-slope afforestation, and (2) without mountain-slope afforestation. The difference between the two is the land surface. The soil type on the mountain-slope is 4 for Exp-1 (Figure 6) and 1 for Exp-2. Everything else is kept the same for the two experiments. Model difference (Exp-1 minus Exp-2) is analyzed especially the stratification and velocity field. Afforestation decreases the downward motion over the valley (i.e., reduction of the mountain-valley circulation) and stratification (destabilzation). The maximum reduction of the stratification is over the valley (-8^{o}K/km). Such conditions favor the dispersion of valley urban air pollutants and improvement of the air-quality (Figure 7).

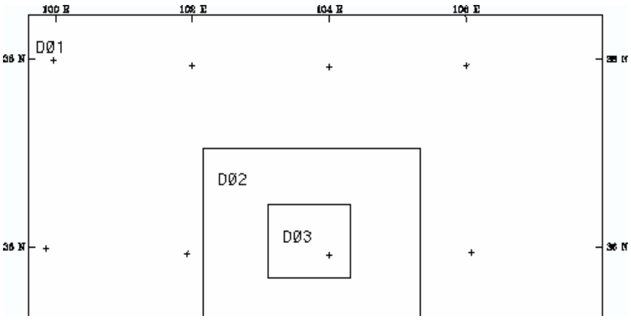

Figure 5. Triple nesting grid system.

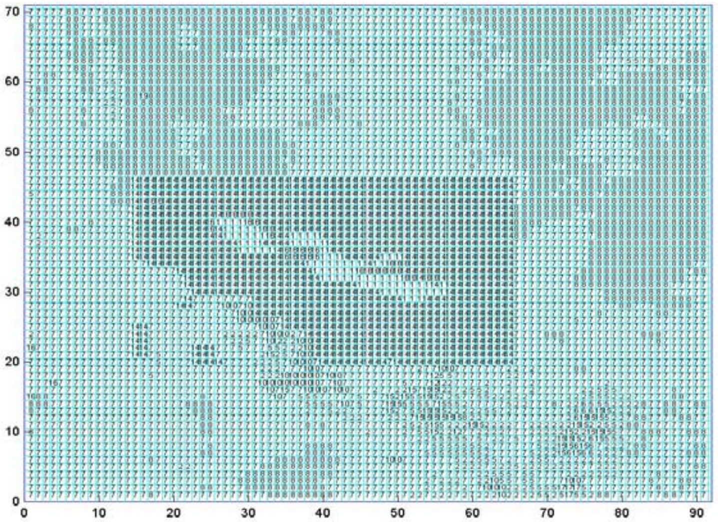

Figure 6. Surface condition for mountain-slope afforestation with the soil type-4. The soil type-4 is replaced by type-1 for experiment without mountain-slope aforestation.

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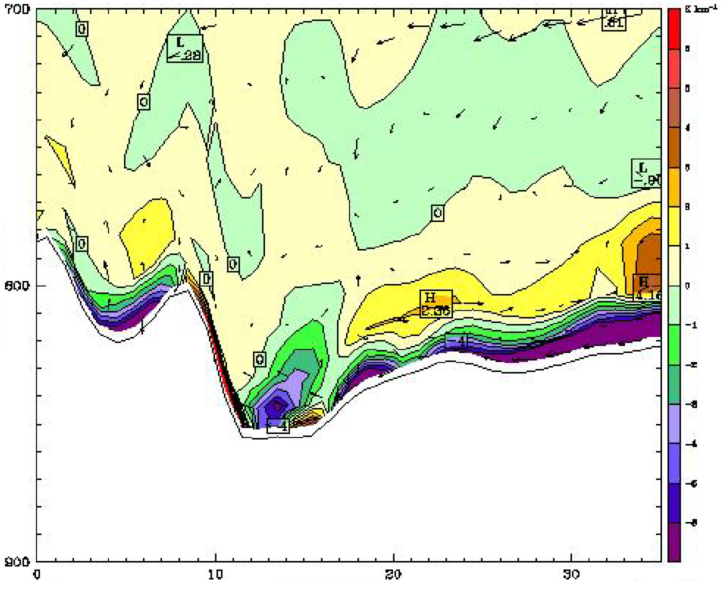

Figure 7. Latitudinal cross-section along 103.8°E of differential (Exp-1 minus Exp-2) stratification (color contour) and (v, w) velocity vectors.

5. AIR POLLUTION MODEL

5.1. Model Description

The Hybrid Particle and Transport (HYPACT) model developed by the Mission Research Corporation (Walko et al., 2001) is used to predict the dispersion of air pollutants in 3-D, mesoscale, time dependent wind and turbulence field. HYPACT allows assessment of the impact of one or multiple sources emitted into highly complex local weather regimes, including mountain-valley and complex terrain flows. In this study, the modeling flow chart is shown in Figure 8. The NCEP data is used to initialize the mesoscale model (RAMS), which provide the velocity field as input to the dispersion model (HYPACT).

5.2. Pollutant Sources

Emission rates from the ground pollutant sources (industrial and residential) were measured such as SO_2, NOx, CO, TSP, etc.. RAMS/HYPACT is integrated from Dec 1, 2000 with the observational pollutant sources to Dec 31, 2000 (Figure 9).

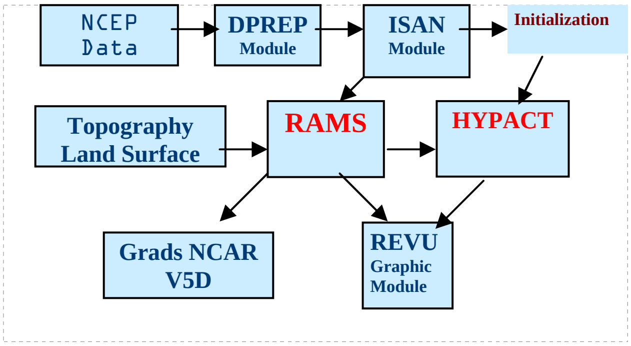

Figure 8. RAMS/HYPACT modeling flow chart.

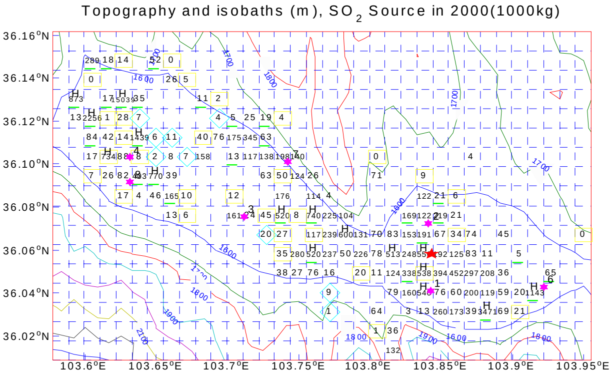
Topography and isobaths (m), SO_2 Source in 2000(1000kg)

Figure 9. SO_2 sources.

5.3. Model Verification

During the prediction period (Dec 1-31, 2000), eight observations of SO_2 were conducted on Dec 25, 2000. Except station-1, the predicted and observed SO2 concentrations agree with each other quite well (Figure 10).

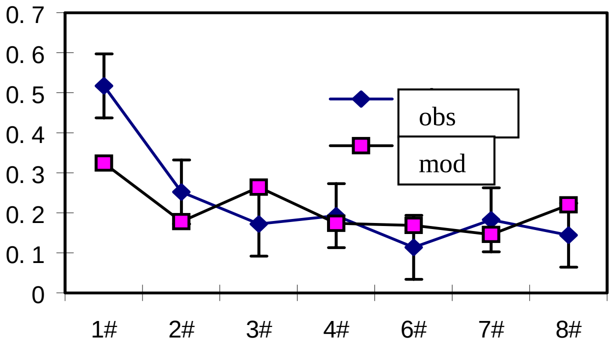

Figure 10. RAMS/HYPACT model verification. The horizontal axis represents station number, and the vertical axis represents observed and predicted SO_2 concentration (unit: mg/m^3).

5.4. Predicted Temporal and Spatial Variability of Air-Pollutants

The RAMS/HYPACT model predicts the air-pollutant concentrations. Here, we show an NOx spreading event from 07h Dec 11 to 07h Dec 12, 2000 as an illustration. Two NOx plumes (concentration > 0.1 mg/m^3) occur at 07h Dec11. On Dec 11, the atmosphere has weak stratification. The plumes disperse to high altitudes. In the morning of Dec 12 (07 h), the stratification strengthens. The two plumes spread horizontally in the valley and cause high NOx concentration.

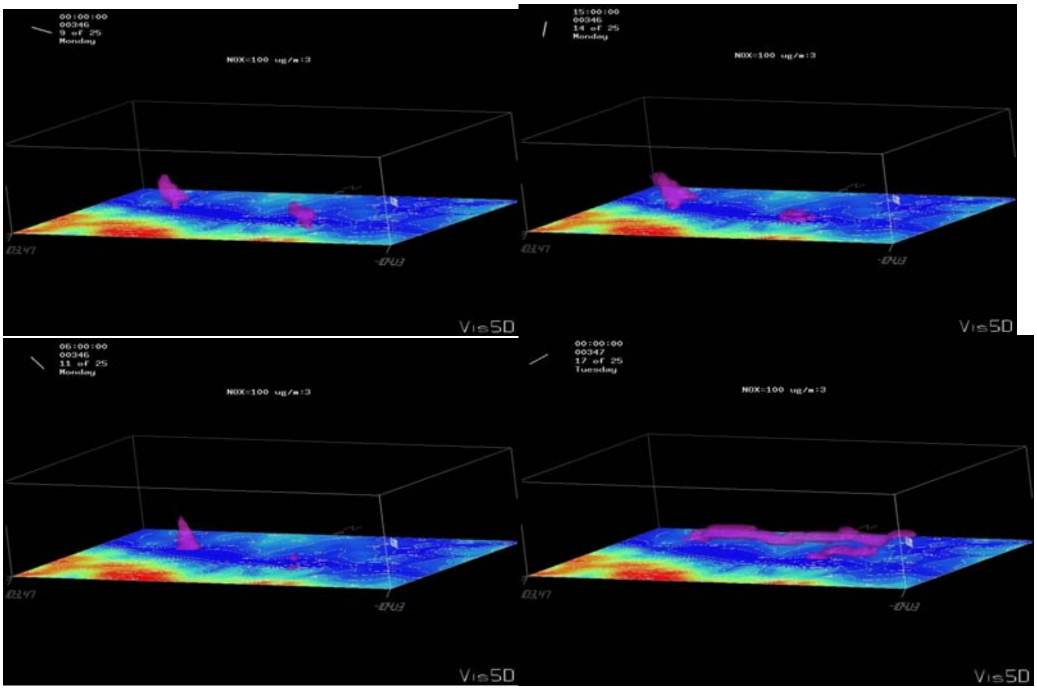

Figure 11. Temporal variation of NOx plumes (concentration > 0.1 mg/m^3): (a) 7 h, Dec 11, (b) 13h, Dec 11, (c) 22h, Dec 11, and (d) 7h, Dec 12, 2000.

6. CONCLUSIONS

This study shows that the mountain-slope afforestation improves the air quality through destabilizing the atmosphere, enhancing the upward motion over the valley, and providing sinks for pollutants. Besides, the RAMS-HYPACT model has capability to predict the transport of pollutants.

7. ACKNOWLEDGEMENTS

This work was jointly supported by the National Natural Science Foundation of China Major Programs No. 40305020, and the Naval Postgraduate School. The data for this study are provided by the program entitled “Air Pollution and Control in Lanzhou” jointly sponsored by the local government of Gansu Province and the Chinese Academy of Science.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

SIZE-RESOLVED SOURCE APPORTIONMENT OF AMBIENT PARTICLES BY POSITIVE MATRIX FACTORIZATION

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ABSTRACT

The size- and time-resolved aerosol samples were collected using an eight-stage DRUM sampler from 29 March to 29 May in 2002 at Gosan, Jeju Island, Korea, which is one of the representative background sites in East Asia. The size-resolved 3-hr average concentrations of 19 elements including S, Si, Al, Fe, Ca, Cl, Cu, Zn, Ti, K, Mn, Pb, Ni, V, Se, As, Rb, Cr, Br were then analyzed using the positive matrix factorization (PMF) technique, in order to identify the possible sources and estimate their contribution to particulate matter mass. Fifteen sources were then resolved in eight size ranges (0.07~12 □), including Chinese aerosol, soil dust, sea salt, biomass burning, coal combustion, oil heating furnace, residual oil fired boiler, municipal incineration, nonferrous metal source, ferrous metal source, gasoline vehicle, diesel vehicle, copper smelter, and volcano emission.

Key Words : Drum sampler, Size distribution, Trace element, PMF, Source apportionment

1. INTRODUCTION

Generally, it is necessary to identify the aerosol sources and estimate their influence on ambient PM concentration, in order to formulate effective control strategies for ambient particulate matter. For that reason, source apportionment has been derived from various statistical methods, such as chemical mass balance (CMB), factor analysis, and multiple linear regression methods. Among them, receptor modeling using aerosol chemical composition data is a reliable method, which can provide information on aerosol sources. However, the commonly used multivariate receptor models such as principal component analysis (PCA) has several drawbacks. The factors of PCA are not always physically realistic, because negative values may appear among factor loadings and factor scores. In addition, PCA can’t handle missing and below detection limit data often observed in the environmental measurements.

Positive Matrix Factorization (PMF) method (Paatero and Tapper, 1994) complements the weak points in the previous receptor modeling. Adjustment of the corresponding error estimates also allows it to handle missing and below detection limit data. Moreover, non-negative constraints are implemented in order to obtain more physically explainable factors (Paatero, 1993).

Composition of ambient aerosol varies with size even in the fine size range (<2.5 □) depending on the type of anthropogenic source. Therefore, more size-segregated composition data are needed in the fine size range in order to improve the accuracy of anthropogenic source apportionment. From this point of view, PMF analysis has been performed in this study on the Gosan aerosol data collected by a DRUM sampler which has merit to collect the fine particles in five stages below 2.5 □. Therefore, it is expected that size-segregated aerosol data collected by a DRUM sampler with high time resolution will improve the efficiency of PMF analysis.

2. SAMPLING AND ANALYSIS

Ambient aerosol collection using an eight-stage Davis Rotating Unit for Monitoring (DRUM) sampling system was made at the western tip of Gosan, Jeju Island, Korea (33^{o} 17’ N, 126^{o} 10’ E, 70m asl), which is a representative background site in East Asia, from 29 March to 29 May 2001. During the measurement period, two Asian dust (AD) outbreaks were observed on 8-10 April and 17 April. In this study, aerosol data pertaining to those AD periods were not subject to PMF and ACWT analysis in order to focus on the estimation of anthropogenic aerosol sources.

The DRUM sampler collects size-resolved aerosol samples on Apiezon^{TM} coated Mylar^{TM} strips in eight stages, having the equivalent aerodynamic cut-off diameters 0.07, 0.26, 0.34, 0.56, 0.75, 1.15, 2.5, 5.0, and 12 □ (Cahill et al. 1985). The DRUM sampler was operated continuously during the 61-day sampling period. The collected aerosol samples were then analyzed for inorganics (19 elements between aluminum and lead) using synchrotron X-ray fluorescence (S-XRF) at the Lawrence Berkeley National Laboratory Advanced Light Source (Perry et al., 2004). A detailed description of the sampling and analysis methods is provided by Cahill et al. (1993).

3. DATA ANALYSIS BY PMF

Positive Matrix Factorization (PMF) method was developed by Paatero (Paatero and Tapper, 1993; Paatero, 1994) to provide flexible modeling approach that effectively uses the information in the data. In PMF, all data matrix X of dimension n rows and m columns, where n and m are the number of samples and species, respectively, can be factorized into two matrix, namely G (n×p) and F (p×m), and the residual part E, where p represents the number of factors extracted.

$$X = GF + E \qquad (1)$$

G is source contribution matrix with p sources, and F is a source profile matrix. PMF provides a solution that minimizes an object function, Q based upon uncertainty for each observation (Paatero, 1994), which is defined as

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{s_{ij}} \right)^2 , \tag{2}$$

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} , \tag{3}$$

where s_{ij} is the uncertainty in the measured data x_{ij}. PMF uses a least squares approach to solve the factor analysis problem with integrating non-negativity constraints into the optimization process, meaning that sources cannot have negative species concentration ($f_{kj} \geq 0$) and sample cannot have a negative source contribution ($g_{ki} \geq 0$). The solution of Eq. (2) is obtained using an iterative minimization algorithm PMF2 (two way PMF) (Paatero, 1994). PMF2 uses the error of measurement in the data to provide optimum data point scaling and permits better treatment of missing and below-detection-limit values. For measurement values below detection limit, x_{ij} was replaced by half of the detection limit and an error corresponding to a relative uncertainty of 100% was assigned to the original error estimate.

A robust mode of PMF2 has been selected for handling outlier data, in order to degrade the disproportional affect of excessively large data points, especially for analyzing environmental data. This can be achieved by introducing a filter function h_{ij} in Eq. (2), the least-squares minimization of Q (Paatero, 1994),

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{h_{ij} s_{ij}} \right)^2 \tag{4}$$

, where

$$h_{ij} = \begin{cases} 1 & \mathit{if} \left| e_{ij} / s_{ij} \right| \leq \alpha, \\ \left| e_{ij} / s_{ij} \right| / \alpha & \mathit{otherwise.} \end{cases} \tag{5}$$

The parameter α is called the outlier threshold distance, and the value $\alpha=4$ was chosen in the present study as done by Lee et al. (1999) and Hien et al. (2004). The other important parameter of PMF2 was F_{peak}, which can be used to control rotations and yield more physically realistic solutions (Paatero et al., 2002). In this study, the rotation was controlled by F_{peak} until an appropriate distribution of the edges is achieved and G space plotting for PMF modeling reveals the independence of the contributions reducing the rotational ambiguity.

4. RESULTS AND DISCUSSIONS

4. 1. Determination Of The Number Of Factors And Rotational Freedom

The information from the scaled residual matrix (**R**) in PMF is used to reduce the ambiguity, due to manual judgment on the number of factors. For each specific number of factors, two parameters are obtained from **R**: *IM*, the maximum individual column mean, and *IS*, the maximum individual column standard deviation (Lee et al., 1999), where

$$IM = \max_{j=1\ldots m} \left(\frac{1}{n} \sum_{i=1}^{n} r_{ij} \right) , \tag{6}$$

$$IS = \max_{j=1\ldots m}\left(\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(r_{ij}-\bar{r}_j)^2}\right). \qquad (7)$$

When the number of factors increases to a critical value, *IM* and *IS* will sharply drop. Figure 1a and 1b show the variation of *IM* and *IS* with different number of factors in eight size ranges. Finally, four to eight factors were found to generate the most reasonable results. After the source profiles were identified without transformation, PMF was run with different F_{peak} values in order to find out a range within which the objective function *Q* value in Eq. (4) remains relatively constant (Song et al., 2001). The largest element in **Rotmat**, a rotational matrix in PMF, is also used to reveal if factors have excessive rotational freedom (Lee et al., 1999). Figure 2.c and 2.d show the variation of *Q* value and largest element in **Rotmat** with the different F_{peak} values. As a result, F_{peak} values of –0.4 ~ –0.9 provided the most physically reasonable source profiles in the eight size ranges.

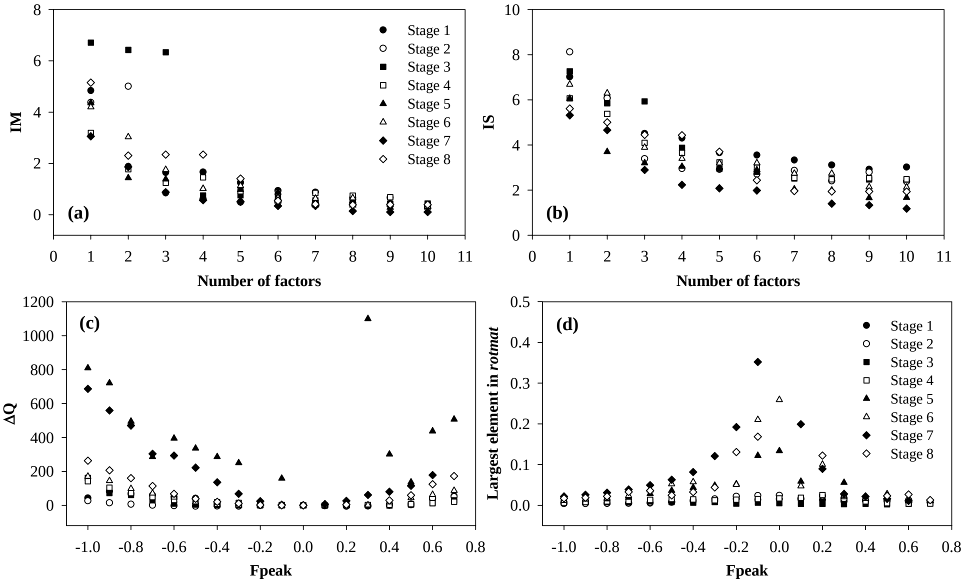

Figure 1. Determination of the number of factors and rotational freedom in eight size ranges by (a) maximum individual column mean (IM), (b) standard deviation (IS) of standardized residuals, (c) Q, and (d) largest element in the rotational matrix.

4. 2. Source Profiles And Temporal Variations

Overall, fifteen distinct primary sources were resolved for the ambient aerosols collected at the Gosan site in spring of 2001 excluding AD periods. Secondary sources were not resolved in this study, because the chemical composition data of secondary particles including sulfate, nitrate, ammonium, and organic carbon matters was not used in PMF analysis. The parameters and results of PMF analysis are summarized in Table 1. The resolved sources include not only natural sources such as soil dust, sea salt, Chinese aerosol, and volcano emission, but also eleven anthropogenic sources such as biomass burning, municipal incineration, coal combustion, oil heating furnace, residual oil fired boiler, gasoline vehicle, diesel vehicle, nonferrous and ferrous metal sources, and copper smelter. The influence of most anthropogenic sources was observed in the fine size range (0.07~1.15 □) while the coarse particles (1.15~12 □) mainly originated from natural sources. Especially, several anthropogenic sources such as gasoline vehicle, diesel vehicle, nonferrous metal source, and residual oil combustion were only resolved in the ultra-fine size range (0.07~0.75 □).

Table 1. The sources identified in each of eight size ranges.

	Source	Major components	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
1	Chinese soil	Si, Al, Fe, Ca, K, S, Pb	+	+	+	+	+	+	+	+
2	Soil dust	Si, Al, Fe, K, Ti, Ca	+	+	+					
3	Sea salt	Cl, S, K, Br	+	+	+					
4	Biomass burning	S, K, Cl, Si, Al				+	+	+	+	+
5	Municipal incineration	Cl, Fe, S, Al, Ca, Zn, Br, Pb	+				+		+	
6	Coal combustion	S, Si, K, Zn, Ca, Fe, As, Se				+	+	+	+	+
7	Oil heating furnace	S, Si, K, Ca, Fe, V, Pb			+	+	+			
8	Oil fired boiler	S, V, Si, Ni						+	+	+
9	Gasoline vehicle	S, Si, Ca Fe, Zn, Cl, K					+	+	+	+
10	Diesel vehicle	Si, S, Al, K								+
11	Ferrous metal source-C	Fe, Zn, Cu, Pb	+							
12	Nonferrous metal source	Cu, S, Zn, Fe, Cr, Pb							+	+
13	Ferrous metal source-F	Fe, Si, Al, K, Zn, Mn		+	+	+	+			
14	Copper smelter	S, Si, K, Fe, Zn, Cu, As, Pb						+	+	
15	Volcano emission	Si, Al, S, K, Ca, Fe, Ti					+			
	Number of samples		411	411	411	411	411	335	381	411
	Number of factor		5	4	5	5	8	6	8	7
	Q (Chi square)		37015	31996	30992	37007	12773	23331	5067	12175
	Fpeak		-0.4	-0.5	-0.9	-0.7	-0.7	-0.6	-0.7	-0.7

The profiles of fifteen sources were determined by taking an average of the similar profiles in different size ranges. The average mass profiles, obtained from PMF analysis, are shown in Figure 2 with the known profiles from the previous works. The resolved source profiles had very similar chemical composition to the corresponding existing source profiles: Chinese aerosol (He et al., 2001), soil dust (EPA profile 41340), marine aerosol (Watson, 1979), volcano emission (Davis et al., 1981), oil heating furnace (Mamoro et al, 1979a), oil fired boiler (EPA 13505), coal combustion (Mamuro et al., 1979a), field burning (EPA profile 42320), municipal incineration (EPA profile 17106), gasoline vehicle (Watson et al., 1994), diesel vehicle (Watson et al., 1994), nonferrous metal source (Mamuro et al.,1979b), ferrous metal related sources (Watson, 1979; Mamuro et al., 1979b), and copper smelter (Small et al., 1981). At this time, the known source profile and the resolved one didn't have exactly the same composition, because the source composition is slightly different from each individual emission source and the known profiles from previous works are simply averaged source composition regardless of aerosol size range. Figure 3 represents the corresponding temporal variations of these possible sources. The mass concentration of each source was calculated from the sum of scaled intensity values in the resolved size ranges. Overall, apparent differences in temporal variations of these anthropogenic sources confirm the independence of the estimated source contributions.

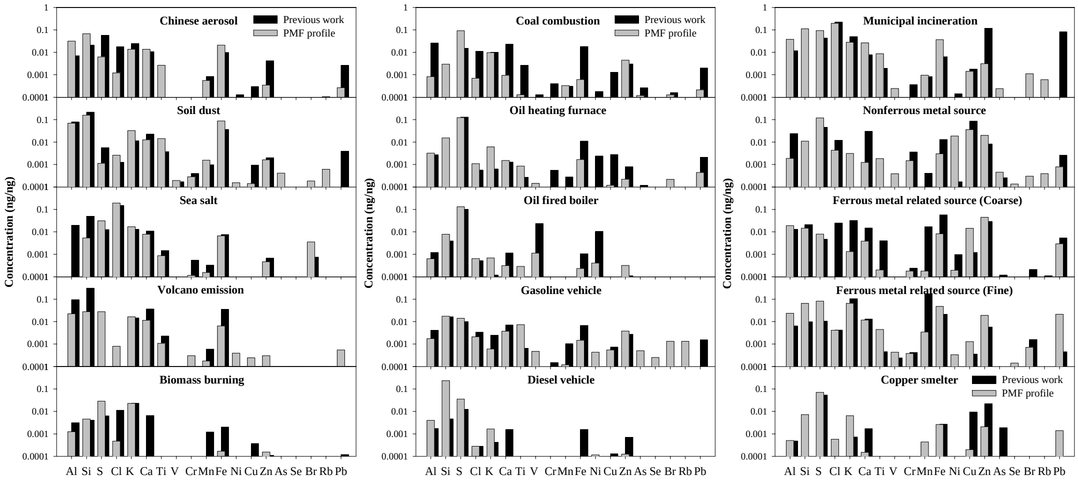

Figure 2. Average source profiles resolved from the size-segregated aerosol samples in this study and the corresponding known profiles.

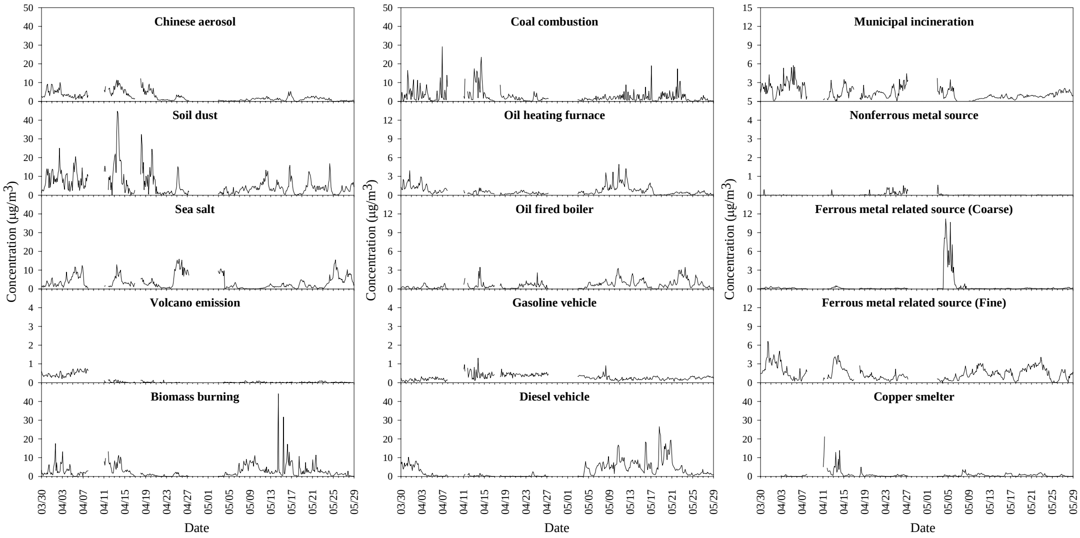

Figure 3. Temporal variations of total mass concentration by each of the resolved sources during the non-AD periods.

Chinese aerosol source usually has higher concentration of S and higher ratio of Ca to Al than general soil sources influenced by various industrial activities (He et al., 2001). This difference helped to identify these factors into different sources in the PMF analysis. These sources commonly contain the characteristic elements Si, Al, Fe, Ca, K and mainly contributed during the first half of the measurement period, especially before and after the AD outbreaks. However, they had different patterns in the temporal variation and size distribution; Chinese aerosol source has lower values and relatively small variations during the entire measurement period while soil dust reveals many sharp peaks over the entire measurement period. The sea salt factor characterized by high Cl and Br was also resolved in the same coarse size range as the soil dust source.

The factors characterized by high S and V in the fine size range (0.07~2.5 □) could be represented by oil combustion source (Watson, 1997). However, these factors were separated into two different sources such as residual oil fired boiler and industrial oil heating furnace sources in order to account for the differences in their chemical composition. In the ultra-fine size range (0.07~0.56 □), the factor containing larger amount of V and Ni represents the influence of residual oil combustion source (Swietlicki and Krejci, 1996). The factor characterized by K, Ca, and Pb in the relatively large size range (0.56~2.5 □) represents the industrial oil combustion source (Kang, 2002). The resulting different temporal variations of the two sources support the separate treatment of these sources.

The coal combustion factor shows the presence of S and As in the fine size range (0.07~1.15 □). Biomass burning source was characterized by K, S and Cl (Song et al., 2001) in the same size range. The municipal incineration source was described by Cl, S, Fe, Br, and Zn (Kang, 2002) in both coarse (5~12 □) and fine size ranges (0.26~0.76 □).

The motor vehicle sources were classified further into gasoline and diesel vehicle sources. The gasoline vehicle source, represented by S, Si, Ca, Fe, Cl, was resolved in the fine size range (0.07~0.75 □). On the other hand, the diesel vehicle source characterized by Si, S, Al, K was only resolved in the ultra-fine size range (0.07~0.26 □). The factor associated with S, Cu, Zn, and Pb which represents the industrial emission source mostly from the non-ferrous smelter (Lee et al., 1999) was resolved in the ultra-fine size range (0.07~0.34 □). The ferrous metal source, mainly loaded with Fe, Mn, and Zn, was resolved in both coarse (5~12 □) and fine size range (0.56~2.5 □). In two size ranges, the ferrous metal related source revealed significantly different source composition and temporal variation, indicating that the detailed emission source and the source region are different in each size range. The other metallurgical source, copper smelter, was also resolved in the fine size range (0.56~0.75 □). Finally the volcano emission source, containing large amount of Al, Si, K, Ca, and Fe, was resolved in the fine size range (0.56~0.75 □).

The effectiveness of PMF analysis has been evaluated by the comparison of the predicted primary PM mass with the measured one as shown in Figure 4. The measured primary PM mass was obtained from the sum of element mass concentrations measured in eight size ranges, while the predicted one was calculated from the sum of scaled source contribution values for each sample. The correlation coefficient between the measured and predicted primary PM masses was 0.82, indicating that the resolved factors effectively accounted for the most of the variations in mass concentration of particulate elements.

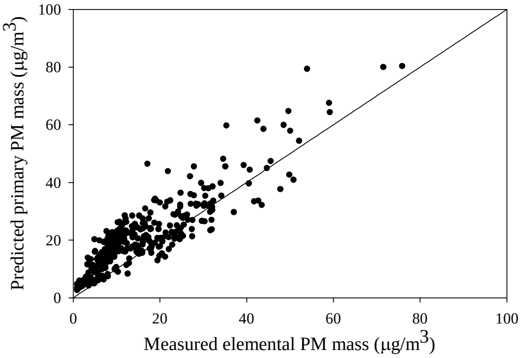

Figure 4. Comparison of the predicted primary PM mass from PMF analysis with the measured one.

4. 3. Source Contributions

The average contribution of each source to the measured total PM mass during the non-AD periods are shown in Figure 5. On average, the estimated fifteen sources from PMF analysis contributed to about 53% of total PM_{12} mass. At this time, soil dust contributed 11%, the largest portion of PM_{12} mass, and natural sources including soil dust, sea salt, and Chinese aerosol occupied about 23%. On the other hand, anthropogenic sources contributed to rather larger portion than natural sources, accounting for 30% of total PM_{12} mass. Especially, the contributions of diesel vehicle, biomass burning, coal combustion, ferrous metal source, and municipal incineration were large in the order, accounting for 6.7%, 6.1%, 5.4%, 3.0%, 2.7%, respectively.

Considering the fact that water soluble ion and carbon components are not included in PMF analysis, the rest fractions of total PM_{12} mass (47%), which can't be described by estimated sources, could be the portion of secondary aerosol components such as ammonium sulfate, ammonium nitrate, and secondary organic carbon matters

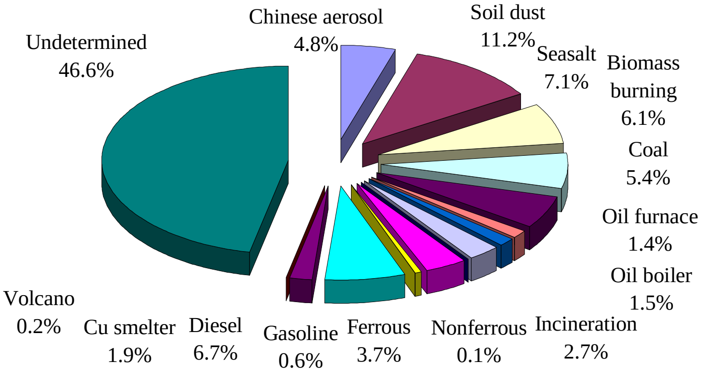

Figure 5. Average source contributions to the total particle mass concentration.

Temporal variations of the total PM_{12} mass and the estimated source contributions are shown in Figure 6, where the contribution by each source is accumulated. It shows that many large peaks in total PM mass are described by the contributions of the resolved sources from PMF analysis. However, the undetermined fraction of

PM$_{12}$ mass reveals rather different temporal variation from those estimated by sources, implying that this fraction originated not from primary emission sources but from secondary particulate matter. In addition, the contributions of various sources reveal different temporal variations, according to the aerosol size range. Source contributions in three different size ranges are assessed separately in Figure 8. Figure 8.b shows that the contribution of natural sources including soil dust, sea salt, and Chinese aerosol was dominant, making up for 79% in the coarse size range (2.5~12 □). On the other hand, the contribution of anthropogenic sources, such as coal combustion, biomass burning, and diesel vehicle, sharply increased in the fine and ultra-fine size range (0.07~2.5 □) as shown in Figure 8.c and 8.d. Especially, the contribution of diesel vehicle (52%) was mainly observed in the ultra-fine size range (0.07~0.56 □) while the coal combustion source (33%) contributes mostly in the fine size range (0.56~2.5 □). The effect of anthropogenic sources increased up to 98% of the total contribution in the ultra-fine size range (0.07~0.56 □).

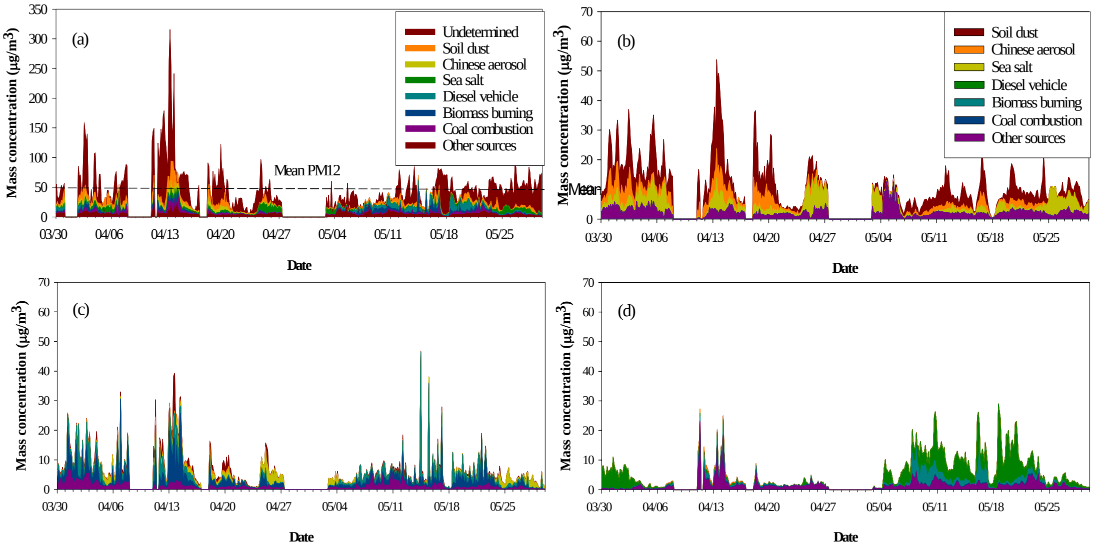

Figure 6. Temporal variation of PM mass contributed by different source types (a) in total size ranges, (b) in the coarse size range (2.5~12 □), (c) in the fine size range (0.56~2.5 □), and (d) in the ultra-fine size range (0.07~0.56 □).

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

DETERMINING OF GEOGRAPHICAL AND TOPOGRAPHICAL CHARACTERISTICS AND OF URBAN ROUGHNESS ELEMENTS IN TEHRAN FOR AIR QUALITY MODELING

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ABSTRACT

One of the most important problems in mega cities like Tehran is air pollution. Air quality management systems are well developed in industrial and in many developing countries such as Iran. Air quality models are coupled with numerical weather prediction (NWP) models in order to forecast urban air quality temporally and spatially temporal and local forecasting of urban air pollutants. In fact NWP models outputs are air quality models inputs. Some basic and important steps are required to implement such models. In this article, we try to do these basic steps for a case study of urban air quality in greater Tehran area. First step is introducing meteorological and urban air pollution monitoring stations network. Then Tehran's geographical characteristics are discussed. In next the step we determine topographical aspects of the region. Tehran is surrounded by mountains; therefore this is located in a valley and air ventilation is the most important factor for diluting polluted air. In the next step, some various locations such as industrial, commercial, residential and vegetation ones are determined in greater Tehran area. Finally, urban roughness lengths are estimated using urbanization information in the area.

Keywords: Air Quality Management, Air Quality Modeling, Numerical Weather Prediction, Roughness Length.

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

AIR POLLUTION IN URBAN AREA COULD HIGHLY ALTER THE BIOCHEMISTRY OF HUMAN TEARS!

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ABSTRACT

Human eyes are subjected to many man made and natural environmental pollutants. Emissions of motor vehicles, for example, are a very major source of heavy metals. On the other hand, many chemicals originated from industrial and agricultural activities as well as dust and various pH conditions are other causes of air pollution. Stability and functionality of tear film plays an important role in ocular surface diseases. Dry-eye patients typically suffer from discomfort, burning, irritation, photophobia and blurred vision. They are subjected to increased risk of corneal infection and resulting irreversible tissue damage. Analysis of tear film components, especially tear protein profiles has played a significant role in diagnostic of ocular surface diseases and in development of new therapies. The aim of this piece of research was to study the effect of environmental pollutants to the stability of tear proteins. 100 healthy volunteers, 50 lived in Rasht, a city in North of Iran near Caspian Sea (group I), and 50 (group II) lived in south of Tehran, the Capital of Iran with highly polluted air due to industrial activities and congested traffic. The subjects, all male and aged 20-30 years old, filled a questioner in order to get some information about their health and eye disorders history. Total tear proteins and lysozyme concentration were measured and the proteins separated by sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE). The results showed some alternations in tear protein pattern of group II compared to group I. The number of electrophoretic bands in tears of group II, i.e. people living in highly polluted air conditions was about 25% more than non-smokers. The activity of lysozyme and total tear proteins were also higher in this group. The results indicate that the environmental conditions and presence of some toxic metals in the air increase the production of tear immunoglobulin and activity of lysozyme. It is not surprising that the incidence of dry eye syndrome be higher in this second group.

Key words: Human tears, air pollution, dry eye, lysozyme activity.

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

PHOTOCHEMISTRY OF REDUCED SULFUR COMPOUNDS IN A LANDFILL ENVIRONMENT

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ABSTRACT

The photochemical conversions of RSCs compounds (e.g., DMS, CS_2, H_2S, DMDS, and CH_3SH) to a further oxidized form, SO_2 were evaluated in the landfill site in Daegu, Korea during a wintertime period (e.g., 13-16 Jan 2004) using a photochemical box model. The chemical species of RSCs, which may exert influences on the SO_2 production depending on sampling conditions, were found to include DMS, DMDS, and H_2S. RSC contribution to the observed SO_2 levels was insignificant in the sampling sites investigated. The photochemical conversion of the RSCs in the landfill can account for about 15% of the observed SO_2, on average.

Key Words: RSCs; H_2S; SO_2; landfill; Daegu

1. INTRODUCTION

Landfill has been used as a final depository to dispose of most industrial, construction, and municipal wastes in most countries (e.g., US, UK, Mexico, Turkey, etc.) (OECD, 2002). In the landfill, waste degradation takes place under anaerobic conditions, with an initial stage of acidic stabilization and ending in malodorous gas emissions in the surroundings (Vandergheynst et al., 1988). Landfill facilities are considered to be important sources for a wide range of trace gases including methane (CH_4), volatile organic compounds (VOCs), and reduced sulfur compounds (RSCs).

The major RSCs found in the atmosphere are carbon disulfide (CS_2), dimethyl sulfide (CH_3SCH_3, DMS), and hydrogen sulfide (H_2S) (Berresheim et al., 1995; Watts, 2000). In the case of landfill, other RSCs, which include methyl mercaptan (CH_3SH), dimethyl disulfide (CH_3SSCH_3, DMDS), and so on, also constitute significant portions of trace gas emissions (Kim et al., 2005). The concentrations of RSCs in the landfill sites were significantly higher than those in the ambient air by three orders of magnitude (Kim et al., 2005). However, the data for RSCs in this potential source area are still extremely sparse; thus quantitative knowledge of sulfur gas speciation is lacking. Recently Muezzinoglu (2003) found that ambient SO_2 concentrations were affected closely by both total organic sulfur compounds and certain individual components such as DMS and H_2S emitted from polluted creeks carrying wastewaters from industrial and residential areas. Hence, investigations of the absolute and relative distributions of RSCs and their photochemistry may be highly valuable in evaluating the sulfur gas cycle in strong source environments such as landfills. For instance, acquisition of the SO_2 yield rate from RSC oxidation in landfills can be valuable in assessing their impact on the formation of secondary particles in the urban air.

In this study, the oxidation chemistry of RSCs was investigated using the full scale oxidation mechanisms of RSCs, particularly for DMS and DMDS. In addition, the photochemical conversion of RSCs and their impact on the distribution of stable end-product SO_2 were assessed based on a photochemical box model.

2. METHODS

For the model computation, 5 selected RSCs (e.g., H_2S, DMS, CS_2, CH_3SH, and DMDS) were measured along with SO_2. To better explain their relationships, atmospheric trace gases O_3, NO_X, CO, CH_4, and non-methane hydrocarbons (NMHCs) were also continuously measured concurrently with the meteorological parameters of temperature, relative humidity, solar radiation, and so on. RSC measurements were made 2 times per day (e.g., morning period (10:00-10:45) and afternoon period (16:00-16:45)) from all eight sampling sites in the studied landfill located in Daegu Korea. This study was conducted during a winter period, from January 13-16 2004 (Fig. 1).

The landfill is located in Bangchun district, approximately 10 km west of the central area of Daegu city. Eight sampling locations were chosen for the collection of ambient RSCs samples in the study area as shown in Fig. 1. The studied landfill was built in 1990 and is still in operation, with waste undergoing sanitarization before burial. It is partly covered in its upper part and landfilling is still progressing in the rest of landfill area.

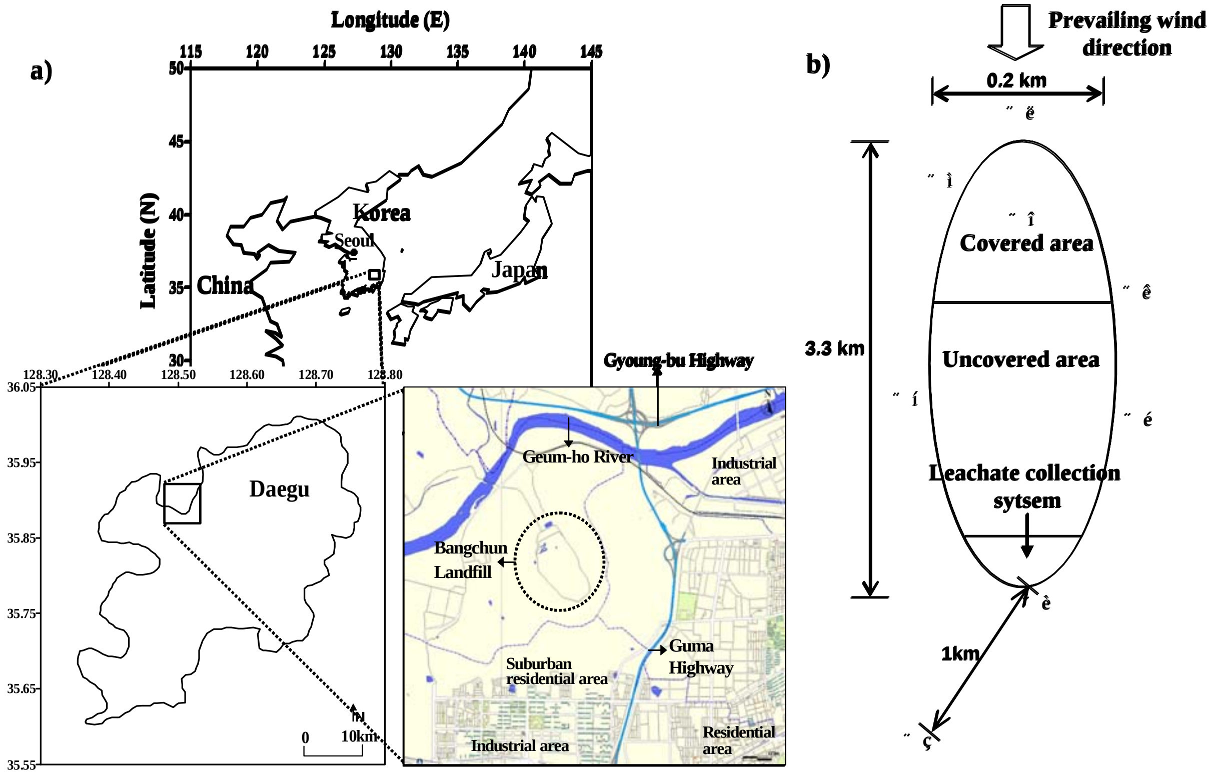

Figure 1. a) Location of sampling area (35°52' 07" and 128°31' 00") in Daegu, Korea and b) characteristics of landfill: site 1=residential area; site 2=near the landfill gate; sites 3-7=circumference of landfill; and site 8=within landfill area; northerly wind is dominant during sampling period; a slope of landfill is 15°; and total area of 596,764 .

Landfill gas samples were collected by the vacuum sampling method using a 10-liter Tedlar bag sampler (SKC corp. USA). These samples were then brought to the laboratory for analysis within 24 hours to minimize the possibility of RSC loss due to long-term storage. The RSCs were determined by a GC system (Donam Instruments, Model DS 6200) equipped with a pulsed flame photometric detector (O.I. Co., Model 5380).

For the analysis of the RSC oxidation pathway, the diurnal profiles of OH and NO_3 were generated by the photochemical box model (PCBM), which includes a full spectrum of $HO_x/NO_x/CH_4$/NMHCs interactions. The PCBM was chemically constrained to the observed input data sets of O_3, NO, NO_2, CO, SO_2, CH_4, (and DMS). In brief, this model contains: 1) 59 HO_X-N_XO_Y-CH_4 gas kinetic/photochemical reactions; 2) 146 NMHC reactions; and 3) 12 heterogeneous processes. Concentrations of SO_2 derived from the RSC oxidation chemistry were calculated using a mass-balance approach. These procedures are based on Eq. (1).

$$\frac{d[SO_2]_{OXD}}{dt} = \{P(DMS) + P(H_2S) + P(CS_2) + P(DMDS) + P(CH_3SH)\} - L(SO_2)[SO_2]_{OXD}$$

(1)

where $[SO_2]_{OXD}$ represents SO_2 concentrations produced from each respective RSC of interest; P(DMS), P(H_2S), P(CS_2), P(DMDS), and P(CH_3SH) are the photochemical production rates of SO_2 from the oxidation of their respective RSC counterpart; and L(SO_2) is the photochemical loss frequency of SO_2. The total first-order loss parameters of SO_2, L(SO_2) include gas-phase chemical losses, the physical removal processes defined by the wet/dry deposition to the surface, the scavenging by aerosols and cloud/fog droplets, and the dilution by vertical transport. Values of L(SO_2) were taken to correspond to SO_2 lifetimes (i.e., $\tau(SO_2)$) of 6, 12, and 24 hours. These L(SO_2) values were chosen based on Bae and Kim (2003), who reported the relative contribution of SO_2-to-sulfate conversion processes (i.e., oxidation by OH, liquid phase oxidation by H_2O_2, O_3, and O_2 in the presence of catalytic metal ions, and absorption of aerosol surface) in the urban area. The full sulfur chemistry model used in this study includes the sum of 88 gas-phase reactions and 9 heterogeneous reactions of sulfur species. The significant fractions of DMS and DMDS oxidation mechanisms were adopted from Yin et al. (1990).

3. RESULTS AND DISCUSSION

3.1 The distribution of RSCs in- and outside landfill site

A statistical summary of all RSCs measured during the study period is provided in Table 1. Comparing the magnitude of RSC concentrations, their values tend to decrease in the order of H_2S, DMS, CS_2, CH_3SH, and DMDS. H_2S varied from 0.01 to 27 ppbv with a mean value of 4 ppbv (a median value of 2 ppbv). Distribution of RSCs in the landfill was somewhat different from that in the ambient air of the Seoul metropolitan area, which was reported by Shon and Kim (2005). For instance, H_2S concentrations in the landfill were significantly higher than those in the ambient air by a factor of more than 10. Mean H_2S concentration in the ambient urban air of Seoul was 0.1 ppbv. However, our H_2S level in the landfill was significantly lower than that measured in polluted creeks in Turkey having a median value of 25 ppmv (Muezzinoglu, 2003). The spatial distribution of RSCs can be used as a clue to explain the impact of strong source processes on the surrounding environment. As shown in Fig. 1, it is reasonable to expect that sites 2 through 8 are more sensitive to the landfill's influence than site 1. In Table 1, the spatial distribution of RSCs is summarized in terms of the site number. In general, most RSC concentration levels in site 1 were significantly lower than those within the landfill boundary (sites 2-8; e.g, up to one order of magnitude for site 8), as those measured in site 8 were significantly higher. However, CH_3SH and DMS concentration levels in site 1 were not notably different from those determined in the landfill boundary (e.g., sites 3-7). In addition, except for H_2S there were no distinct differences in concentrations of most RSCs between morning (e.g., 10:00-10:45 LST) and afternoon (e.g., 16:00-16:45 LST).

Table 1. A summary of RSCs and environmental parameters measured during the field campaign in the Daegu landfill site.

Site No.	H_2S[a]	CH_3SH[a]	CS_2[a]	DMS[a]	DMDS[a]	Temp(°)	NO_2[b]	NO_X[b]	O_3[b]	SO_2[b]	CO[c]	CH_4[c]	NMHC[c]
1	883±815[d]	24±18	99±58	236±193	37±71	0.2±2.3	16±13	26±29	24±11	8.5±5.5	0.3±0.2	60±23	0.6±0.4
	(576)[e]	(22)	(70)	(148)	(9)	(-0.2)	(15)	(19)	(24)	(8.5)	(0.3)	(55)	(0.7)
	10-2057[f]	6-54	48-184	89-597	4-183	-2.8-3.7	1-38	1-80	6-38	2.0-15.0	0.1-0.6	35-97	0.1-0.9
2	442±341	27±11	135±69	264±181	31±43	0.5±2.3	17±15	29±35	24±12	7.8±5.5	0.3±0.2	48±16	1.8±1.1
	(620)	(33)	(115)	(167)	(11)	(0.1)	(14)	(18)	(23)	(7.0)	(0.3)	(44)	(1.7)
	26-760	10-36	45-215	125-542	5-107	-2.7-4.2	1–44	1-98	5-40	1.0-15.0	0.1-0.5	29-73	0.8-2.9
3	848±525	15±8	98±10	100±14	6±2	0.1±2.5	17±12	26±26	23±11	7.8±5.3	0.3±0.1	60±23	1.0±1.1
	(1110)	(14)	(104)	(99)	(7)	(-0.7)	(16)	(20)	(23)	(6.5)	(0.3)	(60)	(1.0)
	245-1191	7-23	87-104	87-115	4-8	-3.0-4.2	2–39	2-76	6-37	2.0-14.0	0.1-0.5	32-98	0.2-1.8
4	1282±605	22±6	103±48	193±139	11±4	0.1±2.6	16±12	25±26	25±12	7.8±5.3	0.3±0.1	65±25	0.8±0.1
	(1111)	(22)	(101)	(147)	(11)	(-0.7)	(14)	(18)	(25)	(6.5)	(0.3)	(71)	(0.9)
	782-2333	15-31	33-158	108-437	5-15	-3.0-4.2	2-38	2-75	6-41	2.0-14.0	0.1-0.5	35-98	0.7-1.0
5	3572±2565	31±23	99±43	196±150	13±7	0.1±2.9	16±14	25±29	24±12	8.2±5.1	0.4±0.2	77±29	4.2±3.2
	(2928)	(27)	(101)	(139)	(11)	(-0.8)	(12)	(17)	(25)	(7.5)	(0.4)	(90)	(5.1)
	607-7566	8-62	47-158	108-462	7-24	-3.5-4.0	1-40	1-82	6-41	2.0-15.0	0.2-0.5	31-102	0.6-6.8
6	4989±3615	50±60	149±89	255±227	60±73	0.7±1.9	18±14	29±30	23±11	7.7±5.0	0.4±0.2	50±16	1.7±1.4
	(4318)	(22)	(119)	(138)	(20)	(0.4)	(15)	(19)	(24)	(8.0)	(0.4)	(48)	(1.2)
	1503-11289	18-171	65-317	98-669	5-170	-1.9-3.6	1-40	1-83	6-36	1.0-14.0	0.1-0.6	29-72	0.7-3.3
7	6112±5813	75±70	98±32	296±173	73±76	0.7±2.2	18±14	30±32	24±11	8.5±5.3	0.3±0.2	52±15	1.3±0.5
	(3384)	(42)	(95)	(280)	(49)	(0.3)	(15)	(20)	(23)	(9.0)	(0.3)	(52)	(1.3)
	427-14485	21-183	61-151	125-608	7-200	-1.9-3.8	1-42	1-91	6-38	1.0-14.0	0.2-0.5	29-68	0.8-1.7
8	13169±8944	80±93	192±96	1897±3799	81±137	0.1±2.9	15±14	24±28	25±13	7.3±5.8	0.3±0.2	60±27	4.5±2.3
	(9079)	(47)	(179)	(308)	(28)	(-0.4)	(12)	(15)	(26)	(6.0)	(0.3)	(57)	(4.5)
	5457-27005	17-265	71-334	99-9625	9-358	-4.0-4.3	1-39	1-78	6-42	1.0-14.0	0.1-0.5	32-97	2.9-6.1

a: unit in pptv; b: unit in ppbv; c: unit in ppmv; d: mean ± 1σ; e: (median); and f: min.- max.

Typically, n=6 in each site for each RSC; n=96 (e.g., 4 days × 24 (hourly mean)) in each site for meteorological parameters and trace gases (NO_x, O_3 etc.)

3.2 Contribution of the RSC oxidation to SO_2 levels in landfill sites

Contribution of the oxidation of individual RSCs (e.g., $[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, $[SO_2]_{CS2}$, and $[SO_2]_{H2S}$) to the observed SO_2 levels is given in Fig. 2. Overall, the proportion of SO_2 concentrations, total $[SO_2]_{OXD}$, converted from the oxidation of 5 RSCs, was episodic depending on the sampling period, ranging from <1 to 80% with a mean value of 13%. The total $[SO_2]_{OXD}$ during the first two days (e.g., Jan 13-14) was significantly higher than that during Jan 15-16, by a factor of 15 on average. In addition, the major compounds of RSCs which make significant contributions to total $[SO_2]_{OXD}$ were DMS, DMDS, and H_2S. As shown in Fig. 2, the significant contribution of RSC oxidation to observed SO_2 levels occurred on Jan 13, ranging from 30 to 80% with a mean value of 45%, based on our standard model runs (23% for the minimum case). The significant fraction of total $[SO_2]_{OXD}$ was derived by DMDS oxidation on that day. However, the RSC contribution in most sites on the other days was insignificant (e.g., <10%), except for sites 5-8 (15-50%) on Jan 14, based on our standard model runs as well as the maximum case runs.

In order to identify the source contribution of SO_2 in the landfill, the correlation patterns between RSCs and SO_2 were examined. In most cases, there were no clear correlations between them. However, there was a case with a clear correlation (e.g., r^2=0.53) between DMS and SO_2 during the study period. The strong negative correlation between the RSC and SO_2 may be expected with a sampling resolution significantly less than 1 day if the following conditions are met: (1) the oxidations of RSCs are the significant source of SO_2 in ambient air and (2) SO_2 production from non-chemical sources (i.e., anthropogenic sources or transport) is not significantly larger than that by RSC oxidation. In field experiments, there have also been some reports for the strong negative correlation between DMS and SO_2 in the clean marine boundary layer (MBL) (Bandy et al., 1996; Davis et al., 1999). In contrast, there was no strong correlation in the MBL on Jeju Island, Korea, which was occasionally influenced by the long range transport of air mass from China and/or the Korean peninsula, according to our previous study (Shon et al., 2004). The atmospheric SO_2 levels on Jeju Island during the sampling period could not be explained solely in terms of DMS oxidation. A clear correlation between these two sulfur species was not noticed previously in the anthropogenically influenced regions such as a coastal site in Brittany, France (Putaud et al., 1999), the Western North Atlantic Ocean (Berresheim et al., 1991), and the Arctic BL (Leck and Persson, 1996)). Meanwhile, there was a weak negative correlation between DMDS and SO_2, although the relative contribution of DMDS oxidation to the total $[SO_2]_{OXD}$ is higher than that of DMS oxidation.

The contribution of DMS oxidation, $[SO_2]_{DMS}$, ranged from 5 to 37% of oxidized SO_2 levels from total RSC (i.e., total $[SO_2]_{OXD}$) with a mean value of 16%, depending on measurement points and the time period. There were significant temporal variations in relative contribution of DMS oxidation. In other words, although the absolute levels of total $[SO_2]_{OXD}$ on Jan 13 were relatively higher, the relative DMS contribution, $[SO_2]_{DMS}$, was significantly lower than those on the other days (e.g., Jan 14-16) by a factor of 3. For spatial distribution of $[SO_2]_{DMS}$ at the sampling sites, sites 1-4 showed similarity in $[SO_2]_{DMS}$ levels; however, sites 5-8 showed slightly lower levels by a factor of 2.5.

In the mean time, the contributions of DMS oxidation by the major oxidants, OH and NO_3 during the study period ranged from 32-62 and 38-68%, respectively. For DMS oxidation by OH, the addition channel during the study period was dominated by cold temperatures. The branching ratios of abstraction and addition channels were 35 and 65%, respectively. Our model simulation indicated that the significant fractions of SO_2 converted from DMS oxidation by OH were produced by the abstraction channel under high NO_x conditions, although the addition channel favors cold temperature.

For DMDS, its contribution to the oxidation pathway (e.g, the ratio of $[SO_2]_{DMDS}$ to total $[SO_2]_{OXD}$) was highly variable, ranging from 12 to 91% with a mean value of 42%. The higher contribution of its oxidation to both total $[SO_2]_{OXD}$ and observed SO_2 levels occurred only during the first day of the sampling period. On the other days, the contribution of its oxidation to total $[SO_2]_{OXD}$ was high, but its contribution to the observed SO_2 levels was insignificant (e.g., <10%). For CS_2, the contribution of its oxidation, $[SO_2]_{CS2}$, to total $[SO_2]_{OXD}$ was negligible (e.g. <4%). In addition, the contribution of CH_3SH oxidation, $[SO_2]_{CH3SH}$, to total $[SO_2]_{OXD}$ was insignificant, ranging from 1 to 11% with a mean value of 4%. In contrast, the contribution of H_2S oxidation, $[SO_2]_{H2S}$, to total $[SO_2]_{OXD}$ fell in a wide range from <1 to 78% with a mean value of 37%. A high contribution of its oxidation to both total $[SO_2]_{OXD}$ (e.g., 78%) and observed SO_2 levels (e.g., 40%) existed only in site 8 on Jan 14. Its contribution to the total $[SO_2]_{OXD}$ was relatively high (e.g., 43% on average) during most study periods, except for the day of Jan 13 (e.g., 5%), but that to the observed SO_2 levels was insignificant (e.g., <4%) .

4. CONCLUSION

In this study, the environmental behavior of RSCs in landfill conditions was investigated in terms of their temporal and spatial distributions and through their oxidation pathways. The results of the ambient measurements indicated that the distribution patterns of RSCs in the landfill were clearly different from those commonly observed in the ambient air (i.e., significantly higher H_2S levels in the landfill). In addition, the photochemical conversions of RSCs of DMS, CS_2, H_2S, DMDS, and CH_3SH to SO_2 were examined using a photochemical box model with the data collected at the landfill site during the winter period. At the end of the study, it was found that the ratio of the SO_2 in the air obtained from the oxidation of the 5 selected RSCs to the overall SO_2 concentration measured directly in the air was not uniform. Rather, it was dependent on the environmental conditions of the day such as the magnitude of each RSC level. In general, the RSC contribution to SO_2 observations was insignificant in most sites. DMDS and H_2S may also exert influences on the SO_2 production depending on sampling conditions, but there were no clear correlations between these RSCs and SO_2.

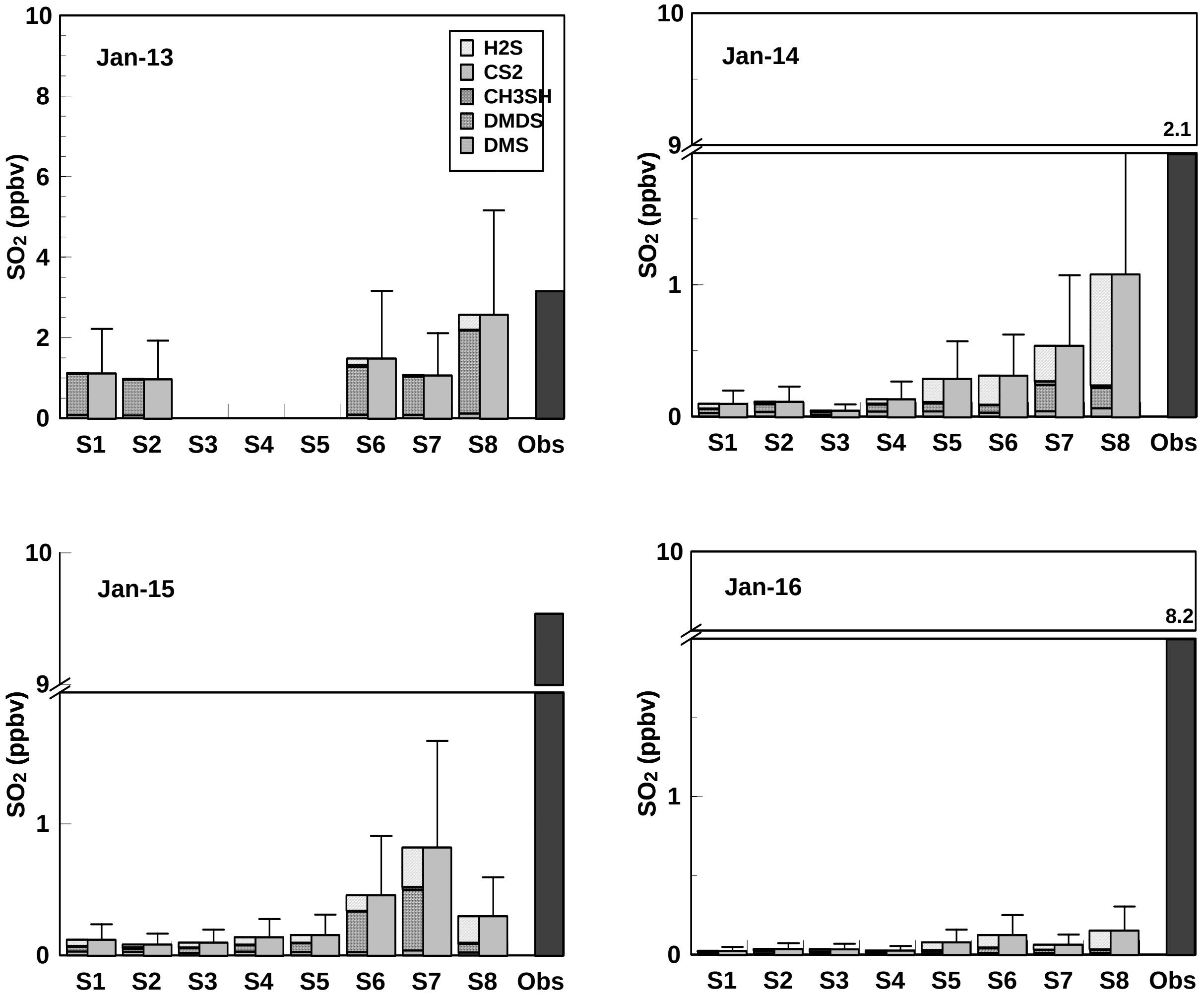

Figure 2. Comparison of observed SO_2 with model simulated values ($[SO_2]_{OXD}$). S1-S8 represent site numbers and Obs (the last bar in black) represents the mixing ratio of observed SO_2. The first bar represents the contribution of individual RSC to observed SO_2 ($[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, $[SO_2]_{CS2}$, and $[SO_2]_{H2S}$). The best estimate for $[SO_2]_{OXD}$ (our standard model run, sum of $[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, $[SO_2]_{CS2}$, and $[SO_2]_{H2S}$) is defined by the

second solid bar with a vertical line and corresponds to $\tau(SO_2)$=0.5d. The top of the vertical lines within each second bar defines the upper limit of model estimates (corresponding to $\tau(SO_2)$=1d) for the mixing ratio of SO_2 when produced from RSC oxidation.

5. ACKNOWLEDGMENTS

This research was supported by the Climate Environment System Research Center, sponsored by the SRC program of Korea Science and Engineering. The second author would also like to thank supports made by a Korea Research Foundation Grant (2003-015-C00680).

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

TRANSPORT OF OZONE IN DOWNWIND AREA FROM SEOUL METROPOLITAN AREA IN KOREA

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ABSTRACT

Recently, high ozone episode occurred frequently in Korea. Moreover ozone episode frequently occurred not only in the city but also in background area where local anthropogenic sources are not important. It analyzed frequency exceeding 100ppb ozone at monitoring stations in Seoul and background area during 2001-2004. Mean of occurrence frequencies for 29 Seoul station and for 12 background stations during 2001-2004 were 7.2, 13.3 respectively. So, it should be noted that ozone concentration in the background area are higher than that of in the city.

Key Words : ozone, transport, background concentration

1. INTRODUCTION

Ozone pollution in urban areas has important implications for health and environmental management. Recently, ozone concentration greatly increases in Korea(fig. 1). As metropolitan area in Korea, the population of Seoul and its surrounding cities is about 20 million people. However ozone episode frequently occurred not only in the city but also in background area where local anthropogenic sources are not important. In the present study, the aspects of high ozone episode in selected background stations were analyzed.

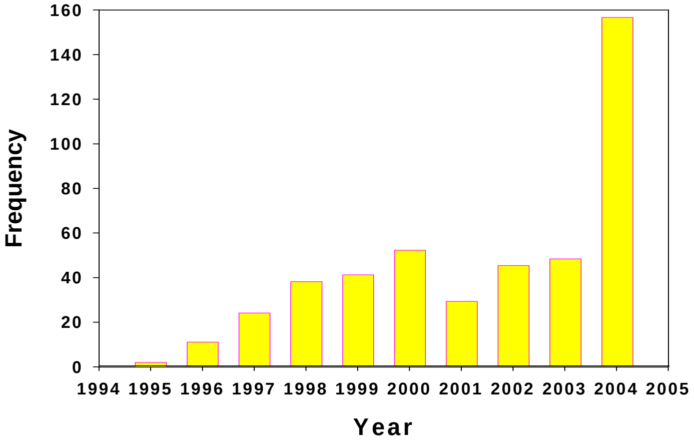

Figure 1. Total frequency of ozone warning (over 120ppb) in Korea(1994-2004)

2. DATA AND ANALYSIS

According to direction of wind in metropolitan region, it becomes the downward region of metropolitan area. The monitoring stations in background of the Seoul Metropolitan are presented in fig. 2. Inside Seoul city, there are 29 monitoring stations. We selected the ozone episode cases, i.e., daily maximum ozone concentration exceeded 100ppb during 4 years(2001-2004).

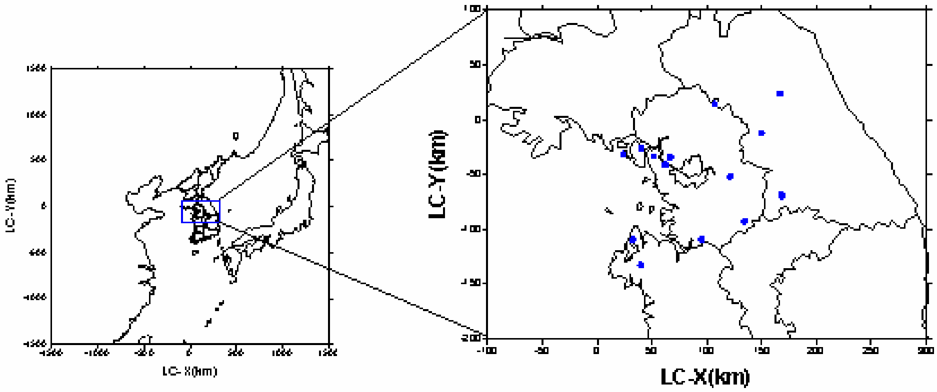

Figure 2. The monitoring sites(●) of   O3 in the study area.

3. RESULTS

3.1 Characteristic of high ozone occurrence in background stations

Table 1 shows frequency of high ozone exceeded 100ppb. In particular, high concentration ozone much occurred in station number 6(132113), 7(632121) and 9(131441) at late afternoon (after 17 LST).

Fig. 3 shows exceeding frequency 100ppb ozone at monitoring stations in Seoul and background area during 2001-2004. Mean of occurrence frequencies for 29 Seoul station and for 12 background stations during 2001-2004 were 7.2, 13.3 respectively. So, it should be noted that ozone concentration in the background area are higher than that of in the city.

Chuncheon is a small city located in northeast region of Seoul Metropolitan area and population is about 250 thousand people. When wind condition was southwestly, daily maximum ozone concentration occurs at late afternoon (after 17 LST) in Chuncheon. When high concentration happened in Chuncheon after 17 LST, ozone concentration in Seoul were much lower than in Chuncheon.

Table 1. Frequency of high concentration ozone (100ppb over) in the study area.
(unit : day)

	station no.	total freq. over 100 ppb	2001	2002	2003	2004	before 16(LST)	After 17(LST)
1	831481	36	12	9	15	0	19	17
2	823691	13	4	1	6	2	10	3
3	131473	12	0	7	0	5	10	2
4	131451	13	-	10	3	0	6	7
5	132401	3		3	0	0	0	3
6	132113	18	8	8	2	0	3	15
7	632121	14	4	5	4	1	3	11
8	632122	13	0	1	6	6	7	6
9	131441	15	1	1	13	0	3	12
10	131341	23	3	9	5	6	14	9
11	534421	12	-	5	4	3	9	3
12	534422	12	-	2	8	2	4	8

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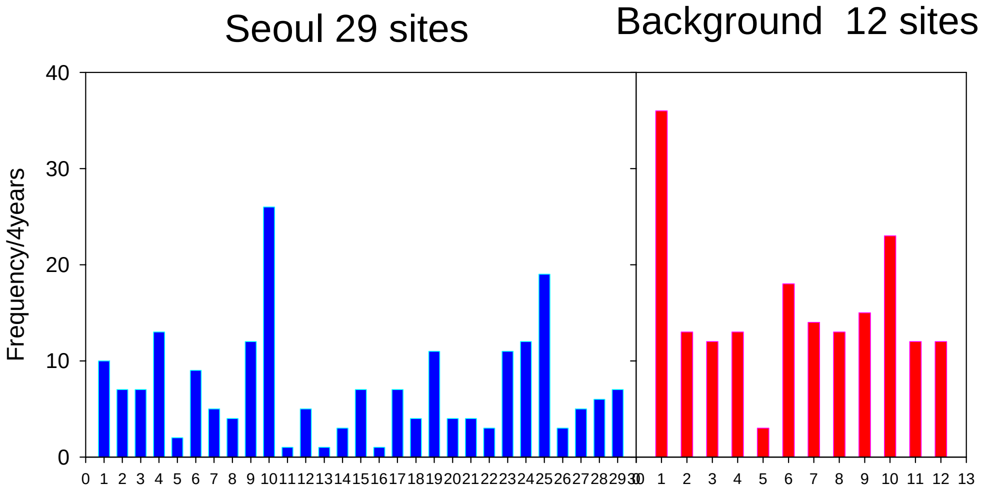

Figure 3. Frequency of exceeding 100ppb ozone at air pollution monitoring stations in Seoul(left) and background stations (right) during 2001-2004.

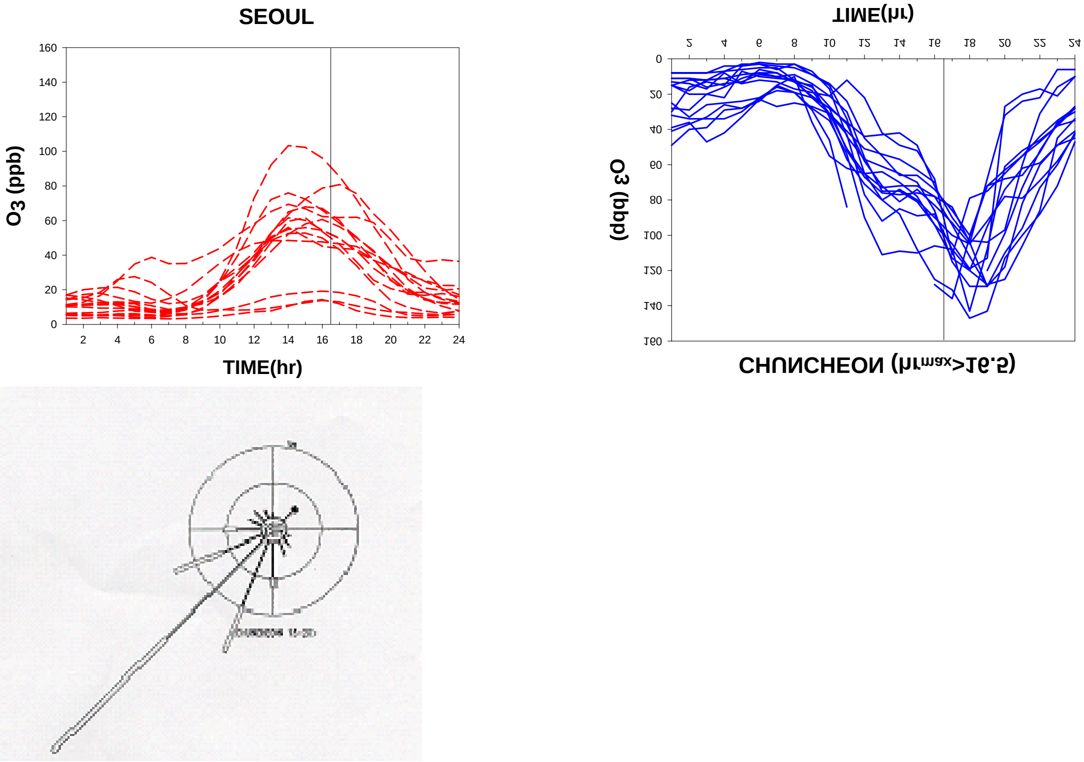

Figure 4. Diurnal variations of ozone concentration in Seoul (left of upper) and Chuncheon(right of upper) for days daily maximum ozone concentration exceed 100ppb in Chuncheon. The wind rose(down) in Chuncheon at daytime(13-20 LST) shows southwesterly wind.

3.2 Occurrence time delay of high ozone concentration

Fig. 5. show variations of average ozone concentration in 5 cities(A:Incheon, B:Bucheon, C:Seoul, D:Guri, E:Chuncheon) for 18 days when daily maximum ozone concentration exceeds 100ppb in Chuncheon. As monitoring station moves from A to E, the daily maximum ozone concentration increases gradually and occurrence time of daily maximum ozone concentration delayed gradually.

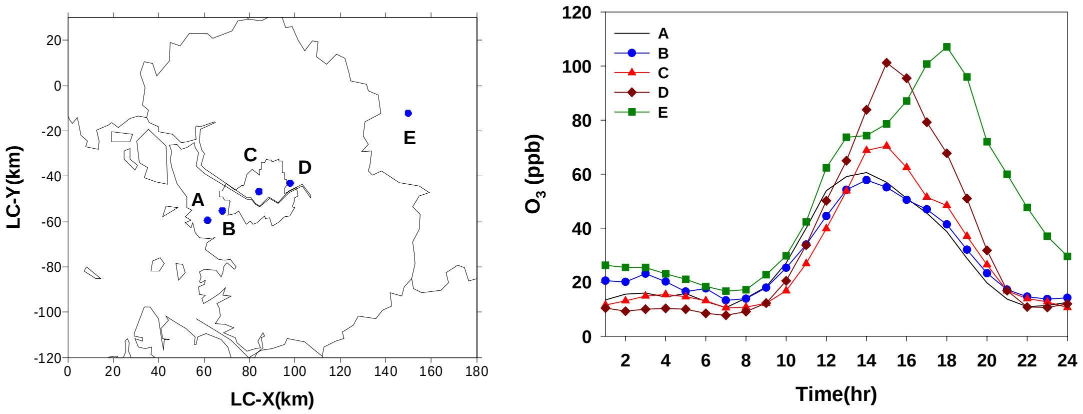

Fig. 5. Variations of ozone concentration in 5 cities averaged for 18 days when daily maximum ozone concentrations were exceeded 100ppb in Chuncheon during 2001-2004.

ACTIONS TAKEN IN ISTANBUL TOWARDS THE AIM OF PREVENTING AIR POLLUTION

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ABSTRACT

In this study, the efforts performed in Istanbul as of the year 1984 until the year 2005 (the month of April) as regards the air pollution and the precautions taken for reducing the air pollutants are described. The point that has been reached concerning air pollutions as of the year 2005 is summarized.

Keywords: Sulfur Dioxide, Quality Fuel, Quality Burning Systems, Coal, Inversion

1. INTRODUCTION

In the year 1972, the United Nations General Assembly adopted the day 5, June as the 'World Environment Day' in order to 'engage in worldwide activities towards the aim of marking the interest of humanity in protecting and developing the environment with regards deepening the environmental awareness'. For that reason, every year on 5, June, special training programs at schools, parades, special cleaning campaigns, tree-planting activities are carried out throughout the world. The volunteers work in campaigns for using recycled paper as well as making efforts for increasing their effectiveness among workplaces and political circles.

In our country, there are many official and voluntary institutions and organizations taking actions in the issue of environment. The 'Environment Clubs' that are being set up or intended to be formed in schools can also be deemed voluntary environmental organizations.

Our subject matter being the environmental pollution, we can give a brief account of the information on air pollution as follows:

What is Air Pollution, What are its Sources?

Clean air is composed of 78% nitrogen, 21% oxygen and 1% other gases, substances like dust and vapor. These ratios are referred to as the natural components of the air. The presence in the air of foreign substances at such an intensiveness and duration that it might be harmful to the human health, organic life and ecological balance due to a disruption in these ratios leads to air pollution.

So, as for the question 'What are the sources are that lead to pollution?', these sources are:

Natural Sources

Examples for the natural sources which cause air pollution:

a) Volcanoes-Volcanic activities,
b) Fires in forests,
c) Deterioration of the flora and fauna in open country etc.

Synthetic Sources

The artificial sources that lead to air pollution are those sources which are formed as a result of human activities. These are:

a) Use of fuel in residences for heating purposes,
b) Industrial activities,
c) The use of motor road vehicles for transport, that is, traffic.

a. Air pollution due to the use of fuel in residences for heating purposes

There is a continuous flow of heat from an object or an environment with higher temperature to an object or an environment with lower temperature. Therefore, the temperature of the object or environment which has lower temperature decreases. If the temperature gap between two objects or environments is high, then the temperature transferred shall also be high. This basic rule also applies to human beings. People burn the food that they intake using oxygen and the body produces heat.

However, people lose heat and get cold in winter months when their environment is colder than themselves. To meet the need for establishing a balance between the heat produced by the human body and the heat lost by it, various heating devices (stoves, heaters etc.) are used.

The smoke that is exuded from the chimneys as these fuels are burned in our stoves and heaters also pollutes the air. The gases that emit from the stoves or heater furnace chimneys are called general pollutants.

These are;

- Carbon monoxide (CO)
- Sulfur dioxide (SO2)
- Nitrogen dioxides (NOx)
- Particulate substances (soot, lamp black and dust) are referred to as general pollutants.

b. Prevention of the Air Pollution due to Environmental Reasons

The fuels burned in factories to meet the need for energy as well as the pollutants occurring as a result of the operation in the factory are released into the air via chimneys and lead to environmental pollution.

So, how can both development and environmental protection be ensured at the same time?

The workplaces and factories must take the necessary measures in order not to pollute the environment. For example, clean fuel should be used, filtering systems ought to be set up, the raw materials that are able to be recycled should be used, the awareness of the staff concerning the environment should be raised, work should be performed to enhance green areas, technological innovations must be followed or implemented. Most importantly, the necessary permits absolutely have to be obtained from authorized institutions. Controlling institutions must also control such places very frequently.

Our Directorate controls the Non-Sanitary Enterprises based on the authority it derives from the laws. In cases where those enterprises which are detected to emit dirty smoke from their chimneys or releasing emissions, our directorate demands from the highest civilian authority in the Zone that judicial action to be taken against them according to the Environmental Code number 2872.

In order for the pollutants stemming from industrial zones and workplaces to be minimized, 2 teams generally resume their control every day, these controls are also performed at night when necessary.

The industry in our city has huge part in air pollution. Ranking the first among the pollutions stemming from the industry are fuels used for energy as well as non-fuel processes and various operations.

c. Air Pollution due to Traffic

The fact that a single vehicle turns the 15 m^3 of clean air that is the daily need of a human being into air which is harmful for inhalation can gives us enough idea about the extent of air pollution caused by hundreds of thousands of vehicles in cities.

Today in Istanbul, more than 2 million motor vehicles registered in traffic roam the streets and avenues of the city. These vehicles which might release pollutant gases and particulates in the air are increased another fold in their pollutant features due to poor maintenance, inattentive use and oldness in many of the cases, thus they constitute important sources for pollution.

Two types of engines are used in vehicles being and diesel. The sources in vehicles which lead to air pollution vary according to the type of the engine.

The primary pollutant sources in a vehicle that works with a gas engine are as follows:
Exhaust pipe (the actual source)
Fuel tank
Carter ventilation
Carburetor
Brake linings and Tires

As for the vehicles with diesel engines, the primary pollutant source is the exhaust pipe. Three types of smoke is emitted from the exhaust pipes of vehicles with diesel engines.

Black Smoke: It is the smoke formed by fuel granulates that are not entirely burned. It indicates that the viable conditions for burning do not exist.

Grey-White Smoke: It is the smoke formed by the substances which are wastes of full burning. It indicates that the viable conditions for burning do exist.

Blue Smoke: It is a mixture of unburned fuel and oil, it generally indicates that the engine needs maintenance.

The pollutants stemming from vehicles are divided into two as general and special pollutants. The gases carbon dioxide (CO_2), vapor (H_2O), hydrogen (H_2) and nitrogen (N_2) , which are found in the exhaust gases are not deemed to be pollutant

The carbon monoxides (CO), particulate substances (soot, dust, granulate etc.) and hydro carbons in the exhaust gas are deemed to be general pollutants.

The lead (Pb) compounds in gas vehicles is a significant pollutant.

2. EFFORTS FOR PROVIDING ISTANBUL WITH QUALITY COAL

The specifications and amounts of coals used in Istanbul before the year 1995
In Istanbul, air pollution started to manifest itself as of the year 1985 due to the rapid population increase and the use of low quality fuel.

Since the steam coals sold in Istanbul for heating purposes included more than 1% of sulfur on a dry basis, they had carcinogenic effects due to the poly-aromatic hydrocarbons that they contained and the air pollution levels increased the steps of II. warning, selling of steam coals was banned in Istanbul for heating purposes as of 1, March, 1993.
However, the air pollution continued to pose a problem since an effective fight could not be carried out as regards this ban. Furthermore, to recall those days, warnings were made in the newspapers regarding air pollution and people used to go out wearing masks in some regions (Figure 1).

Cumhuriyet

21 OCAK 1993

İstanbul'da 'kırmızı' alarm. Valilik, hava kirliliğinin yoğun olduğu akşam ve sabah saatlerinde çocukların sokağa çıkmamasını istedi.

06-10, 17-21 en tehlikeli saatler. Ancak bu saatlerde çocuklar ya okul yolunda ya da okul dönüşünde. Valilik, uyarmasına karşın okulları tatil etmiyor.

Bilim adamları, üst solunum yolları ve bağlı hastalıklara dikkat çekerek bugünlerde çocukların okula gönderilmemesini istiyor.

Hava kirliliği Denizli, Eskişehir, Konya, Samsun, Erzurum, Kayseri, Diyarbakır, Uşak, G. Antep ve Bursa'da da tehlikeli boyutlarda.

Çocukları evden çıkarmayın

İstanbul Valisi Kozakçıoğlu: 'Hava kirliliği ciddi boyutlara varmıştır. Alınan önlemlere uyulmasını istiyorum'. Belediye Başkanı Sözen: 'Kirliliğin nedeni egzoz. Kömürden kaynaklanan sorun doğalgaza geçilmesi halinde çözülecek. İstanbul'un şansı deniz.'

Figure 1. Extract from the newspaper Cumhuriyet issued on 21, January, 1993.

When it came to the year 1994, one of the most remarkable problems in Istanbul was air pollution. Since the resolution of the City Local Environmental Board dated 31.03.1993 and number 3 was previously taken concerning the coals to be used in Istanbul in order to prevent air pollution, it was necessary that the coals entering the city be controlled according to this Resolution.

In this resolution, the specifications for coals were specified as follows:

Humidity : 18% Max. (for Coal Dry in the Air)
Ash :14% Max.
Total Sulfur :1.7% Max.
Burnable :1.4% Max.
Calorific value :4000 Kcal/Kg
Size :200 mm Max.

According to these values, it was possible for coals with an original humidity rate of 30-40% to enter the city. Before, sample analyses were performed in the Ağaçlı Zone in Istanbul by getting samples from 50 coal quarries, however, it was possible for the coals obtained in those quarries to enter the city since the specifications to be observed in the coals to enter the city were kept on a broad spectrum.

That year, we could request the certificates of origin and make controls on sizes only at the points of entries for the coals entering the city. The size control could not be totally possible, either. Because, larger pieces of coals would be placed on the lower parts and smaller pieces of coals would be placed on the higher parts of the lorries. Some efforts were made, however, there was also a problem of air pollution experienced in Istanbul in the mean time. Hence, our municipality engaged in a search and a scientific study was also commissioned by way of a resort.

In addition to the efforts made by our municipality, the study we commissioned to the Yıldız Technical University shows on the Table 1 that 10% of the emissions polluting the air (PM, SO_2, CO, NOx, HC) were caused by vehicles, 90% by fixed sources, conversely, the residences and the industry.

Also, the study indicates the condition of the liquid and coal fuels used in residences and the industry. While the consumption of coal was equal to that of fuel-oil during the years 1980-81-82, the consumption of coal increased nearly 9 times compared to fuel-oil and amounted to the level of 8-9 millions of tons/year. 80-90% of these coals were received from the Ağaçlı Zone in Istanbul. Coals that complied with the standards for burning were also received from the other coal-bearing zones in our country.

Table 1. Distribution of the pollutant emissions in Istanbul in the year 1990

Pollutant	Total Emission (%)	Fixed Sources (%)	Vehicles (%)
PM	48.10	47.5	0.65
SO2	29.4	29.1	0.26
CO	16.3	9.9	6.64
NOx	3.1	1.6	1.44
HC	3.0	1.6	1.40
TOTAL	100	90	~10

It could also be seen very clearly in the study conducted by Yıldız Technical University that the emission of sulfur dioxide (SO_2) increased in accordance with the rise in the use of coal.

Namely, while the emission of sulfur dioxide (SO_2) sorted by the fuels consumed during the 1980s was equal to the amounts of sulfur dioxide stemming from coal, the amount of sulfur dioxide also increased proportionately in the later years in parallel to the consumption of coal.

Comparing this increase with the sulfur dioxide stemming from fuel oil, the rate of sulfur dioxide due to coal in 1980s was 37%, and the rate of sulfur dioxide due to fuel-oil was 60%, these rates became 78% for sulfur dioxide due to coal and 20% for sulfur dioxide due to fuel-oil in 1993-1994.

Until the year 1994, the rate of sulfur dioxide emission stemming from fuel-oil fell from 60% to 20% within the last decade. It is natural in our city that there will be an increase in the air pollution at the same that as 8-9 millions of tons of low quality coal is used generally for heating.

Actions for increasing the quality of coal
Since the air pollution has assumed the dimensions mentioned above and this stems predominantly from the burning of low quality coal, actions have been taken in the direction of increasing the coal quality and making natural gas more rampant. As it is known, departing from the fact that it is not possible to take natural gas to the entirety of Istanbul in terms of both the amount of gas and technical terms and that the 30-40% of the need for fuel in the city can be met under any circumstances with coal, the quality of coal has been seriously dwelled upon.

Environment and Coal Analysis Laboratory
The samples taken from the entrances to the city, the points of sale in the city as well as the consumer domiciles in order to control whether the coals consigned to Istanbul with certificates of permission conform to the specifications determined by the Local Environmental Board Decision are analyzed in our coal analysis laboratories belonging to our municipality that started their activity in Yenibosna during the winter season in 1997-1998.

Thanks to this laboratory established within the body of our municipality, an increase rate of 30% has been ensured compared to the rate obtained by the university and the complaints by the citizens could be resolved more quickly since the coal analyses could be finalized in a shorter period of time. Thus, it has been also been ensured that the quality of coals be controlled in a more effective manner within a general structure.

As a result of this active work performed as of the year 1995 in order to reduce air pollution in Istanbul, the consumption rate of 8-9 millions of tons of coal marked during the years 1993-1994 fell to approximately 2-2.5 millions of tons in the winter season in 1997-1998 and down to 1-1.5 millions of tons during the winter season in 2004-2005. Even though the expansion of natural gas has had a share in this decrease in the amount, the actual factor was the raise in the quality of coals.

3. AIR POLLUTION MEASUREMENT ACTIONS

In Istanbul, the air pollution is one of the most significant problems brought about by modern life and it had assumed increasingly important dimensions in the past periods due to the rapid population increase, concentration of population caused by migration, faulty selection of locations in urbanization and industrialization, use of low quality fuel, lack of attention paid to heat isolation, non-conformity with standards in the burning devices (stoves and furnaces), use of old burning techniques in the industry, failure to perform the chimney cleansings as required, failure to take enough actions for reducing the emissions caused by traffic, overall lack of knowledge of environmental problems and the inadequate attention paid to the issue in spite of everything.

As a result of these actions taken, the air pollution in Istanbul decreased as of the year 1995, the levels of warning reached before were not to be seen, furthermore, the limit values were not even reached.

Average Values In Winter Seasons

A rate of more than 400 mg/m3 was generally observed during the years 1993-1004 and 3600 mg/m3 was observed on some days.

	SO2	PM(TOZ)
1995-1996 Winter season (October-March) average	100	78
1996-1997 Winter season (October-March) average	81	60
1997-1998 Winter season (October-March) average	69	62
1999-2000 Winter season (October-March) average	43	57
2000-2001 Winter season (October-March) average	37	62
2001-2002 Winter season (October-March) average	33	71
2002-2003 Winter season (October-March) average	33	65
2003-2004 Winter season (October-March) average	23	61
2004-2005 Winter season (October-March) average	19	50

As a result, the air pollution was eliminated to a great extent as a problem in Istanbul. However, our efforts are underway to maintain this situation.

Our Metropolitan Municipality continues its activities briefly for providing quality coal (quality coal, quality fuel-oil), expansion of natural gas, improvement of burning devices (stoves and furnaces), implementing heat isolation in buildings and taking under control the emissions stemming from the industry taking and maintaining under control in order to eliminate these negativities and ensure that the effects leading to the negativities do not resurface.

Parameters taken into consideration for the selection of existing measurement locations

- Climatic conditions
- The topographic structure of Istanbul.
- Position of the industrial zones.
- Condition of the buildings in Istanbul and settlement.
- Vehicle traffic.
- Distribution of population.
- Distribution of natural gas.
- Historical meteorological data obtained from the Atatürk Airport.

Table 2. Location of the Air Quality Stations and Measurement Parameters

	AIR POLLUTANTS					
	SO2	NOx	CO	O_3	HC	PM
Yenibosna	X		X			X
Esenler	X	X	X		X	X
Saraçhane	X	X	X	X	X	X
Alibeyköy	X	X	X		X	X
Beşiktaş	X	X	X		X	X
Sarıyer	X		X			X
Üsküdar	X		X			X
Kadıköy	X	X	X	X	X	X
Ümraniye	X	X	X		X	X
Kartal	X		X			X

Table 3. Air Quality Analyzers/Samplers

	METHOD OF ANALYSIS
SO_2	UV Fluorescent Method (Automatic)
NOx	Chemi-luminescence Method (Automatic)
CO	IR Absorption Method (Automatic)
O_3	UV Photometry Method (Automatic)
HC	Gas Chromotography (FID) Method (Automatic)
PM10 (DUST)	Beta Beam Absorption (Beta Gauge) Method (Automatic)

Figure 2. Ümraniye, Kartal, Sariyer, Üsküdar, Esenler, Beşiktaş, Alibeyköy And Yenibosna, Kadiköy, Saraçhane Air Quality Measurement Stations In Kadıköy, Saraçhane Stations SO_2, PM 10, CO, NOx, THC, O_3 In Esenler, Beşiktaş, Alibeyköy, Ümraniye Stations: SO_2, PM 10, CO, NOx, THC, In Yenibosna, Kartal, Üsküdar, Sarıyer Stations: SO_2, PM 10, CO measurements are made.

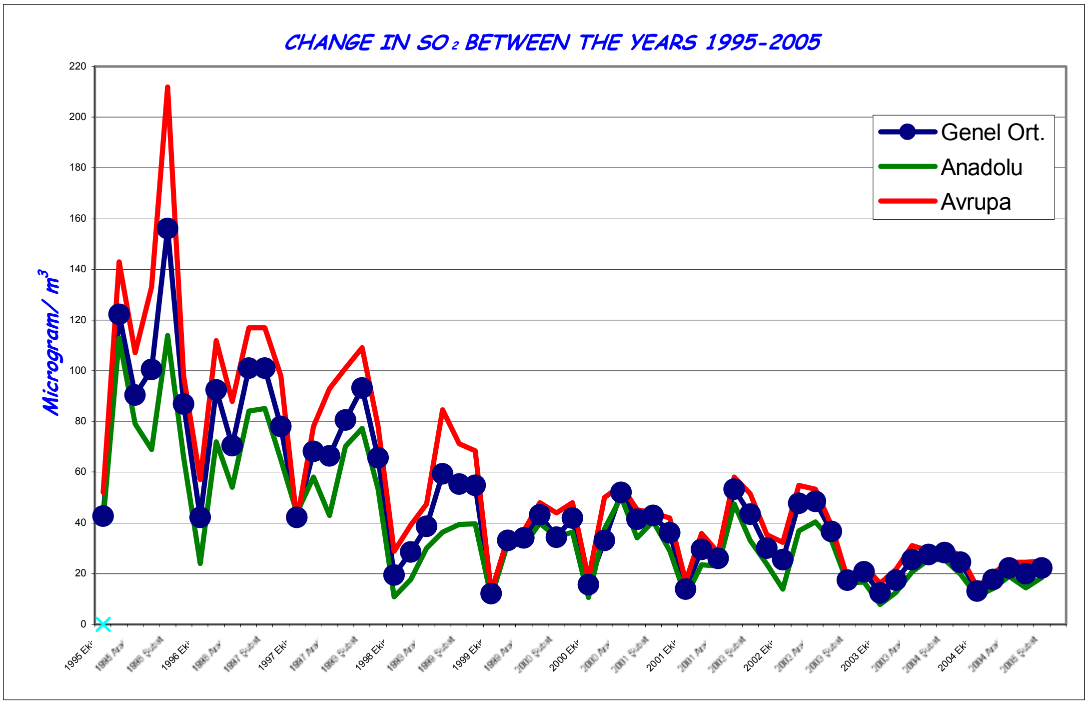

Figure 3: Change in the SO_2 between the years 1995-2005

An examination of the 2004-2005 Winter season (October-March) portrays that the daily threshold values specified in the Regulation for Air Quality Protection, World Health Organization, European Union, EPA and Benelux are not measured on average in the entirety of Istanbul; furthermore, the values are even below these thresholds.

The Measured Air Quality values are sent to the General Directorate of İGDAŞ (Istanbul Gas Distribution Corporation) and to the e-mail addresses of both the Provincial Directorate for Environment and Forest and the General Directorate of İGDAŞ as well as the Press Advisory Office of Istanbul Metropolitan Municipality.

Our measured air quality values are posted every day on our website "http://www.ibb.gov.tr/" \t "_parent", under the link **Air Quality.**

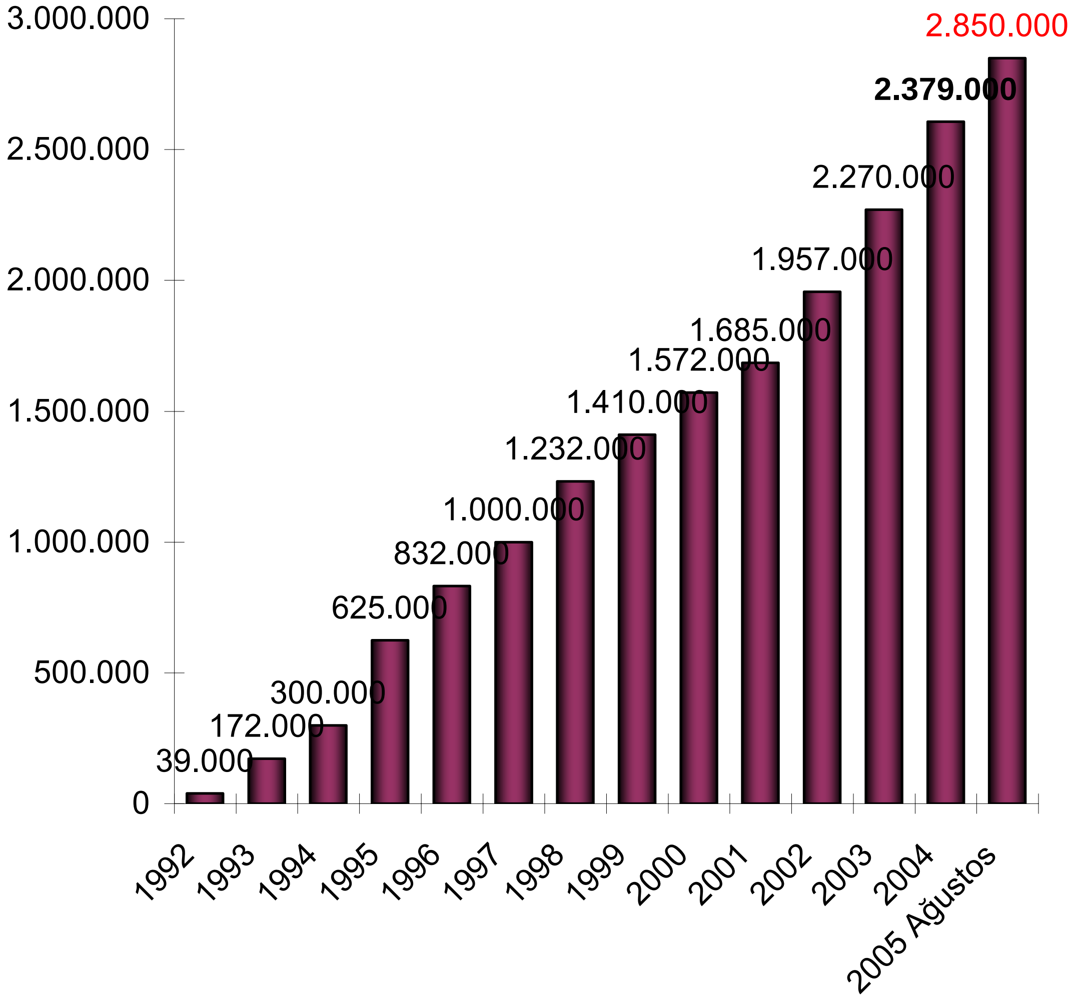

Figure 4. The number of subscribers of İGDAŞ sorted by years

4. RESULTS

We both have to provide heat for ourselves and to avoid polluting the air. Then, we should provide heating without polluting. For that reason, it is necessary that the principles below be obeyed in order to reduce air pollution stemming from heating or to prevent air pollution.

- There should be a fuel saving. The less fuel we consume, the less will be the air pollution.
- We should use clean fuel.
- The fuels should be burned in stoves and heaters in accordance with the technique.
- Heat isolation should be ensured in the buildings and in our houses.
- The furnace attendants should be commonly trained, the attendants who are not eligible should not be allowed to work in furnace rooms.
- The heater and stove chimneys should certainly be cleansed at the beginning of every season.
- The ventilation window of the furnace room should be kept open while the heaters are powered on.
- For the coal furnaces, a furnace cleaning should be performed twice a week; as for the furnaces that use liquid fuel, that is, fuel-oil, the cleaning should be done once a week.
- The faults in the heating installation should be overcome on time.
- The heaters shall be powered when the air temperature outside the building falls down to 12 ºC and below, when the temperature is between 12 ºC- 18 ºC, they shall be heated in a limited fashion and the heaters shall not be powered on once the temperature exceeds 18ºC.
- In the houses; heating ought to be ensured so that the temperature in the living rooms shall be around 22°C and it shall not exceed 15 °C in steps, kitchen and toilet, 20 °C in the bedroom and 26°C in the bathroom.
- If the area of heating of the heater installation is 3000 m^2 and above, a water filter is to be mounted on the furnace chimney.

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İGDAŞ A.Ş., the number of subscribers of sorted by years

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

CHARACTERISTICS OF BENZENE, TOLUENE, AND XYLENE GAS REMOVAL BY A BIOFILTER USING SCORIA

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ABSTRACT

The biodegradation experiments of benzene, toluene, and xylene (BTX) by bacillus culture were carried out. In biofilter experiments packed with scoria as a packing media, benzene and toluene were removed over 90% and xylene was removed over 80% with empty bed contact time (EBCT) between 10 and 60 seconds when each concentration was kept constantly at 600 ppmv. The maximum removal capacities of toluene, benzene and xylene were found to be 760 g/m^3-hr, 720 g/m^3-hr and 450 g/m^3-hr, respectively. The pH in a drain water maintained between 6.0 and 7.0 during the continuous operation for 195 days. The pressure drop had a tendency to increase slightly according to the inlet gas concentration, but was maintained low at about 5 mmH$_2$O/m. The biofilter using scoria media showed an excellent efficiency of BTX removal, and would be able to apply in a full-scale system with economic advantage.

Key Words : Biofilter, Biofiltration. Scoria, Benzene, Toluene, Xylene, *Bacillus* sp.

1. INTRODUCTION

Benzene, toluene, and xylene (BTX) are important industrial solvents that are frequently encountered in industrial operations including the painting and varnishing industries. A large amount of BTX is released into the atmosphere from industrial processes, petroleum refining, petroleum making, containers, and storage tanks every year. BTX vapors are toxic to the liver, kidneys and the central nervous system when they enter the body by skin contact or breathing (Martin et al., 1998; Fishbein, 1985; Dean, 1985). Losing these substances to the ambient air may lead to an advertise impact and endanger public health and environment.

Biofiltration is an air pollution technology that utilizes microorganisms present in the biofilter media to degrade the pollutants in a waste gas stream into water and carbon dioxide. It is a very cost-effective technology for the treatment of large volume of air contaminants with low concentrations of biologically degradable compounds, as compared with the traditional VOC control technologies such as incineration, ozonation, combustion, and adsorption (Ottengraf, 1986). Especially, it is environmentally friendly because the contaminants are completely converted into non-hazardous final products.

The capacity and the durability of the biofilter depend upon the property of the media, and the removal efficiency of the pollutant will be determined by the degradation ability and the specific growth rate of microorganisms. Thus, the packing material plays an important role in biofiltration. The selection of a proper media is very important for high efficient biofiltration. However its selection depends on several factors. The medium should provide an optimum environment for microbial populations. It should have desirable properties such as high porosity, appropriate pore size, good mechanical stability, and an ability to sorb water (Ergas et al. 1992). Another important factor affecting practical application of biofilter media is cost. The less expensive the packing medium, the more desirable it is.

A wide range of packing materials including peat (Acuña et al., 2002; Zilli et al., 2001; Auria et al., 1998), compost (Morgenroth, et al., 1996; Ergas, 1994; Hodge and Devinny, 1994), sugarcane bagasse (Sene et al., 2002), granular activated carbon (Kim, 2003; Den et al., 2002; Abumaizar, 1998), polystyrene particles (Kiared, 1996), porous inorganic matrix (Kim et al., 2000), and polyurethane foam (Thalasso et al., 2001; Moe and Irvine, 1999) have been used in biofilters. However these materials may cause several problems such as compaction and channeling, thus in turn strongly influencing biofiltration performance.

Scoria is abundantly found in Jeju Island, Korea, and especially inexpensive natural porous material. It is a volcanic stone generated from the eruption of a volcano. Since it has a high water holding capacity, a high porosity, and an appropriate intensity, it is considered as a potential medium for biofiltration process. In this study, biofiltration of benzene, toluene and xylene (BTX) compounds has been investigated in a laboratory scale-down-flow biofilter packed with Jeju scoria as a new filter material. The effects of influential factors such as influent gas concentration and empty bed contact time (EBCT) on the removal efficiency were studied, and pH and pressure drop across biofilter bed were measured.

2. MATERIALS AND METHODS

A schematic diagram of a biofilter that was used in continuous experiments was shown in Fig. 1. The biofilter was made from acryl pipe with 150 cm of height and 10 cm of diameter. Scoria of 12 - 17 mm particle size was packed in the biofilter up to 1.2 m height. The packed volume and weight were 10 L and 6.3 kg, respectively. Five check valves were installed from the top of the reactor with 30 cm interval for gas sampling ports, for three media sampling ports were installed from the bottom of the reactor with 25 cm interval. The humidifier was made with acryl (18 cm of inside diameter, 150 cm of height), was packed with a number of pall rings in order to increase the efficiency of humidification. The vaporized BTX gases in the vaporizer were introduced into the top of the biofilter and flew downwards.

Bacillus sludge was used as inoculating microorganism into the biofilter. The sludge was centrifugated for 10 min at 3000 rpm, and washed before inoculation. The cell concentration of 15,000 mg/L as MLSS was inoculated to scoria medium through circulating by nutrient supplying pump for about 3 days. MLSS and MLVSS concentration of bacillus sludge inoculated in biofilter column were 6,720 and 5,130 mg/L, respectively. The final amount of micro-organisms attached to media was 0.517 g-MLVSS/g-dry material.

The composition of a mineral salts medium used in this study were (per 1 L) : KNO_3, 0.2 g; K_2HPO_4, 0.9 g; $(NH_4)SO_4$, 0.125 g; KH_2PO_4, 0.6 g; $MgSO_4$, 0.2 g; $CaCI_2$, 0.07 g; $FeSO_4$, 0.01 g; EDTA, 0.02 g. The nutrients were supplied into the reactor with 10 times dilution and sprayed from the top with a flow rate of 0.5 L/day in regular periods by a timer installed on pump.

Samples were taken at the top (inlet) and at the bottom (outlet) of the biofilter bed. The concentration of benzene, toluene, and xylene were analyzed by GC (Gas chromatography, DS-1200) which installed FID (Flame Ionization Detector). Helium gas flowing at 1 mL/min was used as the carrier gas. The temperature of the oven was 70 at the beginning, and increased from 70 to 150 at a rate of 10 /min and maintained at 150 for 1 min. The temperatures of injector and detector were 150 and 250 , respectively. Pressure drop across biofilter bed was measured by a Durablock Manometer (DWYER, USA), and pH of the drain water from biofilter was measured using a pH-meter (ORION, model 420A).

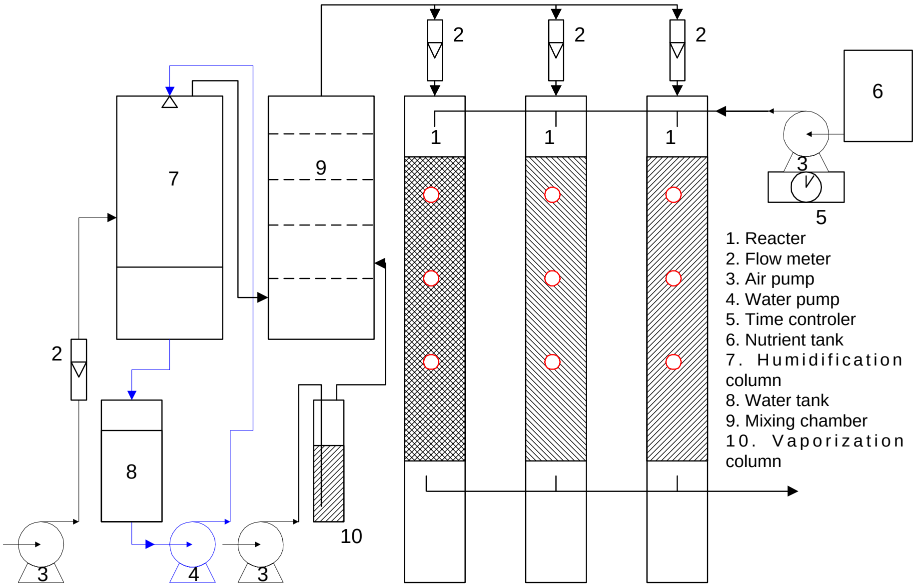

Fig. 1. Schematic diagram of biofilter.

3. RESULTS AND DISCUSSION

Fig. 2 shows the influent and effluent concentrations of each BTX compound along the operation time. Biofilter was operated continuously for 195 days in 3 different phases based on each BTX compound. The first phase began on day 1 and lasted 90 days. Toluene concentration in this phase was increased gradually from 40 ppmv to 1,200 ppmv (Fig. 2(a)). The second phase of the experiment was from day 91-150 using benzene as target gas (Fig. 2(b)). The last phase of the experiment started on day 151 by using xylene as target gas (Fig. 2(c)). At the beginning of the biofilter operation as shown in Fig. 2(a), toluene inlet concentration was fixed at 40 ppmv with 2 min EBCT for adaptation of microorganism and no toluene was detected after 3 days operation. From 9 days after the beginning of operation, the influent gas concentration was gradually increased and operated at 80, 100, 150, 300, 600, 1,000 and 1,200 ppmv for the continuous experiments. In this study, bacillus culture needed 2-4 days of adaptation time for all tested conditions. Kiared et al. (1997) reported that acclimation period of 1 week needed when peat was used as the media. Compared to the study of Kiared et al.(1997), bacillus culture showed fast adaptation for toluene. This reason could be found not only from the property of scoria which provided good environment for microorganisms, but also from the characteristic of bacillus culture which possessed fast adaptation for toluene.

The EBCT was changed from 45 to 5 sec with a fixed concentration of BTX at 600 ppmv. Up to 10 sec EBCT, toluene was removed over 90%. When EBCT was further reduced to 5 sec, toluene was removed about 50%. Also, the inlet toluene concentration was reduced half to 300 ppmv and EBCT was reduced two-fold to 5 sec in order to make the same condition of loading rate into the biofilter as that of 10 sec EBCT at 600 ppmv. With the concentrations at less than 300 ppmv, over 98% of benzene and toluene were removed. Xylene was removed 95% with concentrations at less than 100 ppmv. These results indicated that EBCT was able to be reduced at low influent gas concentrations within the limited loading rate. Hence, this results in an economic advantage in reducing size of the system.

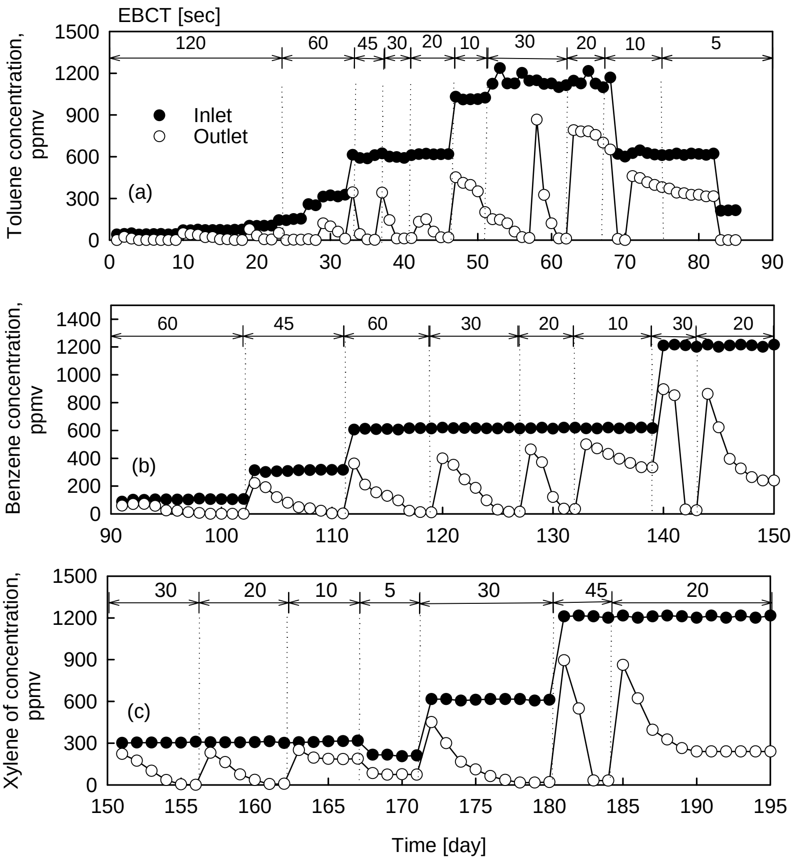

Fig. 2. Influent and effluent concentrations of (a) toluene, (b) benzene, and (c) xylene during operating time in biofilter.

For benzene shown in Fig. 2(b), the experiment started at 100 ppmv benzene with 1 min EBTC, since bacillus sludge was thought to be adapted through that of toluene removal. After 4 days operation, no benzene could be detected, and this phenomenon lasted more than 10 days. The continuous experiments were executed with the increase of benzene concentrations at a range of 100 – 1,200 ppmv. The adaptation time of bacillus sludge was more increased, compared with that of toluene, but it could be done in 4-5 days. In Fig. 2(c), the influent concentration of xylene was initially operated at 300 ppmv with 45 sec EBCT. This operation was done by the assumption that bacillus culture had been already adapted adequately. The influent xylene was gradually changed with the increase of concentrations at 300, 600 and 1,200 ppmv. For xylene, bacillus culture required more adaptation time (4-7 days) than those for other two gases.

The effect of EBCT on removal efficiency for each BTX is shown in Fig. 3. The EBCT was changed from 60 to 5 sec with a fixed concentration of BTX at 600 ppmv. Up to 10 sec EBCT, benzene and toluene were removed over 90% while xylene was removed 80%. When EBCT was further reduced to 5 sec, benzene and toluene were removed about 50% while xylene was removed 40%. This decrease in BTX removal was thought to be from a two-fold loading rate.

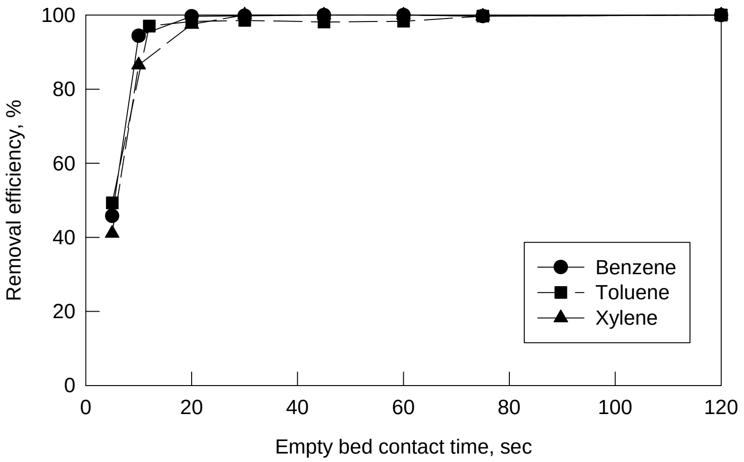

Fig. 3. Removal efficiency of benzene, toluene and xylene as a function of EBCT. (EBCT : 5 - 60 sec, influent concentration : 600 ppm).

Fig. 4 shows the individual elimination capacity of each BTX compound as a function of inlet loading rate. As shown in Fig. 4, the elimination capacity was an increasing function of the inlet load and reached a maximum. This result revealed that a biofilter system used in this study have the maximum loading rate without inhibition to microorganisms for all tested conditions. This is a very important factor in design and operation of a biofilter system, and depends on both the operation condition and the type of media (Angela, 1996). The maximum removal capacities obtained in this study were 760, 720 and 450 g/m^3-hr for toluene, benzene and xylene, respectively. The maximum removal capacities for toluene and benzene were almost the same, but that for xylene was lower.

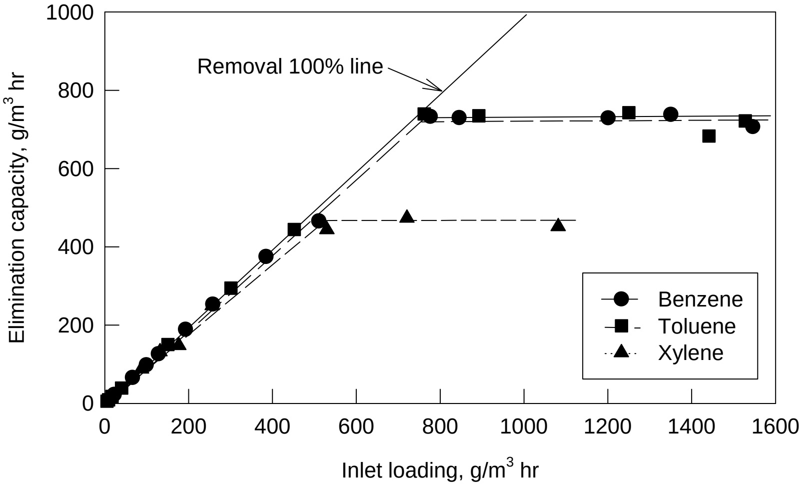

Fig. 4. Elimination capacity of benzene, toluene and xylene as a function of inlet loading rate.

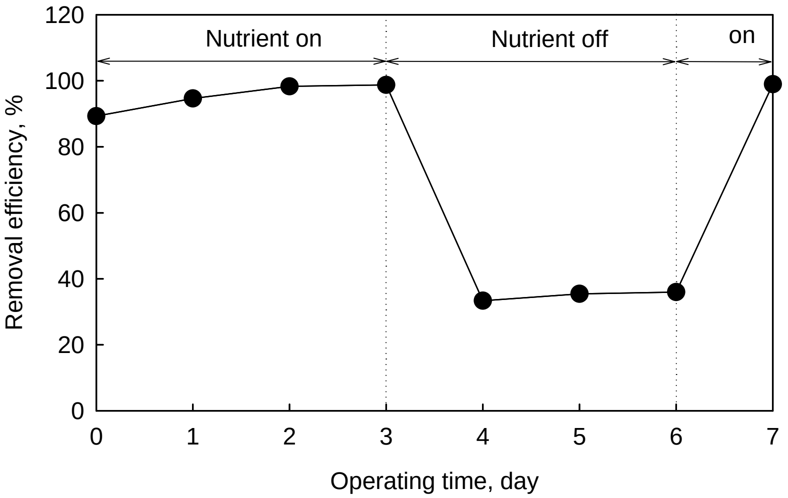

Fig. 5. The effect of removal efficiency of toluene with nutrient solution and without nutrient solution. (Influent concentration of toluene : 1200 ppmv, EBCT : 30 sec).

It has been known that the capacity of a biofilter decreases in a long-run operation when nutrients are not supplied by power failure and other operational problems, and recovering the capacity is time-consuming even though enough nutrients are supplied again (Maria et al., 1999). In Fig. 5, the removal efficiency is shown when the supply of nutrients was shut down in continuous operation and the time to recover the removal efficiency is shown when the supply of nutrients resumed. At an influent toluene concentration of 1200 ppmv with 30 and 40 sec EBCT, the removal efficiency declined from 99% to 40% when the supply of nutrients was shut down for 3 days and it recovered up to 98% within one day when the supply of nutrients resumed. This result indicated that the supply of nutrients other than toluene as the carbon source largely affected the removal efficiency and the removal efficiency quickly recovered in a day when scoria as the media was used in a biofilter.

Variations of pH and pressure drop in the biofilter during continuous operation are shown in Fig. 6. The pH maintained constantly between 6.0 and 7.0 only by intermittent spray of nutrients. The pressure drop across the biofilter bed maintained low at the average of 5 mmH_2O/m during the continuous operation.

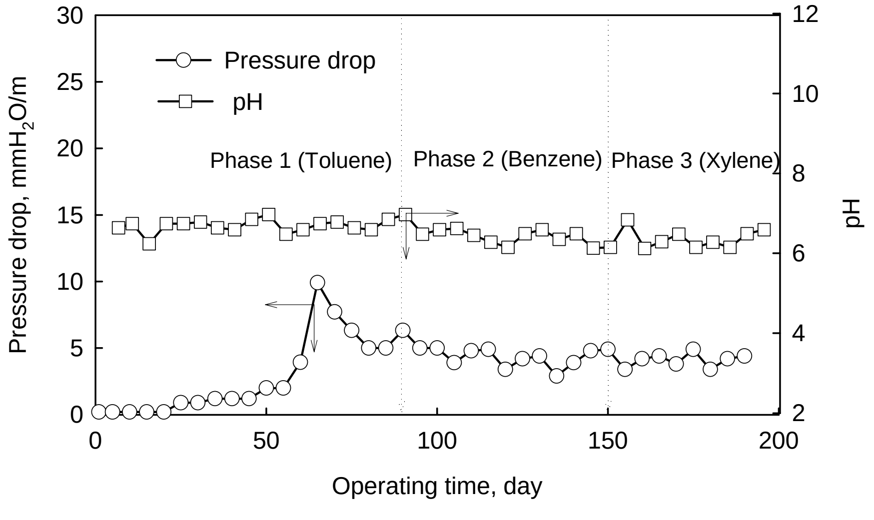

Fig. 6. Pressure drop and pH variations in the biofilter.

4. CONCLUSION

Biofiltration of BTX compounds has been investigated in a laboratory scale-down-flow biofilter packed with a new filter material. Various inlet concentrations and gas flow rates has been tested. Benzene and toluene were removed over 90 % and xylene was removed over 80 % with EBCT between 10 and 60 seconds when each concentration was kept constantly at 600 ppmv. With 5 seconds of EBCT, benzene and toluene at the concentrations below 300 ppmv were removed over 98 % and xylene below 100 ppmv was removed over 95 %. The maximum removal capacities of toluene, benzene and xylene were found to be 760 g/m^3-hr, 720 g/m^3-hr and 450 g/m^3-hr, respectively..

The pH in a drain water maintained between 6.0 and 7.0 during the continuous operation for 195 days. The pressure drop had a tendency to increase slightly according to the inlet gas concentration, but was maintained low at about 5 mmH_2O/m. From all the results, the biofilter using scoria showed an excellent efficiency of BTX removal, and would be able to apply in a full-scale system with economic advantage. Scoria exhibited good physical and mechanical properties as justified by the low pressure drop through the filter bed recorded during all the operation of the biofilter.

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CADMIUM CONTENT IN SUSPENDED PARTICULATE MATTER IN ZAGREB AIR

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ABSTRACT

This paper presents the results of cadmium monitoring in total suspended particulate matter (TSPM) in Zagreb air at two measuring sites (city centre and the northern, residential part of the city) for 20 years (1984-2003). Samples of TSPM were collected over 24-hour periods (noon to noon) on membrane filters (Millipore SSWP 09025, pore size 0.8 μm) at the average air flow rate of 70 L min^{-1}, from approximately 100 m^3 of ambient air. Samples were destroyed in nitric acid and cadmium was determined by atomic absorption spectrometry. Over the 20 years of monitoring, the annual means of cadmium concentrations varied from 0.5 to 5.9 ng m^{-3} in the city centre and from 0.4 to 3.1 ng m^{-3} in the residential part of the city. Cadmium concentrations in the residential part were in average 32% lower than in the city centre. However, cadmium concentrations in Zagreb air were below the recommended value (RV) of 0.01 μg m^{-3}, according to the Law on Air Quality Protection in Croatia. With respect to cadmium in TSPM, Zagreb air is of the 1st category – clean air (concentration levels of air pollution are below RV).

Key Words: heavy metal, air quality monitoring, atomic spectrometry

1. INTRODUCTION

Cadmium is a heavy metal that can be found in ambient air, dust, food, drinking water, tobacco, smoke and working environment. Cadmium in humans often originates from a combination of these sources. Total suspended particulate matter is one of important cadmium sources in the environment.

Cadmium content in TSPM collected from ambient air was measured in the period 1984-2003 in Zagreb, the capital of Croatia. Zagreb is the city with about 1,000.000 inhabitants; it is a cultural and industrial centre of the region.

The purpose of this investigation was to describe cadmium concentrations, trends, and seasonal dependences and to compare the measurements with the concentration limit values defined by the Ordinance on Recommended and Limit Air Quality Values (Ordinance, 1996).

2. MATERIAL AND METHODS

Two sampling sites were chosen for cadmium investigation, representing the city centre and the northern, residential area of Zagreb (Fig. 1). Samples were collected on a daily basis (noon to noon), totalling at least 200 samples per site and per year.

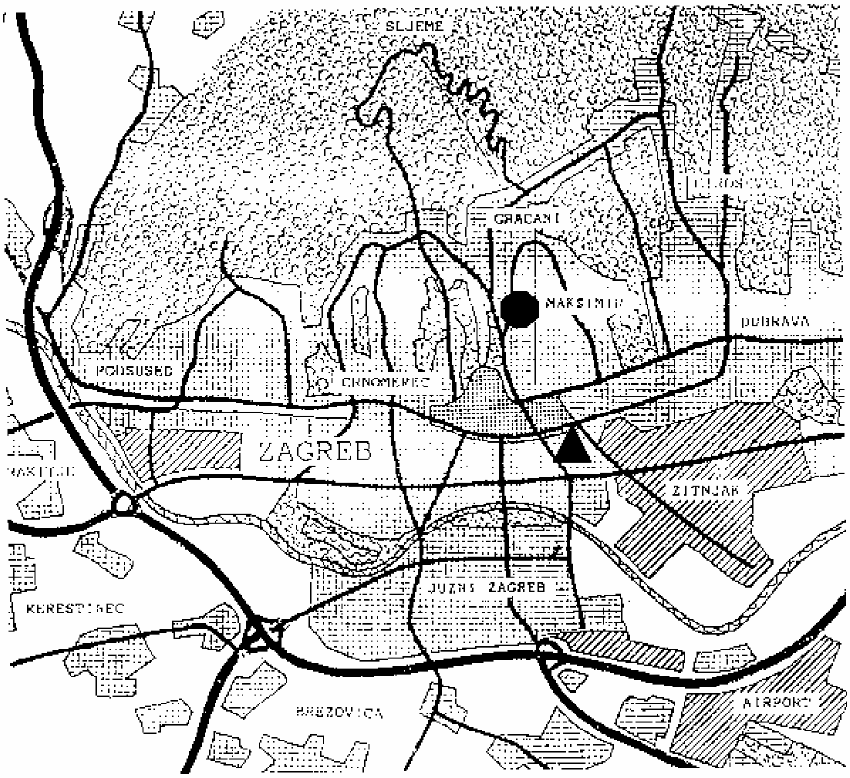

Figure 1. Location of measuring sites (□ - city centre , □ - northern part of the city)

Total suspended particulate matter was collected on membrane filters, 102 mm in diameter, at an average flow rate of 70 L min^{-1}. Prior to mass determination, before and after sampling, filters were preconditioned in desiccator for a period of 24 hours (Hršak, 1994). The samples were destroyed with nitric acid; the acid was evaporated, and the residue was dissolved in 1 M HNO_3. Cadmium content was determined using atomic absorption spectroscopy (Solar 969 AAS).

3. RESULTS AND DISCUSSION

Annual mean cadmium concentrations in TSPM in Zagreb air varied from 0.5 to 5.9 ng m^{-3} in the city centre and from 0.4 to 3.1 ng m^{-3} in the residential part of the city. Figure 2 shows annual trends for cadmium in TSPM in Zagreb air at both sampling sites over the entire measuring period (1984-2003). The decreasing trend of cadmium concentrations in TSPM in Zagreb air was observed from 1984 to 2000, and over the last few years cadmium concentrations were below 1 ng m^{-3}.

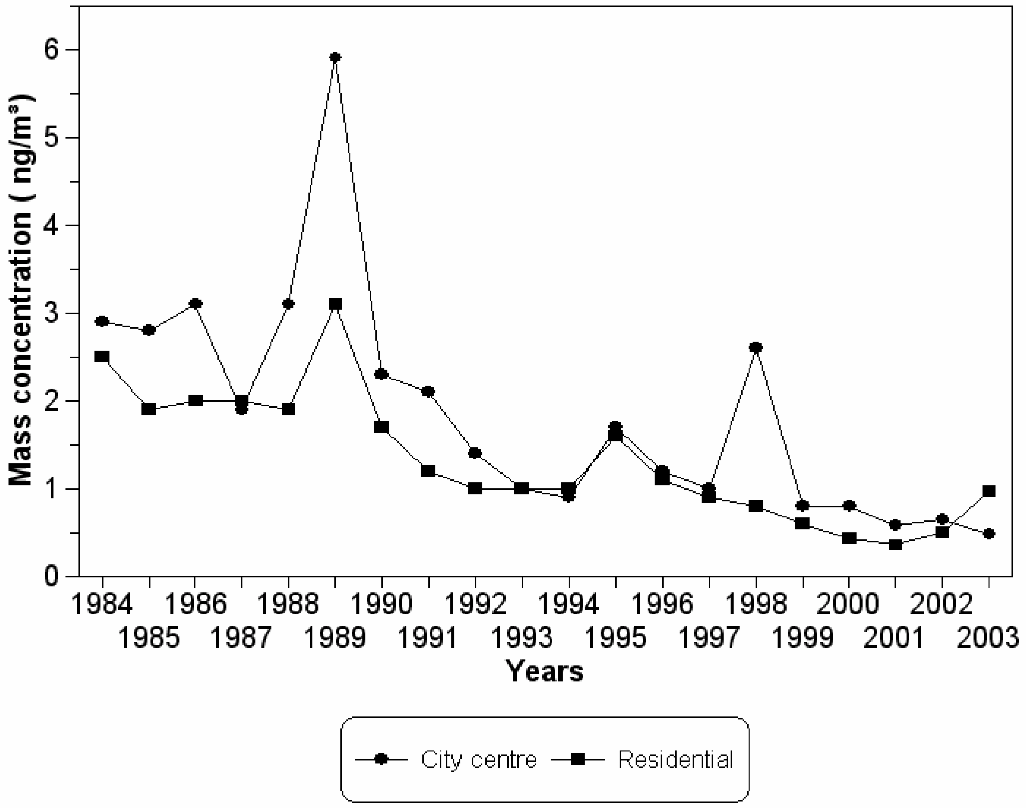

Figure 2. Trend of cadmium in TSPM in Zagreb air

A comparison of cadmium concentrations in TSPM between two sampling sites showed a good correlation (r= 0.591). The value of correlation coefficient and the results of regression analysis (Fig. 3) suggest that transport has an important role in cadmium content in the air; namely, cadmium comes with lead, but in much lower quantity. Also, the results in the residential area were in the average 32% lower than in the the city centre with a high traffic density.

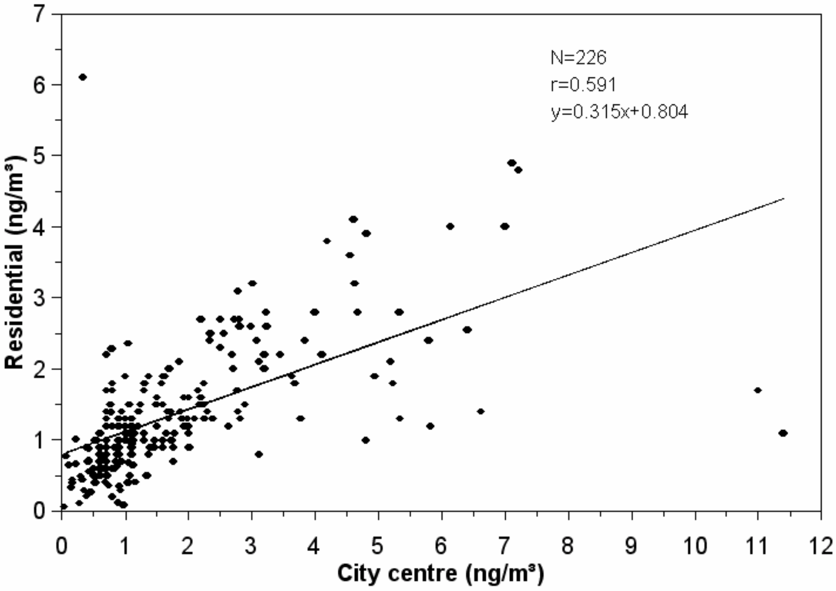

Figure 3. Correlation between cadmium in TSPM in the air in centre and in residential part of the city

Monthly cadmium concentration averages for the city centre and residential area are presented in Figure 4. Generally, monthly averages of cadmium concentrations for the entire measuring period (1984-2003) were low, ranging from 0.98 to 2.9 ng m^{-3}.

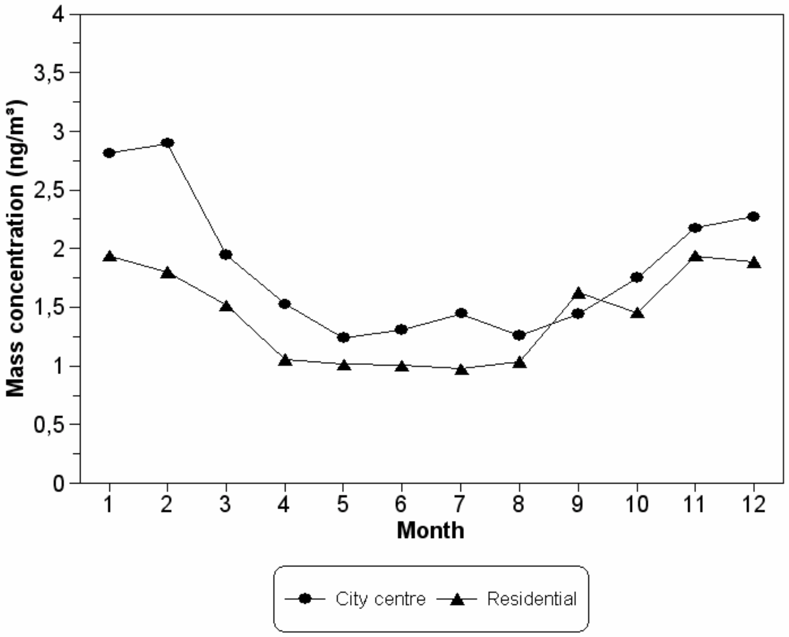

Figure 4. Monthly cadmium concentration averages in TSPM in Zagreb air

Cadmium concentrations in TSPM were higher in winter and lower in summer (Fig. 4). Annual values kept below the recommended value defined by the Ordinance which is for cadmium 0.01 µg m^{-3}.

4. CONCLUSIONS

In the period 1984-2003, cadmium concentrations in TSPM in Zagreb air were low, below the recommended value. Higher values were measured in winter and lower in summer. Cadmium concentrations in TSPM in the city centre were in average 32% higher than in the residential part of the city.

However, cadmium content in TSPM was very low and the air in Zagreb, according to the Law on Air Quality Protection in Croatia (Law, 1995) was in the 1st category – clean air (concentration levels of air pollution are below RV) throughout the measuring period.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

CALIBRATION OF DISPERSION MODELS USING DIFFUSIVE SAMPLERS

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ABSTRACT

A Gaussian dispersion model was used to calculate sulfur dioxide concentrations levels in the vicinity of a remote power plant in Turkey. Whereas emission data for SO_2 were available, a lack of meteorological data had to be tackled. By measuring ambient SO_2 concentrations with diffusion tubes, the input data could be tuned in such a way that the coincidence of calculated versus measured data was satisfactory.

Key Words: Air pollution modeling, diffusion tubes, air quality, sulfur dioxide, model calibration

1. INTRODUCTION

Dispersion models play an important role in air quality management [1]. However, models are only as good as the input parameters: accurate emission factors and meteorological data are indispensable. Such data is often available only to a limited extent, above all in remote areas. In this case, the possibility to compare calculated data with measured data is of great help.

An efficient technique to obtain ambient concentration measurements is diffusive sampling. Diffusive samplers are based on the diffusion of molecules onto absorbent surfaces. They need no power source, are highly portable, and their handling requires no training. Diffusive samplers allow the assessment of spatial air pollution in a cheap and convenient way.

For air quality assessment a wide variety of models has been developed. A dispersion model based on Gaussian theory was used (IMMPROG2000) [2]. Model results and measured passive sampling tube data were compared for the pollutant sulfur dioxide.

2. DISPERSION MODEL

IMMPROG2000 air dispersion modeling software has been developed in line with recommendations formulated by the Swiss Federal Office for Environment, Forest and Landscape [3]. They simulate the concentrations of inert air pollutants emitted from point sources, from vehicles on streets in open terrain and on streets in residential areas. The dispersion model is based on the Gaussian approach which itself is based on an analytical solution of the fundamental advection-diffusion equation describing the transport and diffusion of pollutants in the atmosphere.

The basic equation used to compute ambient concentrations at given points is shown in equation 1:

$$C = \frac{Q}{2\pi\sigma_y\sigma_z u} \cdot e^{\left[-0,5 \cdot \left(\frac{y}{\sigma_y}\right)^2\right]} \cdot e^{\left[-0,5 \cdot \left(\frac{H-z}{\sigma_z}\right)^2\right]} \qquad (1)$$

C	Ambient concentration, [mg/m3]
x,y,z	Co-ordinates, [m]
Q	Emission strength at point (x,y,z), [g/h]
z	Height above ground, [m]
h	Effective source height, [m]
u	Mean wind speed, [m/s]
sy	Standard deviation of the concentration distribution in the horizontal plane, [m]
sz	Standard deviation of the concentration distribution in the vertical plane, [m]

Meteorological data acquired over a period of five years at a resolution of one hour was available. This period includes meteorological parameters such as wind speed, wind direction, solar radiation, inversion layer and cloud cover. From this data, the frequency of stability classes according to Pasquill/Turner were calculated automatically by the model.

3. AMBIENT MEASUREMENTS BY DIFFUSIVE SAMPLING

The passive sampler for sulfur dioxide is based on the principle of the diffusion of sulfur dioxide molecules onto an adsorbing medium, in this case a mixture of potassium carbonate and glycerol. The driving force is the concentration gradient between the surrounding air and the absorbing surface, where the concentration is kept to zero.

The movement of molecules can be expressed by Fick’s law. After integration and rearrangement, equation 2 can be used for calculation of the ambient concentration:

$$\text{concentration } c_u = \frac{Q \bullet l}{D \bullet A \bullet t} = \frac{Q}{SR \bullet t}$$

c:	concentration	[µg/m^3]	D:	diffusion coefficient	[cm^2/sec]
Q:	amount absorbed	[µg]	t:	exposure time	[sec]
l:	diffusion path	[cm]	SR:	sampling rate	[ml/min]
A:	cross section	[cm2]			

The cross section, length of the tube and diffusion coefficient remain constant in a sampling system, and express the sampling rate of a diffusive sampler.

The absorbed pollutants are determined by analysis using ion chromatography.


Figure 1: View of diffusion tube

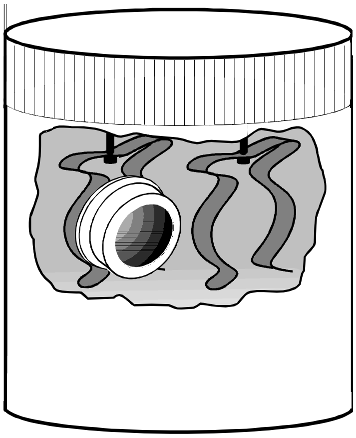
Figure 2: protective shelter

The SO_2 passive sampler is composed of a polypropylene housing with an opening of 20 mm diameter. To reduce wind disturbance a glass fiber membrane is attached, supported by a wire net. To protect the sampler from weather influences, while at the same time minimizing wind disturbance, a specially developed suspension device was used.

Sulfur dioxide measurements were carried out at 20 sites in the vicinity of the power plant. Data was collected over 6 months.

4. CALIBRATION OF MODEL

The dispersion model was adjusted on the basis of 20 monitoring sites. Calibration was used to adjust conditions in the modeling area, such as background concentration and different wind direction. This process is shown in figure 3.

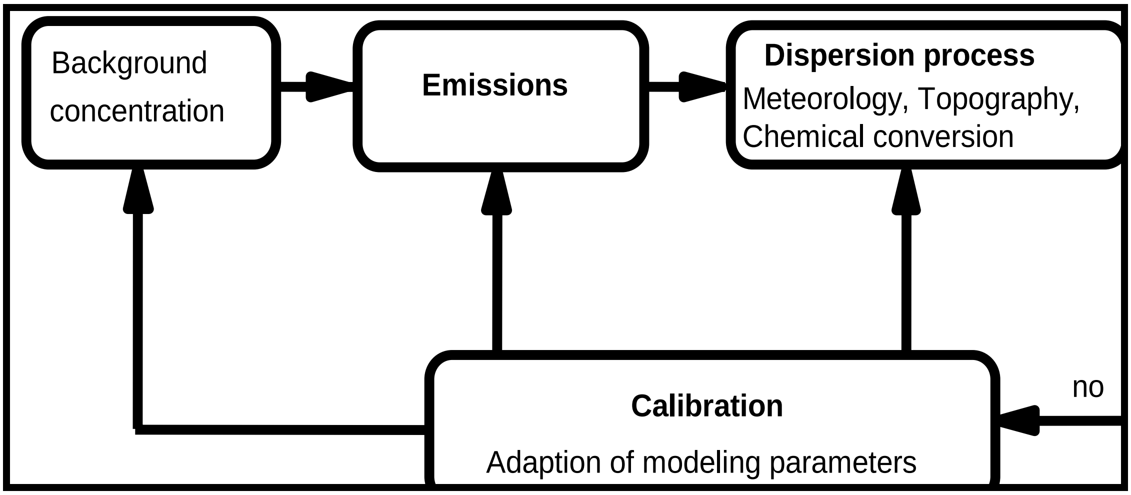

Fig. 3: Calibration process for Gaussian dispersion models.

The mathematics behind the model is fixed, so it was only possible to change the input parameters to bring the calculated and the measured values as close together as possible. A "trial and error" procedure was therefore used. Meteorological data was only adapted in terms of changing wind direction to fit the data to local circumstances. Due to the fact that emission was only given by some point measurements of 1 – 3 hours duration and the model needs stationary emission conditions, emission was adapted to achieve the best fit with measured data.

The following scenarios were calculated

- Fitting of raw data
- Adaptation of wind field
- Exclusion of monitoring points outside of the impact area of the plant

5. RESULTS

5.1 Fitting of raw data

Meteorological data were imported to the model and a first calculation was performed. The result was a negative correlation with the measured data. One reason might be that the meteorological data from the gauging station 50 km away do not correspond well to the actual situation.

Figure 4 shows the map of the point source (BACA_1) and the measuring point of the diffusive samplers (square dots) with computed isolines of sulfur dioxide concentrations. From the dispersion cloud shape the two main wind directions can be seen, one heading north east and the other south west.

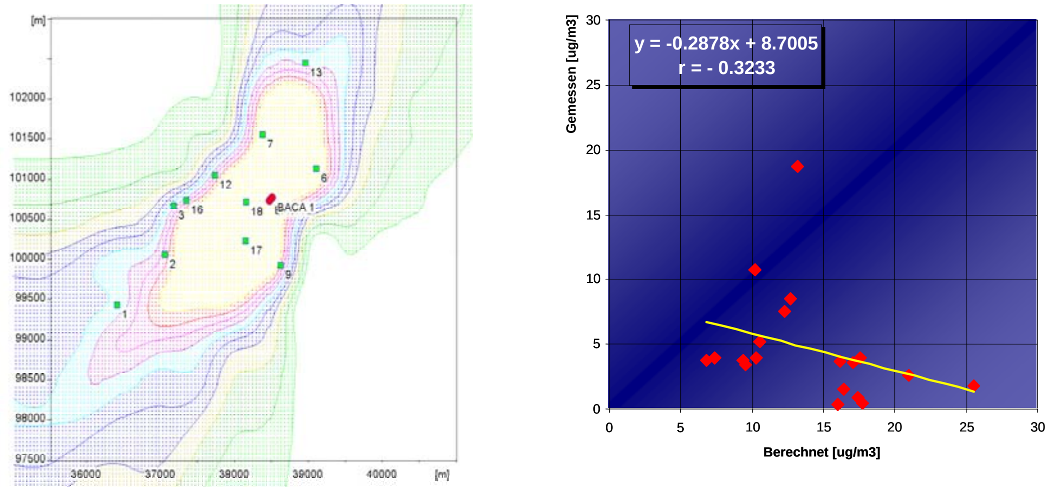

Figure 5: Calculated iso concentration lines in the vicinity of the plant. Right: comparison of calculated values and values measured using passive samplers, using the unreflected input data.

The first result without any adaptation was not satisfactory –with a correlation coefficient of -0.3233

5.2 Adaptation of wind field

A nearby mountain range has a remarkable influence on wind direction. Based on the assumption that the average wind direction distribution at two places - not too far from each other - is the same and that wind direction changes only as a result of local circumstances, the wind field was rotated.

After adjusting the wind direction to local circumstances the correlation coefficient was at least positive (r = 0.3401, see figure 4).

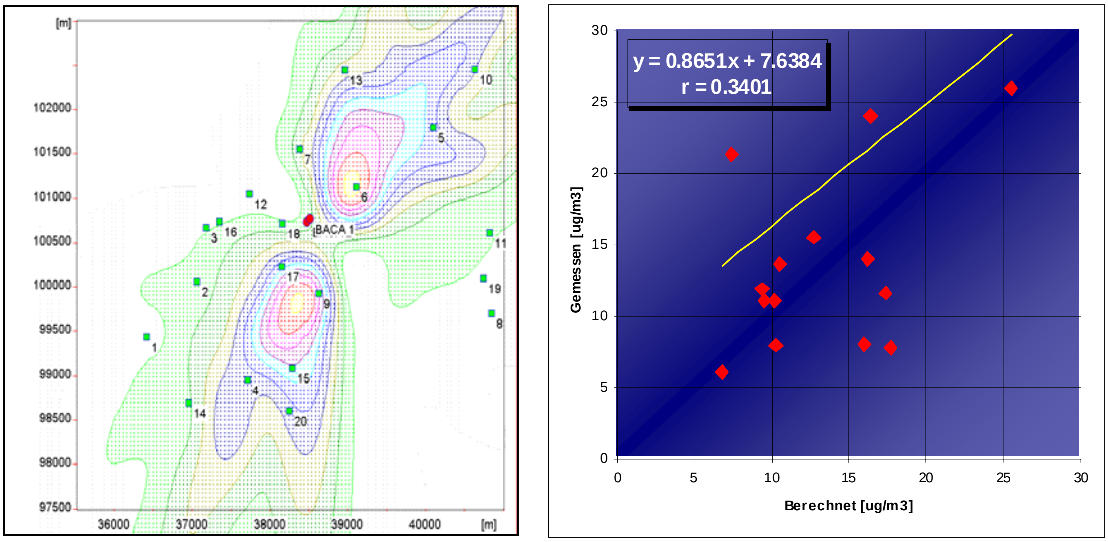

Figure 6: Calculated iso lines in the vicinity of the plant after rotation of the wind field test. The comparison of calculated and measured data reveals a better correlation.

5.3 Impact area of plant

Some other industries that create air pollution are also situated near the power plant. This should also be taken into account. Unfortunately, the lack of information made this impossible. As a consequence, I decided to plot only the points influenced mainly by the power plant. These measuring points could be modeled with only one source (power plant). This gave me an almost perfect correlation with an r = 0.9178 (see figure 5).

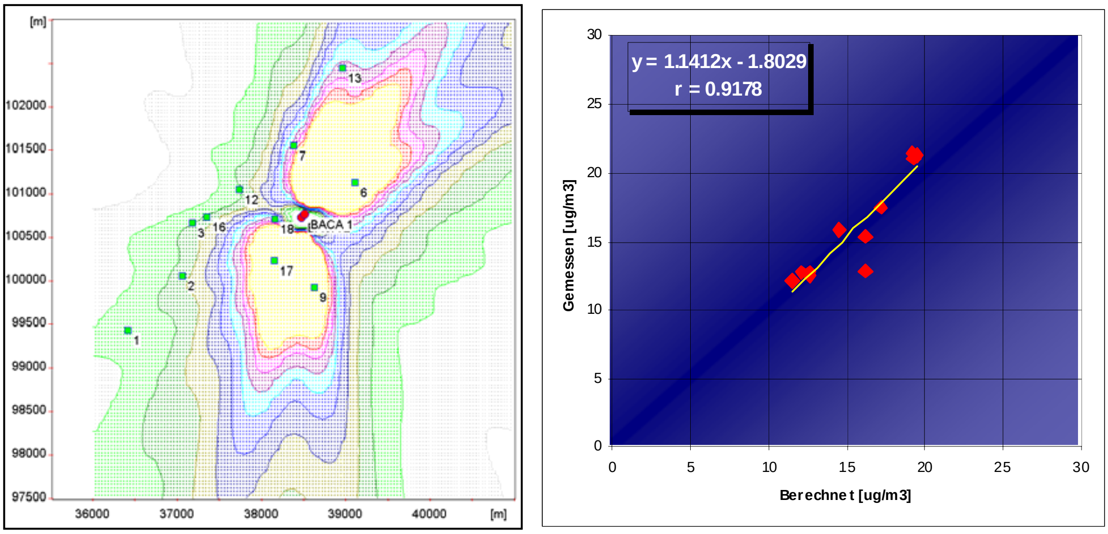

Figure 7: Calculated iso lines, disregarding measurement points outside the power plant's area of influence. The correlation is much better here.

5. CONCLUSIONS

To use models without verifying the results with real data is critical and unsafe. The quality of modeling depends on the input parameters and it is essential to check the outcome with measurements of real concentration values. The model outcome can be improved remarkably by tuning input data.

The tuning of input data also depends on the skill and experience of the person applying the model and is somewhat subjective. Coincidence with ambient data supports the decisions of the model user.

Diffusive samplers are an adequate means of assessing the spatial distribution of air pollutants. Nevertheless, only long-term concentrations can be obtained, and peak values can not be measured.

5. ACKNOWLEDGEMENTS

The authors thank Ekotest Ltd, Ankara (Turkey) which gave substantial support to this work in the form of data collection. The model was supplied courtesy of Airinfo Ltd., Switzerland

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

THE COMBINED NON-LOCAL, BAROCLINIC AND CAPPING INVERSION EFFECTS ON THE TURBULENT AND POLLUTANT CHARACTERISTICS IN THE NEUTRAL AND STABLE PBL

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ABSTRACT

Practically oriented parameterization schemes: bulk Richardson number (Rb-method), resistance law (Rl-method) and combined (Rb-Rl) method, based on their joint and coordinated use are presented. In this schemes are incorporated not only traditional factors, but and new non-local effects caused by the free- flow stability, baroclinicity and rise of capping inversion at long lived PBL regimes (see Zilitinkevich and Esau, 2005).

Using that it is developed flux- calculating techniques, it is established relationships and coordination between a series of surface, PBL and free atmosphere turbulent and stability parameters. It is also given some estimation for pollutant characteristics.
The approaches can be used (considering traditional and non-local effects) as a practical tool in the environmental and weather/climatic modeling applications.

Key Words: non-local effects, capping inversion, turbulent fluxes, resistance law, dispersion parameters.

1. INTRODUCTION

According to Zilitinkevich and Galanca (2000), it has to differ two types of stably stratified boundary layers (SBL) which exhibit essentially different physical nature. The first type involves nocturnal SBL in the middle latitudes, disconnected from the stably stratified free atmosphere by a thick neutrally stratified residual layer (this is traditional short-lived nocturnal SBL). At high latitudes and coastal zones, another type of boundary layers are often observed (King 1990) namely, long-lived SBL immediately adjusting to the stably stratified free atmosphere. Here the two stably stratified layers are essentially interconnected due to the propagation of internal gravity waves and atmospheric surface layer is essentially affected by the static stability of the free atmosphere. This is a striking demonstration on non-local nature of turbulence (Kitaigorodskii and Joffre 1988), (King and Turner 1997), (Mahrt 1999). The key parameter characterizing this mechanism is the Brundt-Vaisala frequency N in the free atmosphere, and also the baroclinicity and the parameters of rise capping inversion over SBL (Zilitinkevich 2005). Accounting the mentioned above effects in the present work it is realized a parameterization method for determination of the main characteristics of the turbulent regime of neutral and long-lived SBL, based on the joint and coordinated use of the following components: bulk-Richardson number method, resistance and heat transfer laws and its universal functions A, B, C. It is also given some application to the dispersion models.

2. PARAMETERIZATION METHODS, REGIMES AND SOME APPLICATION

It is considered three parameterization schemes and some of their applications, which we consecutively introducing.

2.1. Bulk- Richardson number method with accounting of the non-local effects

A starting point for practical calculation of turbulent fluxes in the surface layer is the Monin-Obukhov similarity theory. Zilitinkevich and Galanca, (2000), Zilitinkevich, (2002), developed a theoretical model of the non-local turbulent transport (accounting the internal- wave interaction between the long-lived SBL and the free atmosphere). In stable stratification its results is dependence of the universal functions in surface layer $\varphi_u = (\aleph z / U_*)(dU / dz), \varphi_\theta = (\aleph_T z / \theta_*)(d\theta / dz)$, on the Brundt-Vaisala frequency $N = (\beta (d\theta / dz)|_{z>h})^{1/2}$ above the top h of the SBL (Zilitinkevich and Esau, 2005):

$$\varphi_u = 1 + C_u \frac{z}{L}(1 + C_{NM}^2 Fi^2)^{1/2}, \quad \varphi_\theta = 1 + C_\theta \frac{z}{L}(1 + C_{NH}^2 Fi^2)^{1/2}$$

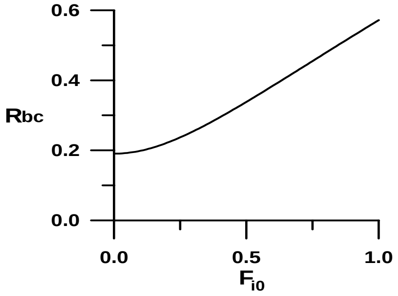

Figure 1.Dependence of Rbc on F_{i0}

where $Fi = NL / U_*$ is the inverse Froude number, $L = \aleph L_{MO}, L_{MO} = -U_*^3 \big/ \beta q \aleph$ is the Monin-Obukhov length scale $\theta_* = -q / U_*$ is the von Karman constant, U and θ are wind component and potential temperature, z is the height, U_* and q are the dynamic friction velocity and flux of potential temperature, $C_u = C_\theta = 2, C_{NM} = 0.06$, $C_{NH} = 0.6$. With considering the above expressions for $\varphi_u, \varphi_\theta$, (Syrakov, 2004), (Syrakov and Cholakov, 2005) developed practical orientated flux calculation techniques, based on the bulk Richardson number:

$$\frac{\beta \Delta \theta}{U_1^2} z_1 = Rb(\lambda_u, \lambda_\theta, S, F_{i0}) = \frac{\aleph^2}{\aleph_T} S \frac{\lambda_\theta + C_\theta \left[S^2 + C_{NH}^2 \frac{1}{Cd} F_{i0}^2 \right]^{1/2}}{\left[\lambda_u + C_u (S^2 + C_{NM}^2 \frac{1}{Cd} F_{i0}^2)^{1/2} \right]^2}, \qquad (1)$$

where $F_{i0} = Nz_1 / U_1$ is non-local parameter, z_1 is a fixed reference height in surface layer (accepted in this study at 10m), $U_1 = U(z = z_1)$, $\Delta\theta = \theta(z_1) - \theta_0$, $\theta_0 = \theta(z = z_{0T})$, z_{0u} and z_{0T} are the roughness lengths, $\lambda_u = \ln(z_1 / z_{0u})$, $\lambda_\theta = \ln(z_1 / z_{0T})$, $S = z_1/L$, β is the buoyancy parameter, $\aleph_T \approx 0.42$. At $S \to \infty$ from (1) we define the critical bulk-Richardson number:

$$Rbc(F_{i0}) = \frac{\aleph^2 C_\theta}{\aleph_T C_u^2} \frac{(1 + C_{NH}^2 F_{i0}^2 A^{-2})^{1/2}}{(1 + C_{NM}^2 F_{i0}^2 A^{-2})}, A = \frac{\aleph}{C_u}\left(1 - \frac{C_{NM}^2}{\aleph^2} F_{i0}^2 C_u^2\right)^{1/2} \tag{2}$$

At $F_{i0} = 0$ from (2) follows the classical result: $Rbc(0) = \aleph^2 C_\theta / \aleph_T C_u^2$ (see Byun, 1990).

Figure1 present the dependence of Rbc on F_{i0}. It is seen that in the case of non-local effects, the critical number Rbc is significantly greater then the corresponding number in the classical case $Rbc(F_{i0} = 0) = 0.19$. This means that at $Rbc(F_{i0} \neq 0) > 0.19$, it can be generated the non-local exchange effects. The proposed method allows determining the drag coefficient $Cd^{1/2} = U_* / U_1$ and potential temperature transfer coefficient $Ct = \theta_* / \Delta\theta$, from the input conventional $\lambda_u, \lambda_\theta, Rb$ and non-local F_{i0} parameters:

$$Cd^{1/2} = Cd^{1/2}\,(\lambda_u, \lambda_\theta, Rb, F_{i0}), Ct = Ct\,(\lambda_u, \lambda_\theta, Rb, F_{i0}) \tag{3}$$

Compared with the traditional case ($F_{i0} = 0$), the non-local effects ($F_{i0} = 0.4, 0.8$) are significant and generate an extended range of the exchange processes of impulse and heat in the surface layer (Figure 2).

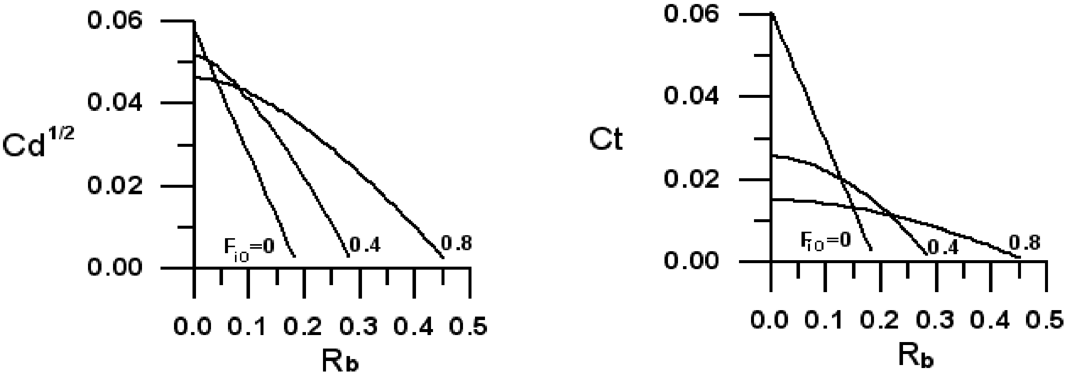

Figure 2. Dependence of drag $Cd^{1/2}$ and heat-transfer coefficient C_t on Rb at different values of non-local parameter F_{i0}.

2.2 Resistance and heat transfer law's functions A, B, C.

On the basis of simple two-layer model of PBL (surface layer (SL) at $z \le h_S$ and the Ekman layer above, where h_S is the height of SL) it is determined the form of the universal functions A, B, C, in neutral and stable SBL considering the mutual effects of stratification, baroclinicity, and non-local factors connected with N and capping inversion (Syrakov, 1990, 2004, 2005):

$$A_k = -\ln(\aleph H_S) + \widetilde{C}_U H_S \widetilde{\mu}_M - B_k \, ; \widetilde{\mu}_M = \left(\mu^2 + \widetilde{C}_{NM}^2 \mu_N^2\right)^{1/2} \tag{4}$$

$$B_k = \varepsilon / H_S \tag{5}$$

$$C_k = -\ln(\aleph H_S) + \widetilde{C}_\theta H_S \widetilde{\mu}_H - 2l B_k \, ; \widetilde{\mu}_H = \left(\mu^2 + \widetilde{C}_{NH}^2 \mu_N^2\right)^{1/2} \tag{6}$$

for basic barotropic case with non-local N effect and:

$$A = A_k + B_k\left[1 - \left(F_1 + F_2\right)\right] + \frac{1}{2B_k}\left[F_1\left(\eta_y + \eta_x\right) - F_2\left(\eta_y - \eta_x\right)\right] + \eta_x H_S \tag{7}$$

$$B = B_k\left(F_1 - F_2\right) + \frac{1}{2B_k}\left[F_1\left(\eta_y - \eta_x\right) + F_2\left(\eta_y + \eta_x\right)\right] + \eta_y H_S \tag{8}$$

$$\left.\begin{aligned} &C = C_k + \Delta C_{cap}, \Delta C_{cap} = \left[\left(\Gamma_\theta - \Gamma_I / 2\right)h - \Delta\theta_I + \Gamma_\theta \Delta h\right]\frac{\aleph}{\theta_*} \equiv \aleph^5 \frac{\widetilde{\mu}_{cap}^2}{\mu} H_I, \\ &\widetilde{\mu}_{cap} = (\mu_N^2 - \mu_{N_I}^2 / 2 - \mu\Delta\theta_I + \mu_{\Delta h}^2, \end{aligned}\right] \tag{9}$$

for the general case with baroclinic- capping inversion effects, where F_1 and F_2 are weight functions:

$$F_1 = \frac{sh(2l)}{ch(2l) - \cos(2l)}, F_2 = \frac{-\sin(2l)}{ch(2l) - \cos(2l)}, l = (H_I - H_S)B_k, \tag{10}$$

with asymptotes at $l \to \pi$, $F_1 = 1$, $F_2 = 0$ (very high inversions-practical non-inversion effect in (4)-(6)) and at $l \to 0$ (maximal inversion effects at very low inversions). Here $H_I = h_I / (\aleph U_* / f)$ is dimensionless inversion parameter, h_I is the down limit of inversion coinciding in this case with the upper limit h of SBL, i.e. $h \equiv h_I$, $H_S = h_s / (\aleph U_* / f)$ is the dimensionless height of SL. $\widetilde{\mu}_M$ and $\widetilde{\mu}_H$ are SBL composite stratification parameters, $\mu_N = N / f$ and $\mu = (\aleph U_* / f) / L_{MO}$ are non-local and conventional internal stratification parameters, $N = \left(\beta\Gamma_\theta\right)^{1/2}$, Γ_θ is potential temperature gradient in the free atmosphere above capping inversion, $\widetilde{\mu}_{cap}$ is new capping (over SBL) inversion composite stratification parameter characterizing its thermal structure; $\mu_{N_I} = N_I / f$, $\mu_{\Delta\theta_I} = N_{\Delta\theta_I} / f$, $\mu_{\Delta h} = N_{\Delta h} / f$, $N_I = (\beta\Gamma_I)^{1/2}$, $N_{\Delta\theta_I} = (\beta\Gamma_{\Delta\theta_I})^{1/2}$, $N_{\Delta h} = (\beta\Gamma_{\Delta h})^{1/2}$, are corresponding Brundt-Vaisala frequencies, $\Gamma_I = \Delta\theta_I / \Delta h$ is capping inversions temperature gradient, $\Gamma_{\Delta\theta_I} = \Delta\theta_I / h_I$,

$\Gamma_{\Delta h} = \Gamma_{\theta}\Delta h / h_I$, $\Delta\theta_I = \theta_{h_I+\Delta h} - \theta_{h_I}$ is the potential temperature increment across the capping inversion (see Zilitinkevich, 2005), Δh is capping inversion depth, above h_I, $\eta_x = (\aleph^2 / f)du_g / dz = M\cos\phi$ and $\eta_x = (\aleph^2 / f)dv_g / dz = M\sin\phi$ are non dimensional internal baroclinic parameters (see Yordanov and Wippermann, 1972), $M = \left(\eta_x^2 + \eta_y^2\right)^{1/2}$, ϕ is the angle between surface and thermal wind. We will note that from the relation $H_I \equiv \mu_I / \mu$, instead of H_I it can be introduced the equivalent parameter $\mu_I = h_I / L$ (in present work we will use H_I). The quantity H_S is determined on the basis of analyze of the dynamic equations of SBL, using the limit- method, we force the change of the moment fluxes in SL, with the height to 10% ($\varepsilon = 0.1$). In barotropic case:

$$H_S = \frac{2\varepsilon^2}{1 + \sqrt{1 + 8\varepsilon^2 \widetilde{C}_U \widetilde{\mu}_M}} \tag{11}$$

Substituting (11) in (4)-(6), we determine the explicit form of A_k, B_k, C_k. In the general case for H_S it is received a more complex equation, which together with (7)-(9); (10) is a system of transcendental equations and after its numerical decision we determine the dependence of A, B, C on the parameters (it is listed the different stratification parameters, which includes in the composite parameters $\widetilde{\mu}_M$, $\widetilde{\mu}_H$ and $\widetilde{\mu}_{cap}$):

$$\mu; \mu_N; M, \phi; H_I; \mu_{N_I}, \mu_{\Delta\theta_I}, \mu_{\Delta h}, \tag{12}$$

describing a wide range series conventional and non-local (long-lived PBL) turbulent regimes.

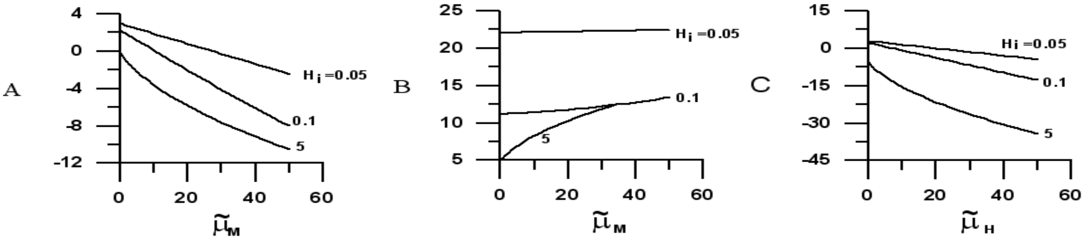

Figure 3. Dependence of A, B, C on composite stratification parameters $\widetilde{\mu}_M$, $\widetilde{\mu}_H$ by different values of inversion parameter H_I

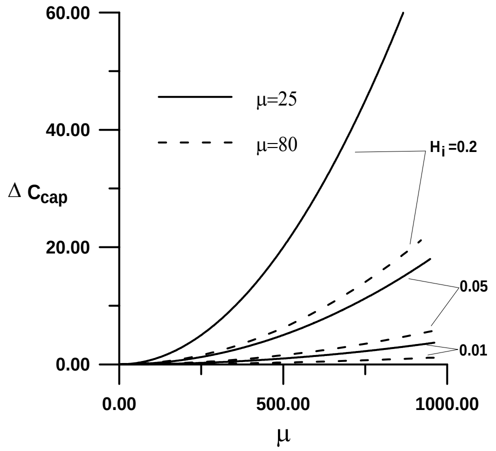

Figure 4. Dependence of ΔC_{cap} from (13) on μ_N at different values of μ and

On the Figure (3) is demonstrated the joint effect of the non-local parameter $\tilde{\mu}_M$ and $\tilde{\mu}_H$, and inversion parameter H_I on A, B, C. With decreasing of H_I, increases this effect. We will notice that this is "clean lid effect" (at $\Delta C_{cap} = 0$). At $H_I = 5$ we have classical non-inversion case. Taking into account also the thermal structure of the capping inversion (in the layer Δh over h_I), at $\Delta C_{cap} \neq 0$, it is considered second additional "capping inversion effect", relatedto the thermal interaction between Δh- capping inversion layer on μ_N by different values of μ and H_I. the correction function ΔC_{cap} from (9). In the capping inversion layer with significantly bigger gradient Γ_I and not very big thickness Δh (i.e. Γ_I significantly exceeds Γ_θ and $\Delta h \le h$);

$$\Delta C_{cap} = \aleph^5 (\tilde{\mu}_{cap}^2 / \mu) H_I , \ \tilde{\mu}_{cap} = -(\mu_{N_I}^2 / 2 + \mu_{\Delta\theta_I}^2)^{1/2} \qquad (13)$$

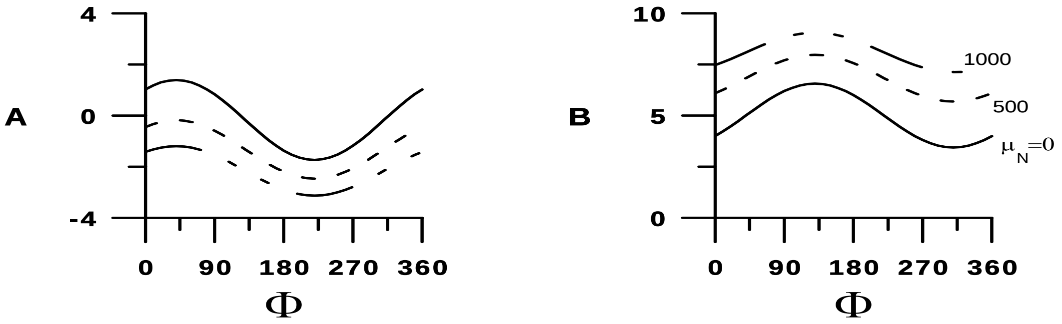

Figure 5. Dependence of A, B functions on baroclinicity parameter ϕ at $M = 10$ and different values of μ_N.

It is seen at Figure 4 that ΔC_{cap} effect can be quite significant and comparable with the basic thermal function C_k from (9). The joint influence of non-local effect at traditionally neutral SBL, (at $\mu = 0$, i.e. $\tilde{\mu} \equiv \mu_N$, (see Zilitinkevich and Esau, 2005) and the baroclinicity on the resistance law's function A and B is demonstrated on Figure 5

2.3 Combined Resistance law's--bulk Richardson method

This method which we will note as (Rb-Rl) method is developed by Syrakov (1990) on the basis of combined parameterization scheme considering the joint and coordinated use of bulk Richardson number method and Resistance laws, for traditional regime of SBL. Here we will generalize the method considering the above studied non-local effects. After some transformation of the resistance and heat transfer laws, considering (1)-(3), we receive the following general relations between the surface (in layer $0-z_1$): $U_1, \Delta\theta, Cd^{1/2}, Ct$ and SBL: $G_0, \delta\theta, \alpha$, parameters (Syrakov (2004), Syrakov, Cholakov (2005)):

$$G_0 / U_1 = F_g\,,\ \ \delta\theta / \Delta\theta = F_t\,,\ \ \alpha = arctg\{B / [\ln(Cd^{1/2}\widetilde{Ro}) - A]\}\,, \qquad (14)$$

where, $f_1 = BC_d^{1/2}$, $f_2 = Cd^{1/2}\left[\ln(Cd^{1/2}\widetilde{Ro}) - A\right]$, $F_t = \dfrac{C_t}{\aleph}\left[\ln(Cd^{1/2}\widetilde{Ro}) - C\right]$, G_0 is modulus of the surface geostrophic wind, $\delta\theta = \theta_h - \theta_0$ (at inversion $h = h_I$), α is the angle of full turning of the wind in SBL, $\widetilde{Ro} = U_1 / fz_0$ is a local Rossby number in layer $0-z_1$; A, B, C functions are gived according to (7)-(9).

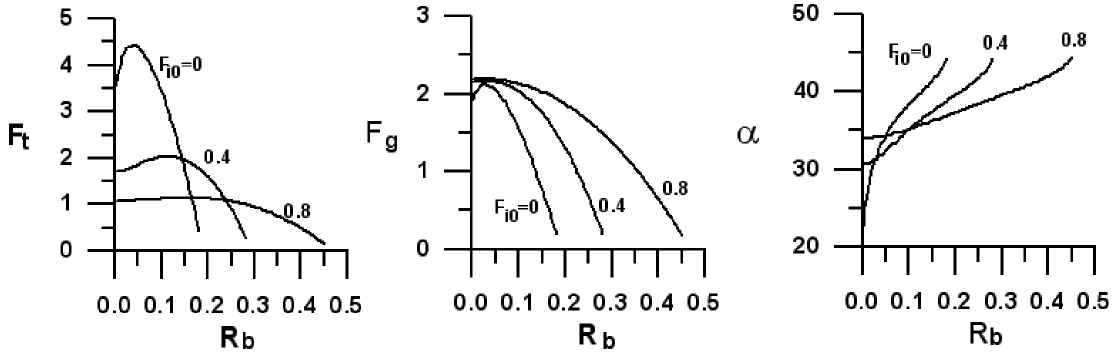

Figure 6. Dependence of F_g, F_t, α from Rb by different values of non-local parameter F_{i0} and $\lambda = 7, \widetilde{Ro} = 3.10^6$.

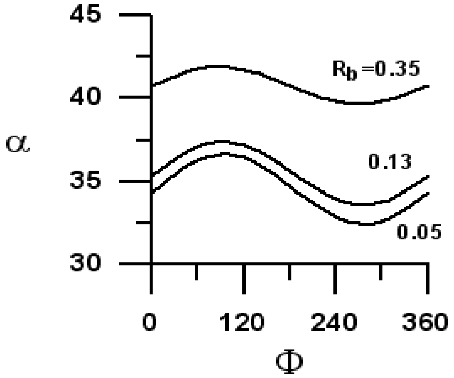

Fig.7. Dependence of α on the baroclinicity parameter ϕ at different Rb and $F_{i0} = 0.8$

Taking into account the relations between the parameters (12) and these in (3):

$$\mu = \aleph^2 \widetilde{Ro} Cd^{1/2} S \exp(-\lambda_u)\,,$$

$$\mu_{N_I} = \widetilde{Ro} F_{i0I} \exp(-\lambda_u)\,,$$

$$\mu_{\Delta\theta} = \widetilde{Ro} F_{i0\Delta\theta_I} \exp(-\lambda_u)\,,$$

$H_I = 1/\aleph C_d^{1/2} Ro_I$, it's easy to see that the right parts of (14) i.e. the explored unknown function F_g, F_t, α depend of the following parameters:

$$\lambda_u, \lambda_\theta, Rb; M, \phi; \widetilde{Ro}, F_{i0}; Ro_I; F_{i0I}, F_{i0\Delta\theta_I}, \quad (15)$$

where $Ro_I = U_1 / fh_I$ is mutual (SL-SBL) Rossby inversion number, $F_{i0I} = N_I z_1 / U_1$ and $F_{i0\Delta\theta_I} = N_{\Delta\theta_I} z_1 / U_1$, are parameters describing the thermal structure of the capping inversion layer with thickness Δh over h_I. Obviously parameters (15) are input for the realization of (Rb-Rl) method. For example on Figure 6 it is shown the joint influence of stratification (Rb) and non-local effects ($F_{i0} \neq 0$) on F_g, F_t and α .For comparison it is also given the conventional case ($F_{i0} = 0$). Influence of baroclinicity at $F_{i0} = 0.8$ (strong non-local effect) at different Rb is demonstrated on Figure 7. As it seen in both cases the non-local effects are significant.

2.4. Application to determination of pollutant characteristics

The proposed parameterization schemes allow different procedures for practical application.

For example, using standard surface input data (at z_1=10m), on basis of Rb- method, are calculated turbulent fluxes, Monin-Obukhov length scale and other main turbulent characteristics.

Generalized variant of Rb method with incorporated non-local effects extending the applicability of parameterization also for the cases of surface layer within long- lived SBL.

Using for parameterization, of resistance laws (Rl-method), as input parameters are used external aerologic-synoptic (diagnostic or prognostic) data. On the basis of combined (Rb-Rl)–method and the proposed practically oriented flux-calculation techniques it is calculated relationships and correspondences between a series of main BL, PBL, PBL-free atmosphere turbulent and stability parameters for conventional and non-local turbulent regimes. Here as input parameters it can be used surface, aerologic-synoptic or from mixed format data.

These approaches are connected with accounting the influence of different above commented conventional and non-local effects, on the dynamical turbulent characteristics. As we have seen above, their dynamical influence is significant. It is natural to be expected, that their influence will take effect over the pollution characteristics.

Here we will consider these dynamical effects on the main pollution characteristics, for example: trajectory, dispersion, skewness of an instantly released cloud in SBL, described with pollutant dispersion model (Syrakov and Ganev, 2003, 2004). This model is based on splitting the diffusion to horizontal and vertical components, taking into account turning of wind in PBL and the other discussed above effects, and incorporating the method of moments (Safman, 1962), (Smith, 1965).Differing from the often met procedures, which a' priory give the dispersion, at this approach they are determined in the frames of the solution of the diffusion problem.

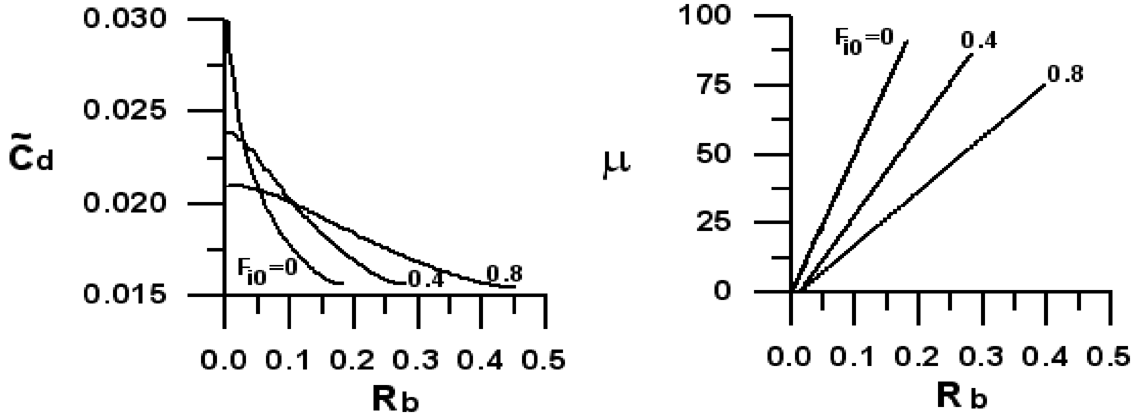

Figure 8. Dependence of geostrophic drag coefficient $\widetilde{C}_d = U_*/G_0$ and internal stratification parameter μ on bulk Richardson number Rb at different values of the non-local parameter F_{i0}.

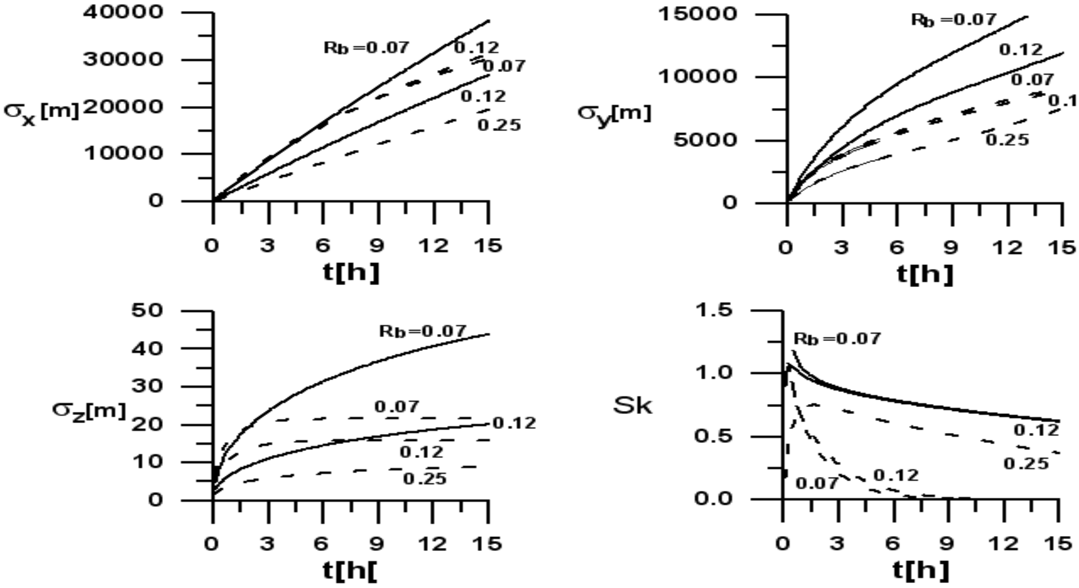

Figure 9. Dependence of dispersion parameters $\sigma_x(t), \sigma_y(t), \sigma_z(t)$ and skewness $Sk(t)$ on non-local parameter F_{i0}: $F_{i0} = 0$ (thick line) (conventional case) and $F_{i0} = 0.4$ (dotted line) by different values of Rb at $\lambda_u = \lambda_\theta = 7$ and $R\widetilde{o} = 3.10^6$.

The necessary for the pollutant model, dynamical parameters: velocity components u, v, vertical turbulent coefficient K_z, are calculated by one dimensional (z,t) - SBL model with formula for mixing length of Blackadar- Delage type. The model has different options for realization. Here we will limit to studying the steady state regime and variance in which as input parameters for the PBL model are used

$\widetilde{Cd} = U_*/G_0$, α, μ, G_0 which are calculated by the (Rb-Rl) method. With the PBL model it is determined the dynamical parameters U, V, K_z , after which on the basis of pollutant dispersion model it is calculated different pollutant characteristics, The algorithm of this procedure is shown in table 1. So for example at input parameters (15): $\lambda_u = \lambda_\theta = 7$, $\widetilde{R}_0 = 3.10^6$ and $F_{i0} = 0,\ 0.4,\ 0.8$ for barotropic($M = \phi = 0$) and without inversion ($F_{i0I} = F_{i0\Delta\theta_I}$) case. Using (Rb-Rl) it is calculated the quantities: α (see Figure 6); $\widetilde{C}_d$, μ (see Figure 8), and using the function F_g (see Figure 6)it is easy to determine G_0 .

With the same parameters $\lambda_u, \lambda_\theta, \widetilde{R}_0$ and $F_{i0} = 0,2$ in an identical way it is calculated and some cases with consideration of the inversion effect: case B (only “clean lid” inversion effect: $R_{0I} = 500$, $F_{i0I} = F_{io\Delta\theta_I} = \Delta C_{cap} = 0$), case C (combined “lid” and ΔC_{cap} effect, $F_{ioI} = 0,135$, $F_{io\Delta\theta_I} = 0,07$). For comparison with cases B and C it is calculated also and the respective to them non-inversion case A (at $F_{i0} = 0,2$). According to the procedure of table 1 it is calculated, for example, the respective pollutant characteristics: dispersion parameters $\sigma_x(t), \sigma_y(t), \sigma_z(t)$ and skewness $Sk(t)$

On Figure 9 is demonstrated the influence of the non-local parameters on the counted parameters. These effects cause folding of the depth of PBL and fast inclining of the skewness $Sk(t)$ to zero. The counted effects increase more in the inversion case, particular in case C when it is counted the joint effects of “lid” and ΔC_{cap} (Figure 10).

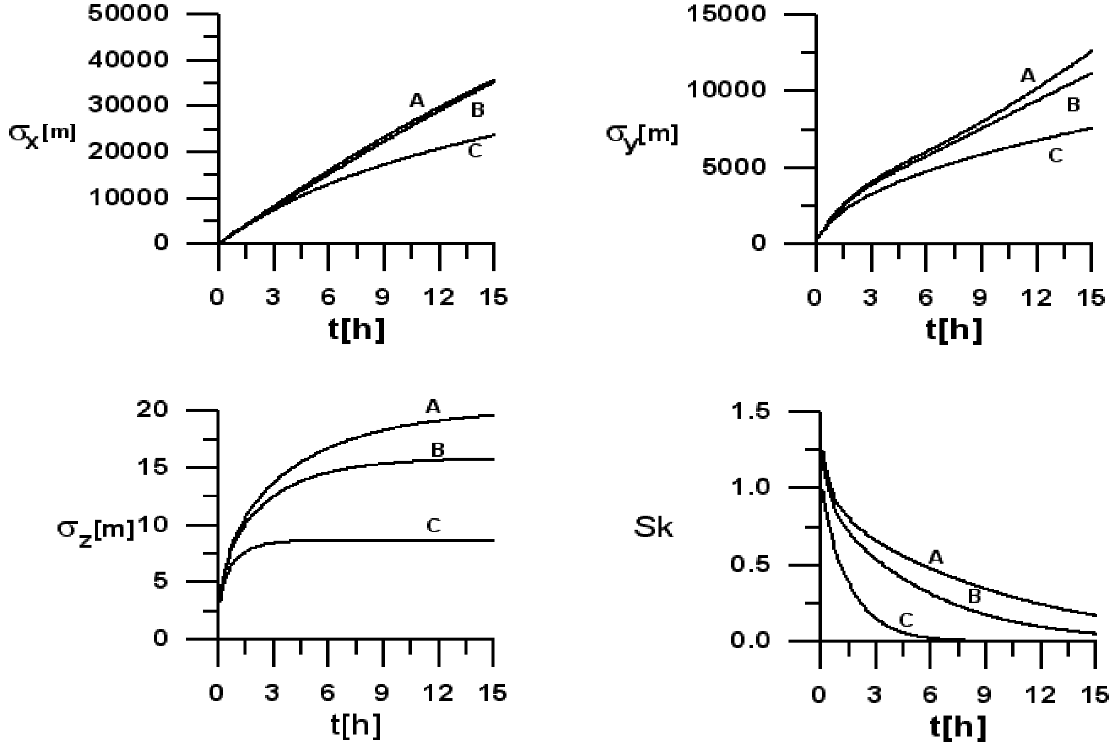

Figure 10. Dependence of dispersion parameters $\sigma_x(t),\sigma_y(t),\sigma_z(t)$, skewness $Sk(t)$ by non-local parameter $F_{i0} = 0.2$, $Rb = 0.12$, on inversion regimes: without inversion (A), only ("clean lid") inversion effect (B) and generalized case with additional ("clean lid") effect" plus thermal structure rise inversion effect (C).

Table1. Procedure for calculation of pollutant characteristics.

Input parameters (15)
(Rb-Rl)-method: determination of Cd,α,μ,G_0
SBL model: determination of $u(z),v(z),K_z(z)$
Pollutant dispersion model and determination of pollutant characteristics

3. CONCLUSION

The most popular (traditional) parameterization schemes from type of Rb-method, Rl-method, etc. are connected with traditional turbulent regimes. The present paper suggests a more general approach including the new non-local and capping inversion effects at long-lived PBL (Zilitinkevich and Esau, 2005), and also suggests combined (Rb-Rl) variant for connection between surface, SBL and free- atmosphere parameters.

In long- lived SBL, the surface layer is strongly affected from free flow stability (parameter N). As difference from the traditional formulation generalized bulk Richardson number Rb and its critical values Rbc are significantly depended on non-local effects. It leads, to incorporating these effects also in turbulent fluxes and other turbulent and stability parameter.

In these conditions the resistance and heat transfer law's functions A, B, C, are advanced accounted with free flow stability, baroclinicity and capping inversion effects. These effects are accounted through corresponding composition stratification parameters ($\tilde{\mu}_H , \tilde{\mu}_M , \tilde{\mu}_{cap}$). It is shown, that capping inversion influence, is formed from two effects: "clean lid" effect and additional connected with thermal structure of capping layer over lower boundary of inversion h_I .

Combined (Rb-Rl) method allows finding coordinated relationships between surface, aerologic-synoptic and free atmosphere entrainment parameter and to use meteorological pre-processors using different input data.

Proposed parameterization schemes and calculated techniques are given in format analogical to conventional, which makes them easy accessible and applicable to determine wide range of dynamical and environmental tasks considering the above mentioned new effects.

4. ACKNOWLEDGEMENTS:

The authors would like to thank to proff. S. Zilitinkevich for the giving us the manuscript of the work (Zilitinkevich, S.and Esau S., 2005.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

CHARACTERIZATION OF POLLUTANT SOURCES AT 10 STATIONS IN ISTANBUL WITH PM$_{10}$ AND EU DIRECTIVES ON FOCAL POINT

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ABSTRACT

Air pollution is an extremely significant issue that should be focused on all around the globe as it affects human health, ecosystems and the environment, destroys aesthetical conditions, gives harm to matters, buildings, and in turn economy.

In this study it is aimed to show the standing of Turkey under the EU directives. Days that exceed limiting PM$_{10}$ values according to the EU directives PM$_{10}$ restirictions are chosen as episode days (PM10>150 µg/m3. İt can be concluded that in nearly all the stations, between 1998-2003, more than 35 days in a year exceed 50 µg/m^3. Furthermore, 247 episode days are chosen according to days, which exceed the PM$_{10}$ value of 150 µg/m^3, of which due to the lack of meteorological data only for 233 days, atmospheric stability conditions are investigated. Furthermore, two test cases representative of summer and winter conditions are investigated in terms of stability conditions and in terms of synoptic fields to capture an approach in defining the source of pollution as local or transport processes. Considering the prevailing synoptic conditions, it is defined either the local sources contribution or the transport processes contribution is the dominant phenomena in generating pollution at the test case days.

Key Words: Air Pollution, PM$_{10}$, Episode Day, Atmospheric Stability, Istanbul.

1. INTRODUCTION

Air pollution is an extremely significant issue that should be focused on all around the globe as it affects human health, ecosystems and the environment, destroys aesthetical conditions, gives harm to matters, buildings, and in turn economy. European Union's approach to this point is very sensitive. It is important in EU member countries to determine the air pollution sources, the contribution of the sources and to define the effects of local sources, effects of meteorology and transport processes like transport of Saharan dust and ocean sprays, in order to set up policies and regulations. If transport processes are dominant, putting regional standards to industrial sources and limiting anthropogenic activities will not be adequate to prevent pollution because there will be pollutants coming from remote sources. Therefore, contributions of sources are important to effectively establish regulations and protect the desired air quality. Countries like Spain is not meeting the demands, causing them to pay to the Union for the pollution they generate. Studies are done therefore by Artinano et al. (2003), Salvador et al (2003) and Viana at all (2005)to identify the sources of pollution in Spain. As Turkey is in a series of steps in becoming a EU member, regulations should be accredited considering the EU directives and source characterization should be found out in order to have a better environment and less economic hardness. With this study, it is expected to predict the kind of pollutant activity affecting Istanbul. Moreover, it is the main purpose of this study to examine and highlight the air quality conditions in Turkey and especially Istanbul considering the European Union (EU) directives on particulate matter other than Turkish regulations.

2. DATA

Data used in this study are air pollutant parameters data and meteorological data. Air pollutant parameters data are obtained from 10 stations in Istanbul owned by the Istanbul Metropolitan Municipality Environmental Protection and Control Unit, namely Alibeyköy, Beşiktaş, Sarıyer, Saraçhane, Esenler, Yenibosna, Ümraniye, Üsküdar, Kartal, and Kadıköy. Data is obtained for the period 1998-2003 and pollutant parameters measured are as follows; SO_2, PM_{10}, CO, NO, NO_x, NO_2, CH_4, THC, nMHC, and Ozone. Meteorological data are obtained from the State Meteorological Service of Turkey, which consits of the following: surface wind speed, total solar insolation, solar insolation period, cloudiness, and surface pressure data.

3. PM_{10} ANALYSIS

PM_{10} values from 1998 to 2003 are examined at 10 stations. Number of days that exceeded limiting PM_{10} values of 50, 100,150, 200, 300, and 400µg/m^3 at these stations on monthly, seasonal and annual basis are obtained (not shown). Table 1 lists number of days that exceed limiting PM_{10} values for the 1998-2003 period in annual base. According to the European Union Directives, daily PM_{10} limit of 50 µg/m^3 should not be exceeded on more than 35 days in a year for the 2005-2010 periods and in 2010 the limiting value will decrease to 20µg/m^3 with not more than annual 7 days exceedance permit. Investigating Table 1, it can be concluded that in nearly all the stations, between 1998-2003, more than 35 days in a year exceed 50 µg/m^3. Furthermore, 247 episode days are chosen according to days, which exceed the PM_{10} value of 150 µg/m^3, of which due to the lack of meteorological data only for 233 days, atmospheric stability conditions are investigated.

4. ANALYSIS OF ATMOSPHERIC CONDITIONS

4.1 Atmospheric Stability

Atmospheric stability is detected using Pasquill stability classes' method. The chosen episode dates are divided into two parts, summertime dates and wintertime dates. Summertime is defined between April and September, for which stability is detected using solar radiation data, wind speed data and the corresponding section of the Pasquill stability classes' chart. On contrary, wintertime is defined between October and March, and stability for this period is detected using cloud cover and wind speed data and corresponding section of the Pasquill stability classes' chart. Stability distributions reveal that the most dominant stability is D, which refers to the neutral case. If there were enough data to measure the atmospheric stability in some other means, it is assumed that the atmospheric stability in episode days would be found as stable. In the study by Chen et al. (2003) wind speeds are quite low (below 2m/s) compared with the surface wind speed data measured at episode days in Istanbul. Only at 10 days of the 240-day long episode days period (with available data to determine atmospheric conditions) in Istanbul are wind speed values below 2m/s. As stability classes are defined according to wind speed in Pasquill Stability Classes Method, it is almost impossible to obtain stable atmospheric conditions in Istanbul with this method.

4.2 Surface Atmospheric Pressure and Synoptic Charts

1000 mb pressure level synoptic charts are examined for two representative episode day periods. These periods are chosen for the summer and winter conditions, namely 1-7 April 2000 and 1-12 February 2002.

On the 1-7 April 2000 period, prevailing winds are northerly and the system is coming from the northeastern and eastern Europe. There is low pressure dominant all over Istanbul, and there is promoted vertical mixing as it is the major characteristic of low-pressure systems(Figure 1). As a result, atmospheric stability is neutral and unstable. It is observed at this period that at times of transition to neutral stability the concentrations increase due to less mixing which is meteorological, but at the other times although the atmospheric conditions promote the mixing of air, and vertical motions, particulate matter concentrations are still high (Table 2). For this reason, this pollution can be linked to local sources contribution. Other air pollutant parameters investigated also show the same reflection (Table 3).

In the 1-12 February 2002 period, there is westerly movement of an anticyclone (high pressure system), and the air from the southern Europe and Northern Africa is carried towards Istanbul with southwesterly prevailing winds. On 8th February 2002 there is a cyclone (low pressure system) coming onto Istanbul from north, and air from northeastern Europe and Siberia is carried towards Istanbul. This is not a long lasting situation as on 9th February 2002; the anticyclone again covers Istanbul with southwesterly winds carrying again the air from the southern Europe and Northern Africa until the end of this period, but the high pressure level in Istanbul is not as much as the previous one although it is still the same field corresponding to the same system, at the end of the period again a cyclone is coming from north causing the pressures in Istanbul to lower(Figure 2).

Table 1. Total numbers of days that exceed limiting PM$_{10}$ values(μg/m^3) for the years between 1998-2003.

İstanbul Air Quality Measuruments Stations	**Years**																	
	1998			**1999**			**2000**			**2001**			**2002**			**2003**		
	TM*	>50	>150	**TM**	>50	>150	**TM**	>50	>150	**TM**	>50	>150	**TM**	>50	>150	**TM**	>50	>150
Alibeyköy	190	159	63	132	61	8	199	85	5	320	86	4	252	180	29	110	79	8
Beşiktaş	210	103	1	200	58	3	-	-	-	93	25	-	218	182	17	110	51	-
Esenler	172	128	23	297	193	8	258	168	22	283	214	17	216	152	24	105	71	6
Kadıköy	-	-	-	-	-	-	-	-	-	-	-	-	179	65	13	112	60	4
Kartal	-	-	-	60	43	5	20	13	-	152	91	-	203	136	9	120	75	3
Saraçhane	150	66	1	283	135	1	167	111	11	242	103	3	236	148	7	118	83	6
Sarıyer	30	5	1	282	93	4	103	54	5	103	68	3	105	61	2	111	43	-
Ümraniye	-	-	-	60	30	2	189	138	9	184	40	-	246	126	10	111	55	1
Üsküdar	-	-	-	-	-	-	-	-	-	48	6	-	301	120	5	110	58	-
Yenibosna	144	129	14	198	159	9	174	105	13	56	19	1	179	119	5	107	74	-

*TM: Total Measurements

Table 2. Variation of PM$_{10}$ concentration (μg/m^3) for the 1-7 April 2000 period with stability classes.

Days	W.speed, m/s	Stability Class	ALİBEYKÖY	ESENLER	SARAÇHANE	SARIYER	YENİBOSNA	ÜMRANİYE
1	1,1	C-D	126	136	121	-	148	154
2	2,2	D	94	98	91	-	93	105
3	1,0	B-C	108	105	86	68	90	96
4	1,1	D	129	114	104	99	108	109
5	2,9	D	189	192	137	227	-	169
6	3,5	D	55	67	57	72	52	61
7	3,7	C	70	43	37	30	53	35

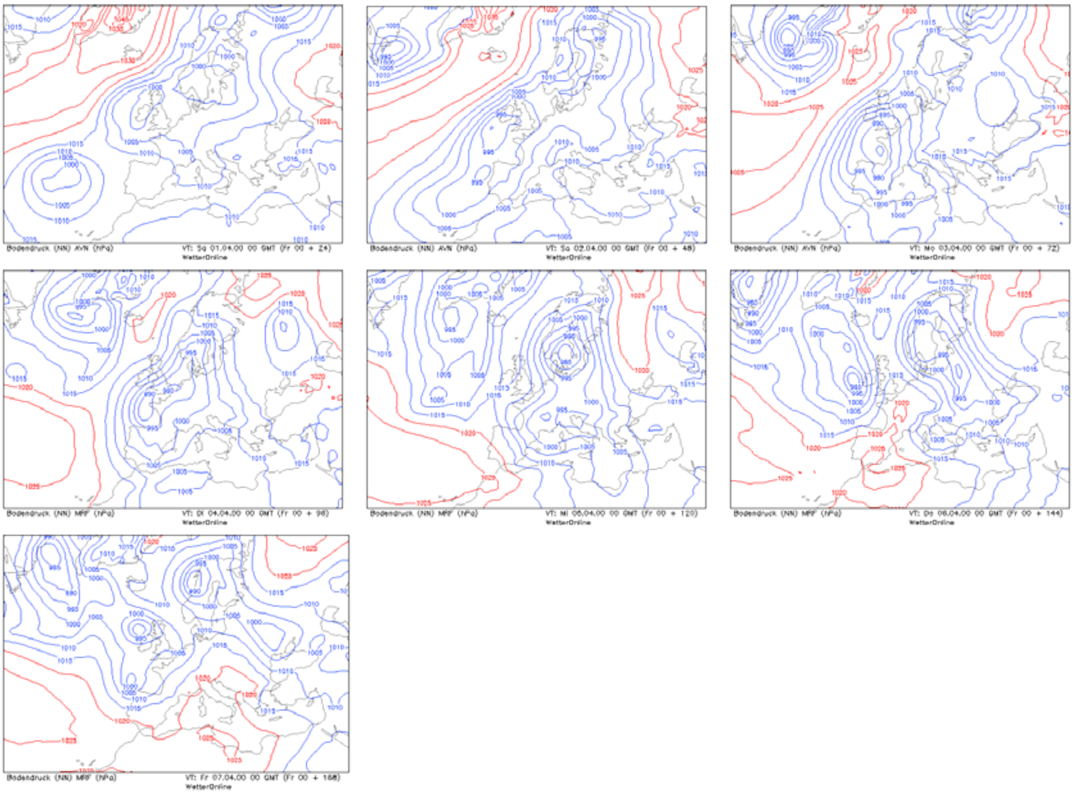

Figure 1. 1000mb Pressure level for 1-7 April 2000 Period

This can be seen as a reflection in PM_{10} concentrations measured at the stations and stability classes in Table 4. There is an increase in PM_{10} levels until 7-8th February, starting with 1020mb and increasing to 1035mb on 5th and decreasing to 1020 again on 7th in Istanbul. After that the cyclone comes from the north and the anticyclone coming for the second time is not as high as the first time, beginning with 1025mb and losing its effect to about 1015 mb with another cyclone coming from the north of Turkey. This in turn causes the PM_{10} concentrations to lower. It can also be observed for other air pollutant parameters, the variation of the other air pollutant parameters in the same period can be seen from the Table 5 in the appendix section.

Anticyclones are high-pressure systems causing a more stable atmosphere by inhibiting vertical motions and as a result increasing the concentrations of pollutant parameters by trapping them in the lower atmosphere. At anticyclonic systems, there is subsidence of air towards the surface; therefore, the pollutants transported from other regions are subsided in the high-pressure centers. What's more, the atmospheric stability coincides with the synoptic chart as expected. It is seen to be neutral and increasing to stable levels as the pressure system gets higher pressure values and becomes neutral on the 8th as there is cyclonic entrance to Istanbul and increasing again to stable atmospheric conditions but not very much as there is another cyclonic entrance at the end of the period.

Table 3. Variation of air pollutant parameters for the 1-7 April 2000 Period

April 2000	BEŞİKTAŞ								ESENLER					ÜMRANİYE						
Days	SO_2	CO	NO	NOx	NO2	THC	CH4	nMHC	SO_2	CO	NO	NOx	NO2	SO_2	CO	NO	NOx	NO2	THC	CH4
1	54	2573	118	175	56	1699	1182	507	59	1099	105	205	100	34	852	12	107	96	2746	2317
2	42	1886	79	121	42	-	-	-	33	483	37	100	63	26	485	5	71	67	1977	1866
3	46	1614	64	113	49	1636	1132	496	43	1210	144	232	88	20	496	10	98	87	2415	2083
4	68	2047	96	156	60	1698	1159	529	55	1211	133	228	95	34	675	4	79	75	2539	1926
5	42	1566	62	103	41	1434	1072	353	32	476	47	101	54	26	368	-	-	-	1967	1830
6	42	1688	81	125	44	1402	1087	306	25	244	14	51	38	14	253	-	-		2396	2210
7	21	1202	65	100	34	1371	1156	207	36	271	28	78	50	12	338	-	-		2349	2304

Table 4. Variation of PM_{10} concentration ($\mu g/m^3$) for the 1-12 February 2002 period with stability classes.

DAYS	W.speed, m/s	Stability Class	Alibeyköy	Beşiktaş	Esenler	Sarıyer	Yenibosna	Ümraniye	Kadıköy	Kartal	Üsküdar
1	1,2	E	136	176	211	93	127	83	81	138	80
2	1,8	D	70	134	139	-	-	84	80	-	48
3	3,6	D	60	99	67	-	--	38	36	-	35
4	4,1	D	54	89	71	56	121	49	50	-	61
5	1,1	F	170	202	298	-	102	145	93	-	128
6	1,1	E	249	164	202	-	71	92	114	-	120
7	0,6	F	257	260	229	99	113	127	166	67	135
8	0,7	None	297	330	464	224	163	205	-	174	185
9	1,4	D	207	173	179	-	40	119	-	-	87
10	0,9	F	182	100	247	-	212	118	-	-	120
11	3,9	D	95	114	77	-	75	62	-	71	81
12	1,3	-	-	112	96	-	37	63	--	60	37

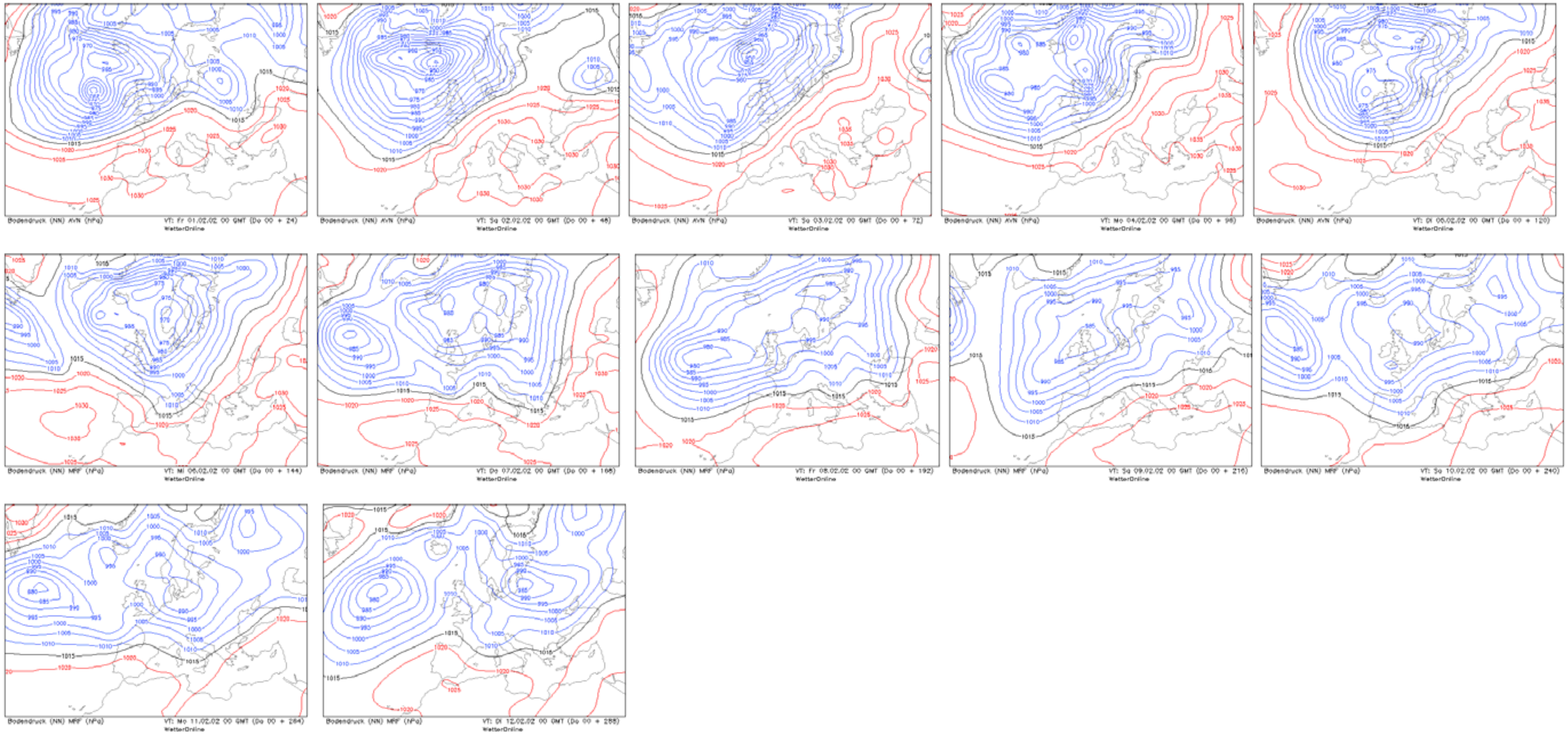

Figure 2. Anticyclone movement for 1-12 February 2002 Period

Table 5. Variation of air pollutant parameters for the 1-12 February 2002 Period

February 2002	BEŞİKTAŞ					ESENLER								**ÜMRANİYE**				
DAYS	SO_2	CO	THC	CH4	nMHC	SO_2	CO	NO	NOx	NO2	THC	CH4	nMHC	SO_2	CO	NO	NOx	NO2
1	78	2642	1484	1186	288	99	1778	104	145	41	1481	1207	266	55	1371	32	59	27
2	44	2438	1693	1428	257	38	-	64	95	32	1349	1249	91	40	1276	24	40	17
3	32	1397	1359	1215	134	23	-	14	36	22	1438	1396	33	15	596	7	17	11
4	23	1740	1351	1214	128	11	567	17	39	22	1537	1503	27	14	533	9	20	12
5	98	2976	1595	1260	326	112	3555	128	186	58	1334	951	373	65	2492	73	109	36
6	104	3149	1580	1199	372	72	2481	105	148	44	1533	1294	230	58	1313	40	64	24
7	73	3593	1615	1191	412	62	3609	216	267	51	1523	1011	505	59	1817	60	85	25
8	135	4658	1910	1288	613	106	7557	453	543	89	2179	1239	931	103	3204	101	149	48
9	58	2059	1372	1169	192	56	2065	115	154	39	1407	1187	210	51	2278	62	95	33
10	68	2915	1325	1210	100	54	4972	265	320	55	1634	1156	469	66	2068	43	70	27
11	66	3356	1271	1106	156	71	2541	118	151	33	1602	1395	140	33	877	11	25	13
12	61	1963	1371	1159	202	48	1311	52	86	34	1189	1002	177	17	771	14	34	19
R^2	0,78	0,79	0,83	0,20	0,94	0,76	0,89	0,89	0,90	0,98	0,67	-0,42	0,94	0,94	0,98	0,98	0,98	0,95

R^2 correlation coefficients are shown the relation levels between PM10 and other parameters for some station.

5. RESULTS

Air pollution is very significant as it affects human health, ecosystems and materials. This is not always a regional phenomenon, with transport processes polluted air can be transported to the region. As a European Union Member candidate, Turkey should monitor the air quality parameters and find ways to control the sources as the parameters are exceeding standards of EU directives. If the pollution is mostly of transport origin, it has to be reported to EU because, even if the regional sources are controlled, pollution can increase to unwanted levels due to transport effects. For these purposes, it is important to find the pollutant fractions of polluted air, and identify whether there is a transport mechanism or not and if there, is the contribution of this mechanism to air pollution.

In this study, using the PM_{10} observations of 1998-2003, it is seen that the number of days exceed limiting values are nearly always exceeding the EU directives. Using meteorological data, atmospheric stability corresponding to the episode days are found and synoptic charts are used to detect the transport mechanisms in two specific periods of the episode days. It is seen that both transport and local sources are contributing to pollution.

In order to be an EU member and most important of all in order to live in a healthy environment with present biodiversity, Turkey must find ways to decrease the amounts of pollutants released into the atmosphere.

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NEURAL NETWORKS BASED MODELLING OF TRAFFIC RELATED AIR POLLUTION

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ABSTRACT

In this study, an artificial neural network modelling has been proposed and employed for modelling of NO_2 pollution on the roadside of Greater London Area. For this purpose, two small programs were written in MATLAB and used for modelling of roadside NO_2 pollution. It was found that the R-value is almost 0.92, and t-test results and P-values were found in the ranges of 0.00-0.30 and 0.5-0.8 for the network outputs, respectively. It was conclude that difference between the means of the measured and predicted values of NO_2 pollution is within the 95.0% confidence level.

Key Words: Artificial Intelligent, Forecasting, Traffic Pollution, NO_2, Roadside.

1. INTRODUCTION

Air pollution is a growing problem because of the increasing urban population causing high density of vehicle traffic, more and more electricity needs, and expanding commercial and industrial activities. The importance of the preventing air pollution has been increasing in recent years, due to increasing knowledge of polluting sources and their pollution levels. NO_2 is one of the environmentally important air pollutants that have been associated with urban air quality problems and mainly released from traffic vehicle exhaust. Nitric oxide (NO) is the primer pollutant from vehicle exhaust and is ultimately converted to NO_2 by reaction with ozone (O_3) in the atmosphere.

The ultimate objective of an air quality management strategy is to achieve acceptable and sustainable air quality for a region. To achieve this aim, prediction and assessment of future air quality is very important. By means of an air pollution model, it is possible to achieve acceptable and sustainable levels of air quality for a region. Precise daily air quality forecast are needed for individual region (i.e., an urban area) when appropriate health advise is to be issued to the public using a health hazard warning system.

An effective local air quality management system that provides authorities with information about current and predicted air quality throughout the area and so enable assessment to be undertaken as to whether pollution levels exceed National Air Quality Standards or are likely to exceed it in the near future. In this regard, air pollution models can be a very effective tool in planning strategies for management of local air quality and can provide a rational basis for the control of air pollution. If properly designed and evaluated, air pollution models play considerable role in any air quality management system.

Classical air quality models can broadly be classified in two groups: physical models and mathematical models, of which can be deterministic or statistical. Deterministic models are based on fundamental mathematical descriptions of atmospheric processes, whereas statistical models are based upon semi-empirical statistical relations among available data and measurements (Zanetti, 1990).

In recent years, Artificial Intelligence (AI) based techniques have been proposed as alternatives to traditional statistical ones in many scientific disciplines. Artificial neural networks (ANN), one of the most popular AI methods, are considered to be simplified mathematical models of brain-like systems. Neural networks are generally trained by means of “training data”, and due their property of generalization, they can learn new associations, new functional dependencies and new patterns.

Artificial neural networks (ANNs) are parallel calculation architectures whose structure is based on the human brain. If suitably ‘trained’ using a set of examples, they can ‘learn’, i.e they can extract the link between the input data and the corresponding output data (Lippmann, 1987). So, ANNs could be used to solve a number of problems of classification and, more generally, black-box identification, in which ‘a priori’ knowledge of the model is not needed (Chen and Billings, 1992). To this we must add the fact that operations are relatively simple and can be performed quite systematically. The learning phase is, in fact, entrusted to special algorithms such as the back-propagation algorithm, which is a simple steepest descent optimization strategy. The term back-propagation refers to the fact that the gradient vector is calculated in the direction opposite to the flow of the output of each node.

Due to these properties, Artificial Neural Networks have been widely used for modeling and forecasting. Especially, the “multilayer perceptron” has been applied within the field of air quality prediction in the last decade. A summarized review of the applications of ANN in the atmospheric sciences has been carried out by Gardner and Dorling (1998). ANN models have been studied by various investigators for SO_2 (Boznar et al., 1993; Chelani et al., 2002; Yildirim et al., 2003), for NO, NO_2 and NOx (Gardner and Dorling, 1999; Perez and Trier, 2001), ozone (Jorquera et al, 1998; Gardner and Dorling, 2000) and PM2.5 (Perez et al., 2000; Perez and Ryes, 2001) concentration forecasting.

This study aims to estimate roadside NO_2 pollution levels depending on meteorological parameters, some air quality data (i.e., O_3 and NO) and total traffic flow by using artificial neural networks (ANN). Its aim is essentially to focus on the usefulness of artificial neural network for the identification of short-term prediction models based on recorded time-series data.

2. MATERIALS AND METHODS

2.1. Artificial Neural Network Models with Backpropagation Algorithm

The backpropagation algorithms (BP) use input vectors and corresponding target vectors to train a neural network (NN). NN with sigmoid layer and a linear output layer are capable of approximating any function with a finite number of discontinuities (Hagan, 1996). Backpropagation algorithms are based on other optimization techniques, such as conjugate gradient and Newton methods. For properly trained backpropagation networks, a new input leads to an output similar to the correct output. This NN property enables to train a network on a representative set of input/target pairs and get good forecasting results.

A two-layer neural network with tangential sigmoid transfer function at hidden layer and a linear transfer function at output layer was used. Due to its highly optimization capability, Levenberg-Marquardt algorithm is used as the backpropagation algorithm. This structure was tested and found as a useful structure for modelling of air pollutants (Karaca et al., 2005). The structure of the neural network used in the study is given in figure 1. This NN has ***k*** input parameters and ***l*** output parameters which are essential for accurate modelling of the air pollution. The input parameters, number of neurons at hidden layer and output layer should be determined according to current data gathered.

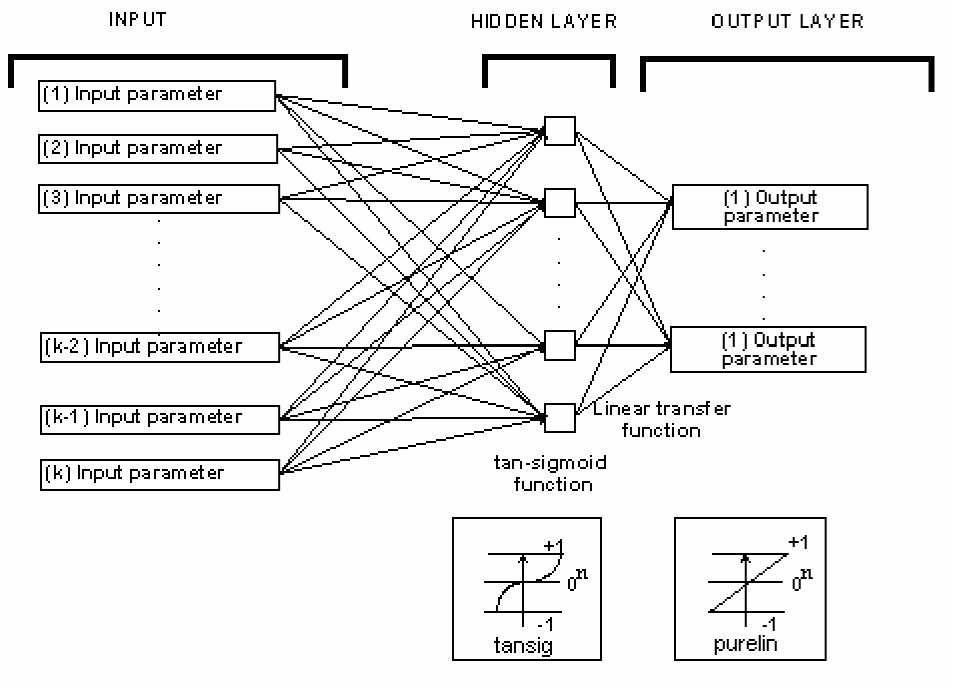

Figure 1. General Structure of a Neural Network.

2.2. Experimental Data

The location of the air quality monitoring station is in Staines site, situated at the edge of the clockwise carriageway of the London orbital motorway, M25 between junctions 13 and 14, to the west of London and the pollutants monitored in 1997. Traffic flows at this site are considerably higher than those at the other locations, with typical daily flows of 175,000 and peak hour flows of between 12,000 and 15,000 vehicles.

The input data includes traffic flow, concentrations of NO, NO_2 and Ozone, and meteorological data. The datasets consist of sequential hourly time series of concentrations and meteorological variables. The time period selected covers year of 1997. All traffic flow, air quality and meteorological data are presented as hourly averaged values.

The relevant traffic flow data was obtained from Highway Agency. This data contains hourly traffic volumes and average driving speed, separately for various vehicle categories (light-duty traffic, busses and other heavy-duty traffic). In this study, hourly total traffic volumes in 1997 were employed for modelling.

The hourly concentrations of NO, NO_2 and Ozone were available for the station of Stainnes during the selected year of 1997. TRL provided air quality and meteorological data from the site for modelling. Hourly meteorological data and air quality data were obtained from the M25 motorway site automatic measuring station. The precipitation (rain) values were obtained from London Weather Centre during 1997.

It is suggested to use TAU as an input parameter instead of wind direction (WD) and wind speed (WS) (Berkovich, 2000). The travel time and the effective travel distance (X) can be calculated as follows:

$$TAU = \frac{X}{u} \quad \text{and} \quad X = \frac{d}{\sin(FI)} \tag{1}$$

Where u is the wind speed and X is effective travel distance, d is the distance from the road (perpendicular) and FI is the angle of the wind with respect to the road axis.

3. RESULTS AND DISCUSSION

3.1. Model Training, Evaluation and Testing

Model building, training and testing are performed using MATLAB compiler. Two small programs were written and used for modelling in MATLAB. The data is divided into two matrix called as P matrix and T matrix. P matrix contains the input parameters of the model and T matrix contains the target of neural network. The values of each parameter were transformed to the interval [0, 1] by using equation (2);

$$V_i' = 1 - \left[\frac{MaxV_i - V_i}{MaxV_i - MinV_i} \right] \tag{2}$$

Where, *Vi* is the transformed ith value of array, $MaxV_i$ is the maximum value of an array, $MinV_i$ is the minimum value of an array, and V_i is the ith value of an array. The input and output parameters used in the models were presented in Table 1.

Table 1. Parameters of NN model

PARAMETERS		**DIMENSIONS/RANGES**
Input Parameters		
1	TAU (Travel Time)	Second (s)
2	TEMP (Temperature)	°C
3	RH (Relative Humidity)	%
4	SR (Solar Radiation)	W/m^2
5	Rainfall	Mm
6	Traffic Flow	total
7	NO	ppb
8	Ozone	ppb
Output Parameter		
1	NO_2	ppb

The available data [N=6658] was divided into section: training, validation, and test subsets, which are randomly chosen by the model. One fourth of the data [1664] was taken for the validation set, one fourth for the test set [1664] and one half for the training set [3330]. The network should have one output neurons since there is one target.

With the purpose of obtaining of maximum efficiency, which corresponds to a neuron number, neurons of the model in the hidden layer were increased one by one from 1 to 100 neurons and the responses of the model were obtained well known statistical indices: Mean Squared Errors (MSE). It was found that there are several local minimum and maximum of MSE values for the model. The relationship between Neuron numbers and MSE is given in figure 2 indicating high error after 15 neurons. However, generally 10-20 neuron regions can be considered as global minimum region. Due to its low error value, finally it was decided to select 15 neurons as the number of neurons for the optimum structure of the model.

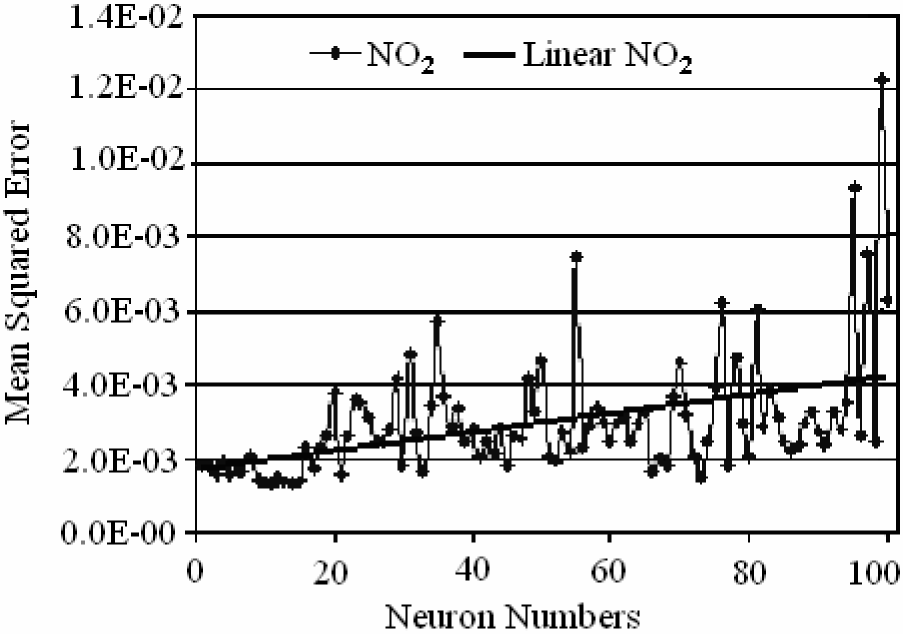

Figure 2. Neuron Numbers vs. Mean Squared Error (MSE) values of network outputs

The training stopped after 97 iterations because validation and test MSE values were reached a steady condition. The training, validation and test errors of the model are given in figure 3. The obtained results are reasonable, since the test set error and the validation set error have similar characteristics, and it doesn't appear that any significant over fitting has occurred.

In order to find performance analysis of the network response, entire data set was put through the network (training, validation and test) and a linear regression was performed between the network outputs and the corresponding targets. All of the outputs seem to track the targets reasonably well, and the R-values are almost 0.92. Performance of the model for NO$_2$ modelling is represented in figure 4 indicating model results are in good agreement with the measured data set.

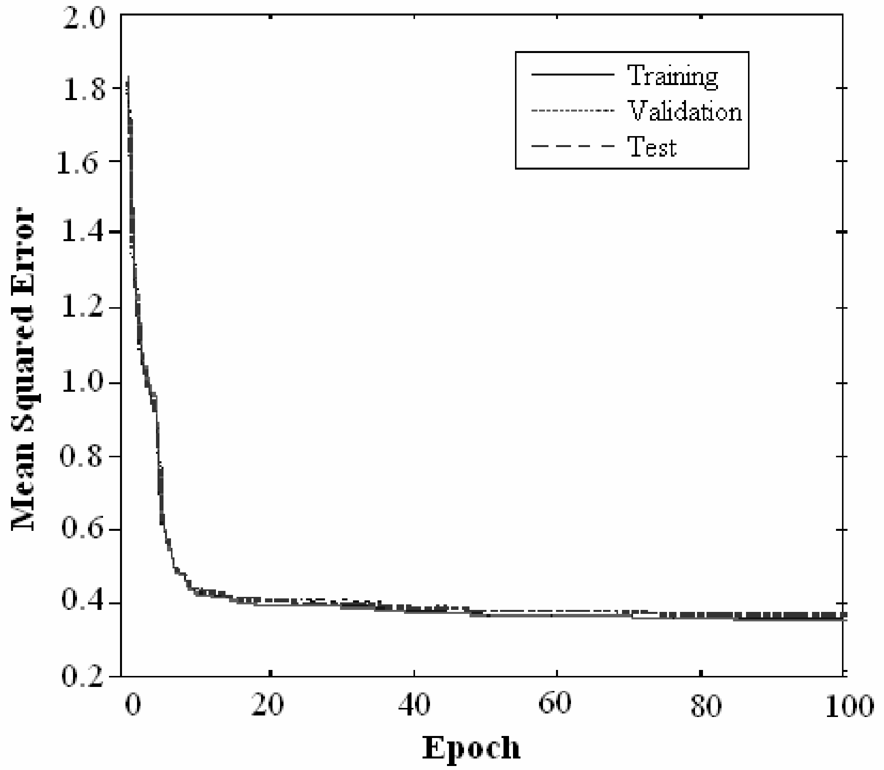

Figure 3. The training, validation and test errors of the training progress.

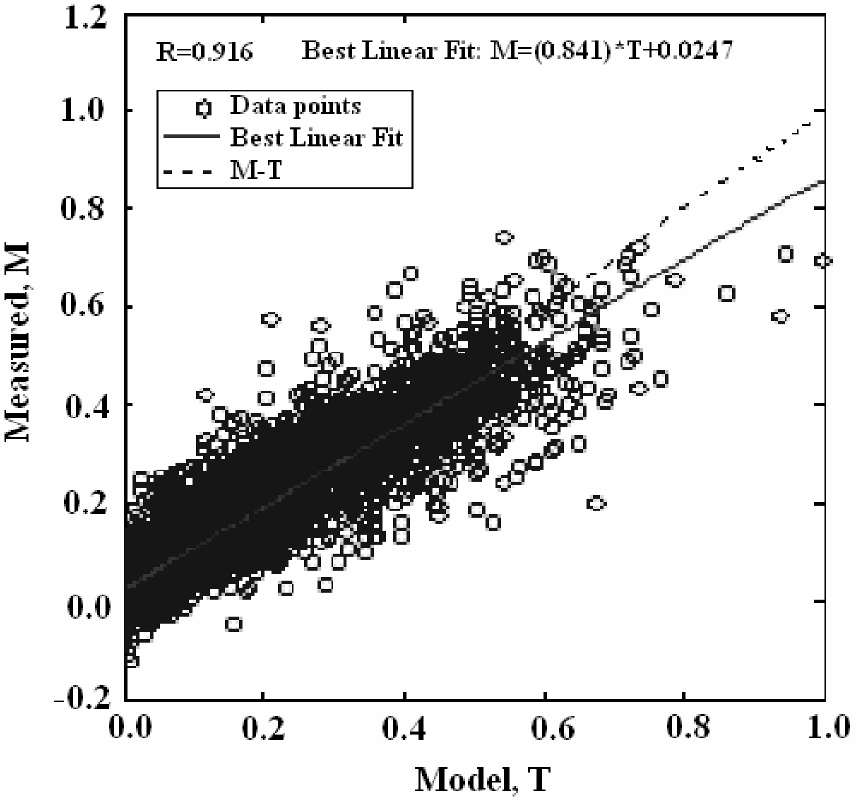

Figure 4. Performance of the model for roadside NO_2 pollution modelling

4. CONCLUSIONS

Entire data set was put the through the network (training, validation and test) and a linear regression was performed between the network outputs and the corresponding targets. All of the outputs seem to track the targets reasonably well, and the R-values are almost 0.92 for NO_2 pollution. The t-test was used to compare the means of the measured and predicted values. T-test results and P-values are found in the ranges 0.00-0.30 and 0.5-0.8 for the network outputs, respectively. Statistically, there is no significant difference between the means of the measured and predicted values of NO_2 pollution at the 95.0% confidence level. They have very good agreements on the trends between forecasted and measured data. It can be concluded that artificial neural networks with backpropagation algorithm are useful neural techniques for the identification of short-term prediction models based on recorded time-series data.

5. ACKNOWLEDGEMENTS

The authors which to acknowledge the Transport and Research Laboratory, UK and the Highway Agency of the UK for providing access to the M25 air quality, meteorological and traffic data.

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PILOT AIR POLLUTION INVESTIGATION AT ZAGREB CROSSROADS

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ABSTRACT

Concentrations of PM_{10}, lead and Benzo-a-pyrene (BaP) contained in PM_{10}, and nitrogen oxides were measured during two weeks at seven Zagreb crossroads (two measuring sites per crossroad) and compared to daily average levels monitored at local network stations. This study was performed as a part of the SILAQ project (Sofia Initiative for Local Air Quality). The results show a small concentration increase in regard to daily concentrations measured at local network stations. Concentrations of all investigated pollutants were higher in the afternoon than in the morning, as a consequence of pollutant accumulation during daytime and dilution over night.

Key Words: PM_{10}, Nitrogen Oxides, Traffic Air Pollutions, Urban Air

1. INTRODUCTION

The air quality surveillance in Croatia started in Zagreb in 1962 with the measurement of deposited matter. PM_{10} and $PM_{2.5}$ measurements were established in 1998, of polycyclic aromatic hydrocarbons (PAHs) in 2000, and a measurement network for NO_2 was established in 1994. The monitoring of spatial and seasonal variations of pollutant concentrations levels in Zagreb (Šega and Fugaš, 1984; Čačković at al., 2001) has started since 1984. In addition, influence of long–range transport on gases concentrations (Klaić, 1996) as well as influence of weather conditions on airborne particle concentrations (Bešlić at al., 2003) have been recently investigated.

Traffic density in Croatian cities (especially in Zagreb) has rapidly increased over the last decade. At the same time, major pollution sources such as heating plants and house heating have become less significant because solid fuel has been replaced with natural gas. In order to estimate the influence of traffic on urban air pollution under these new conditions, this pilot investigation was performed at seven Zagreb crossroads for two weeks and the results were compared with the monitoring network data.

2. METHODS

The investigation was performed at seven Zagreb crossroads from 23 October 2002 to 5 November 2002. Some are situated in the street canyons of the city center, while others are at open space locations. Two samplers were set up at each crossroad to avoid the wind influence on pollutant concentration levels. Two samples were collected daily per measuring site, from 6.00 to 13.00 hrs and again from 14.00 to 21.00 hrs. Portable air samplers (Air Metrics, U.S.A.) were placed at the height of 1.70 meters above the ground level. PM_{10} samples were collected on Whatman quartz filters with the diameter of 47 mm, while gaseous pollutants were collected in Tedlar bags. Cumulative samples were collected throughout the weekdays and weekends, representing weekly averages for weekdays and weekends. Filters were preconditioned for 24 hours before and after sampling, and weighted using microbalance Mettler Toledo MX-5. PAHs were analyzed using the Varian Pro Star high-performance liquid chromatograph (HPLC). Nitrogen oxides were analyzed using the automatic sampler Environnement s.a., model AC 30M.

3. RESULTS

PM_{10} was monitored at one measuring site only, located in the northern, residential part of Zagreb. For this reason, Table 1 shows TSP concentrations in Zagreb center, PM_{10} concentrations in the northern part of Zagreb and at crossroad measuring sites during the weekdays. It should be pointed out that the results obtained at the network measuring sites represent the average of daily samples over weekdays or weekends respectively. The results show higher PM_{10} and TSP concentration levels at the crossroads than at the network measuring stations for both morning (6 – 13 hrs) and afternoon (14 – 21 hrs). Furthermore, the afternoon concentration levels were higher than the forenoon concentrations.

Table 1. PM_{10} concentration levels in $\mu g/m^3$ during weekdays

	TSP	**PM_{10}**	**PM_{10} – crossroads**	
	Center	North	6 -13 hrs	14 – 21 hrs
N	6	10	28	26
AVG	**62.2**	**33.3**	**67.59**	**78.16**
STD	13.10	10.73	26.75	42.77
MIN	43.00	20.84	10.48	10.00
MAX	84.60	61.12	116.19	217.62

Table 2 shows weekend PM_{10} concentration levels at the northern sampling site and crossroads forenoon and afternoon concentration levels. Weekend concentration levels are lower than weekday concentrations because of lower traffic density. But again, higher afternoon concentration levels were observed.

Lead content in PM_{10} determined in the samples collected at the crossroads are shown in Table 3. Again, concentrations measured at the crossroads were higher than those measured at the network site. Higher lead concentrations were determined in the afternoon samples.

Table 2. PM_{10} concentration levels in µg/m^3 during weekends

PM_{10}	North	**Crossroads**	
		6 -13 hrs	14 – 21 hrs
N	4	14	14
AVG	**29.53**	**49.28**	**64.60**
STD	10.27	33.50	50.66
MIN	20.84	4.05	3.57
MAX	46.32	86.84	137.60

Table 3. Lead concentration levels in ng/m^3 at the crossroads, in the city center (TSP) and the southern (PM_{10}) regular monitoring station

Pb	Center	North	**Crossroads - weekdays**		**Crossroads - weekends**	
			6-13 hrs	14–21 hrs	6-13 hrs	14–21 hrs
N	6	10	28	27	14	14
AVG	**69.7**	**62.8**	**74.3**	**110.4**	**53**	**100.2**
STD	27.6	25.8	56.2	64.2	35.4	4.4
MIN	36.4	19.5	0	1.7	2.1	5.5
MAX	106.5	118.9	186.7	229	133.6	315.5

Table 4 shows higher BaP concentrations at the crossroads than at the network station located in the northern part of city. The concentrations were higher on weekdays than on weekends, and in the afternoon than in the morning.

Table 4. BaP concentration levels (ng/m^3)

BaP	North	**Crossroads - weekdays**		**Crossroads - weekends**	
		6 -13 hrs	14 – 21 hrs	6 -13 hrs	14 – 21 hrs
N	14	28	27	14	14
AVG	**1.70**	**2.64**	**3.74**	**1.91**	**2.69**
STD	1.14	0.91	2.77	0.93	1.20
MIN	0.46	0.84	1.05	0.57	0.96
MAX	5.07	4.69	15.68	3.78	4.31

Tables 5-6 show NO and NO_2 concentration levels measured at the crossroads. Higher concentration levels were observed on weekdays and in the afternoon for both pollutants.

Table 5. NO concentration levels measured at the crossroads (μg/m^3)

NO	Crossroads - weekdays		Crossroads – weekends	
	6 -13 hrs	14 – 21 hrs	6 -13 hrs	14 – 21 hrs
N	41	35	12	15
AVG	**183**	**199**	**103**	**130**
STD	58	95	54	89
MIN	56	15	23	24
MAX	319	456	216	358

Table 6. NO_2 concentration levels measured at the crossroads (μg/m^3)

NO_2	Center	Crossroads – weekdays		Crossroads – weekends	
		6 -13 hrs	14 – 21 hrs	6 -13 hrs	14 – 21 hrs
N	14	41	35	12	15
AVG	**42**	**126**	**133**	**65**	**86**
STD	9	43	62	28	48
MIN	27	59	31	27	31
MAX	60	252	279	133	215

4. CONCLUSION

Despite shortcomings (short investigation period and non comparable averaging periods), this investigation suggests that traffic significantly contributes to the air pollution in Zagreb, primarily by exhaust emission as well as by the re-suspension of the dust from the ground.

Samples at the crossroads were collected when traffic density was high. This is the main reason for the higher concentration levels of all pollutants in comparison with regular network site measurements. Higher afternoon pollution level for all pollutants is the result of pollutant accumulation during the day and its dilution over night.

This pilot investigation should serve as the basis for future investigations of traffic influence on local air pollution in Zagreb. The next step would be to establish a correlation between traffic density and pollutant concentration levels.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

FOUR STORMS WITH SUB-EVENTS: SAMPLING AND ANALYSIS

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ABSTRACT

This study investigates the variation in the chemical composition and pH of four precipitation events that was sampled in İstanbul during a) January 21 - 23, 2004 b) November 9 - 11, 2003 c) February 12 - 13, 2004. d) October 27 - 28, 2003. These events lasted 53.3, 47.9, 27.5 and 13.2 hours and the number of collected samples for each event was 22, 14, 7 and 4, in order. Sub-event samplings were carried out for each precipitation event in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps. Precipitation events c and d include rain and snow together where precipitation started as rain and continued as snow after 16th and 3th sub-events. Average concentrations of SO_4^{2-}, Ca^{2+}, Na^+, Mg^{2+}, and K^+ for four precipitation events were found to be 3.90, 2.23, 2.16, 0.63, and 0.45 mg/L, and average pH value was obtained as 5.52. It is interesting to find that high values of pH and maximum concentrations of ions belong to the first samples of four cases. Then the concentration of ions and pH decreased until third and fourth samples. It was also detected that snow flakes were efficient scavenging agents, more efficient than the rain drops, and lead to an increase in the concentration of ions and pH in the samples just after the snowing starts.

Key Words: Acid precipitation, sub-event analysis, rain chemistry.

1. INTRODUCTION

The processes to control the composition of rain are complex and influenced by natural and anthropogenic sources. These processes that result in the incorporation of air pollutants into cloud droplets or the incorporation of the particles below the cloud in falling droplets are poorly understood and difficult to study experimentally. The relation of the chemical composition of precipitation to the associated meteorological conditions can improve our understanding of the causes of acid precipitation.

Wet deposition studies have been popular all over the world and many of them are carried out recently (; Akkoyunlu and Tayanç., 2003; Staelens et al., 2005). These studies investigated the variation of daily and monthly averages of wet deposition chemistry. Sakihama and Tokuyama (2005) studied the effect of typhoons on the behavior of chemical components. The work of Basak and Alagha (2004) was carried out near Büyükçekmece Lake, one of the important drinking water sources of İstanbul city, Turkey and concluded that the dominant anion was SO_4^{2-} and most of this ion came from non-sea salt. Topçu et al. (2002) studied the chemical composition of rainwater in Ankara and they also concluded that neutralization of the acidity plays an important role in that area. Akkoyunlu and Tayanç (2001) established the relationship between the chemical concentration of samples and the meteorological factors by using the trajectory analysis of cyclones.

The aim of this study is to analyze the variation of the chemical composition and pH in four precipitation sub-events that were sampled in İstanbul. In Section 2 the experimental techniques that were used to collect and analyze sub-event samples are explained. In results, the temporal variation of some ionic components and pH in sub-events during the passages of four cyclones are presented and comments on the results are given.

2. EXPERIMENTAL AND METHODOLOGY

This study presents the variation in the chemical composition and pH of four precipitation events that was sampled in İstanbul during a) January 21th - 23th 2004 b) November 9th - 11th 2003, c) February 12 – 13, 2004 and d) October 27 – 28, 2003. Sampling region was Maltepe, which is located on the European side of İstanbul, and has more domestic heating activities in comparison with industrial ones. Sub-event samplings were carried out by using a polyethylene funnel of 0.63 m^2 with circular area onto a polyethylene container. These events lasted 53.3, 47.9, 27.5 and 13.2 hours and the number of collected samples for each event was 22, 14, 7, 4, in order. At least 100 ml precipitation water must be collected in order to conduct all of the analyses. Thus, owing to the variability in the intensity of the precipitation and considering 100 ml precipitation water to be collected, it is impossible to keep the period constant for every sample collection. Sub-event samplings were carried out for each precipitation event in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps. Prior to installations the funnel and collectors used for sub-event sampling, rinsed with distilled water, soaked in a 5% nitric acid bath and then rinsed again with distilled water and dried. After precipitation, the sampled water was removed from the container and brought to the laboratory, and the sampling instrument was cleaned by distilled water and kept closed. Samples were filtered and stored in pre-cleaned polyethylene bottles in the refrigerator at 4^oC prior to chemical analysis.

Concentration of Mg^{2+} was determined by Unicam 919 Atomic Absorption Spectrometer. Concentrations of the SO_4^{2-} were determined by a high performance Dionex model 4001 ion chromatography (IC). Concentrations of Ca^{2+}, K^+ and Na^+ were determined by Jenway Flame Emission Spectrophotometer. A Metrohm-632 pH meter, equipped with a combination glass electrode, was used for pH measurements. The pH meter was calibrated before every measurement using standard pH 4.00 and 7.00 buffer solutions.

A ratio often used to distinguish aerosol sources is the enrichment factor (EF) (Vermette et al., 1988; Ahmed et al., 1990; Singer et al., 1993). This calculation is based on the elemental ratio found between ions collected in the atmosphere or in precipitation, compared with a similar ratio for a reference material, giving important information about the source of the elements. Non-sea salt (NSS) ion concentration is proportional to the enrichment factor. NSS ion concentration gives concentration of ions come from the anthropogenic sources or Earth crust. In this work, NSS ion concentration was calculated by using ratio of the ion, whose NSS concentration was calculated, to the reference ion in the reference material. Sodium was used as reference ion in this work.

3. RESULTS AND DISCUSSION

First Storm

İstanbul was under the effect of a strong cyclone on January 21 – 23, 2004 period deepening up to 994 mb over İstanbul. Significant warm and cold front passages were detected during the passage of the storm and snowing had been started at 25.5th hour after the initiation of precipitation and continued until the end of the storm. This storm was characterized by very low sea level pressure values, decreasing lower than 980 mb at its center located on the Aegean Sea and very low temperatures, -4°C in İstanbul.

Sub-event sampling was carried out during this period that precipitated 53.3 hours. 22 samples were collected during the storm of which the last 7 was snow. First container of the sub-event sampling was removed after 2.6 hour from the initiation of precipitation. Maximum pH level and ion concentrations were measured in this sub-event except SO_4^{2-} and Mg^{2+}. The maximum values of these ions that were measured in snow after 37.2 hours were found to be 6.9, 1.87 mg/L, respectively. Mean concentrations of ions ($SO_4^{2-} > Ca^{2+} > Na^+ > K^+ > Mg^{2+}$) can be ordered as 3.23, 1.95, 1.82, 0.58, 0.40 mg/l. Generally, $SO_4^{2-}$and Ca^{2+} were found to be the dominant ions. High sulfate concentration in samples was thought to be neutralized by the contribution of high concentrations of alkaline compounds. The average concentrations of ions and pH in samples taken between 7.00 and 22.2 hours after the start of rain were relatively lower than those of the initial sub-events and snow precipitation. All of ions have similar variability during the sampling period with a high correlation coefficient except Mg^{2+} and K^+ correlation. The correlation coefficient between these ions was calculated as 0.45. Correlation coefficients of other ions found that ranges between 0.85 and 0.55.

Coarse particles in the atmosphere, that are the primary particles of wind blown dust, can contain high amounts of Ca^{2+}, Mg^{2+}, and K^+ in them and these type of particles are more efficiently scavenged by precipitation than fine particles (Akkoyunlu and Tayanç, 2003). Fine particles of anthropogenic origin were formed by gas-to-particles processes and they can be considered as important sources of the precipitation acidity. With progressing time, concentration of large particles in the atmosphere was decreased by scavenging, thus leading to less and less concentration of suspended particles and in turn less amount of particles transferred into droplets, leading to the decrease in the levels of cations and more acidic wet deposition.

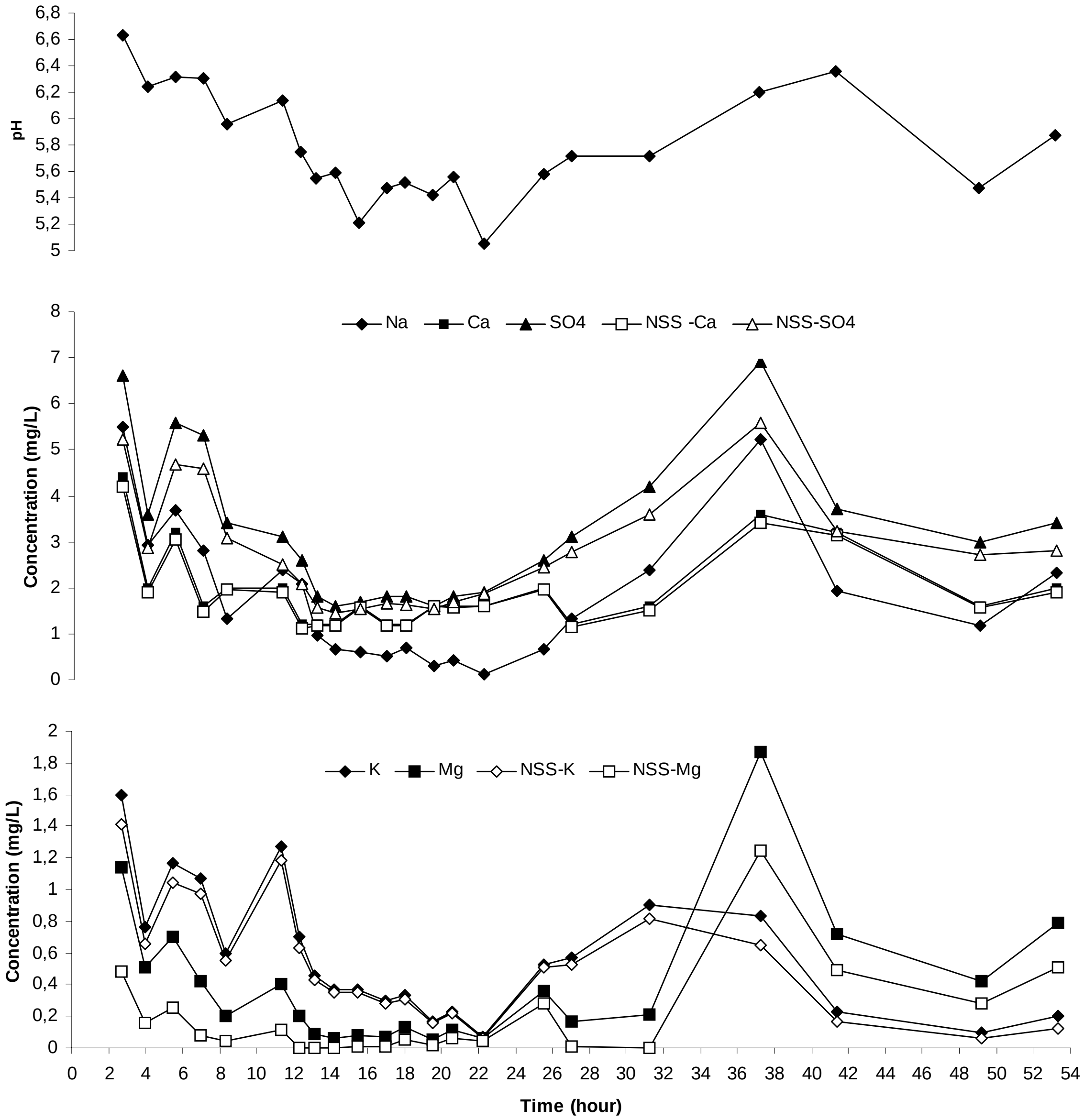

Figure 1. Variability of some ionic components and pH in sub-events as a function of time sampled on January 21 - 23 2004.

Precipitation of the first storm include rain and snow together, where precipitation started as rain and continued as snow after 22.2 hour (15th sub-event) from the initiation of rain. Average concentrations of SO_4^{2-}, Ca^{2+}, Na^+, K^+, and Mg^{2+} for snow precipitation events are found to be 3.84, 2.17, 2.14, 0.48, 0.65 mg/L, in order and average pH value is obtained as 5.85. It is interesting to find that maximum values of pH and maximum concentrations of ions belong to the first samples. It is also detected that snow flakes are efficient scavenging agents, more efficient than the rain drops, and lead to an increase in the concentration of ions and pH in the samples just after the snowing starts.

Second Storm

Other strong cyclone occurred in Istanbul on November 9 – 11, 2003. Precipitation lasted 47.9 hours with some small intervals in between without precipitation. 14 samples collected during the storm. Sub-event sampling was carried out during the period in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps. This storm was characterized by above normal sea level pressure values in İstanbul, decreasing to 1017 mb and normal temperatures with a minimum of 6°C.

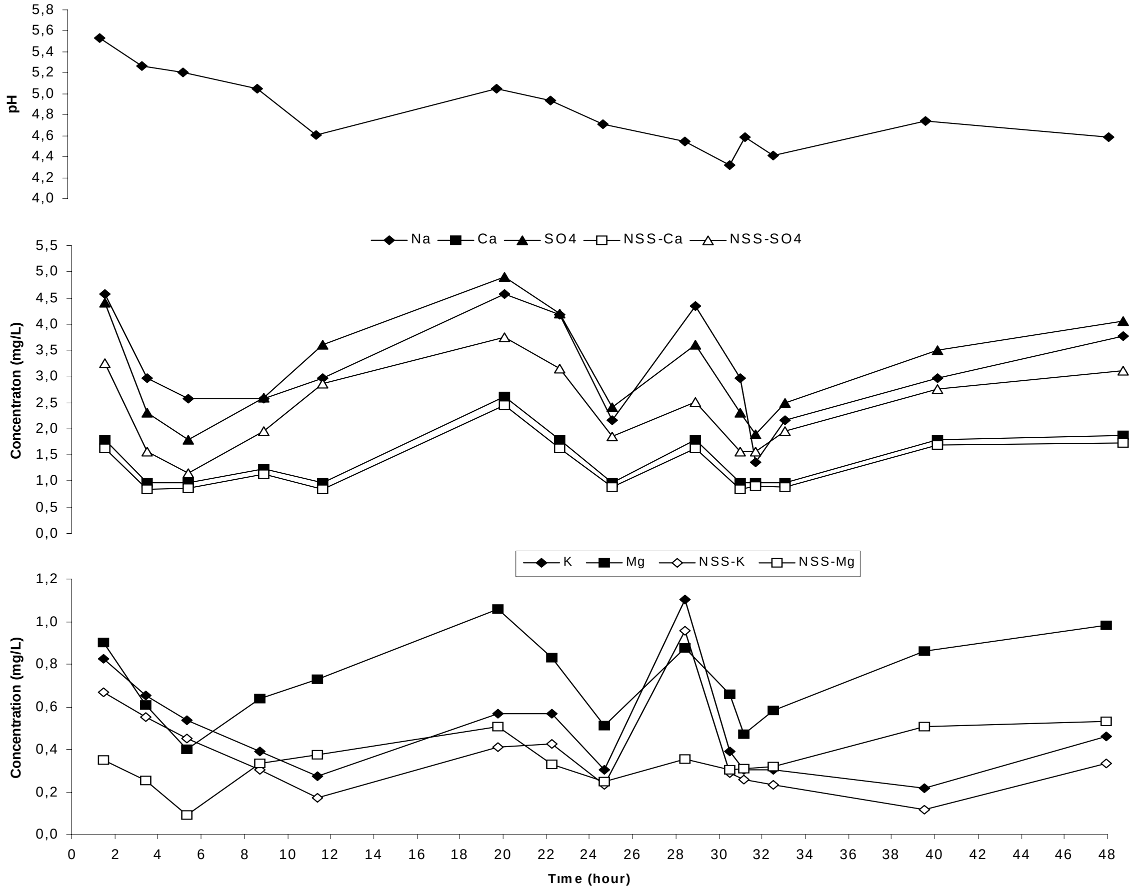

Figure 2. Variability of some ionic components and pH in sub-events as a function of time sampled on November 9 – 11 2003

Figure 2 presents the variation of some ion concentration, NSS concentration and pH in sub-events as a function of time during the passage of the cyclone. First container of the sub-event sampling was removed after 1.5 hour from the initiation of precipitation. High concentration and pH was found in this container, in addition, the sub-event sampled at 19.7th hour after the start of precipitation produced the maximum concentrations of ions except K^+. While there was no significant front passages in this period of rain event, mixing of air was observed. From satellite picture animations and 500 hPa geopotential height animations the mixing was clearly be seen over western Black Sea region between 11.2 – 32.5 hour period. This situation may lead to the fluctuation of concentrations during this period of precipitation.

Besides that SO_4^{2-} and Ca^{2+} have maximum NSS concentrations, generally SO_4^{2-} and Na^+ were found to be the dominant ions in total concentrations (Table 1). There existed high correlation coefficients between all ions except K^+. The correlation coefficients between K^+ and others ranged between 0.35 and 040. Mg^{2+} has very high correlation with SO_4^{2-} and Ca^{2+} with coefficients as 0.94 and 0.90, in order.

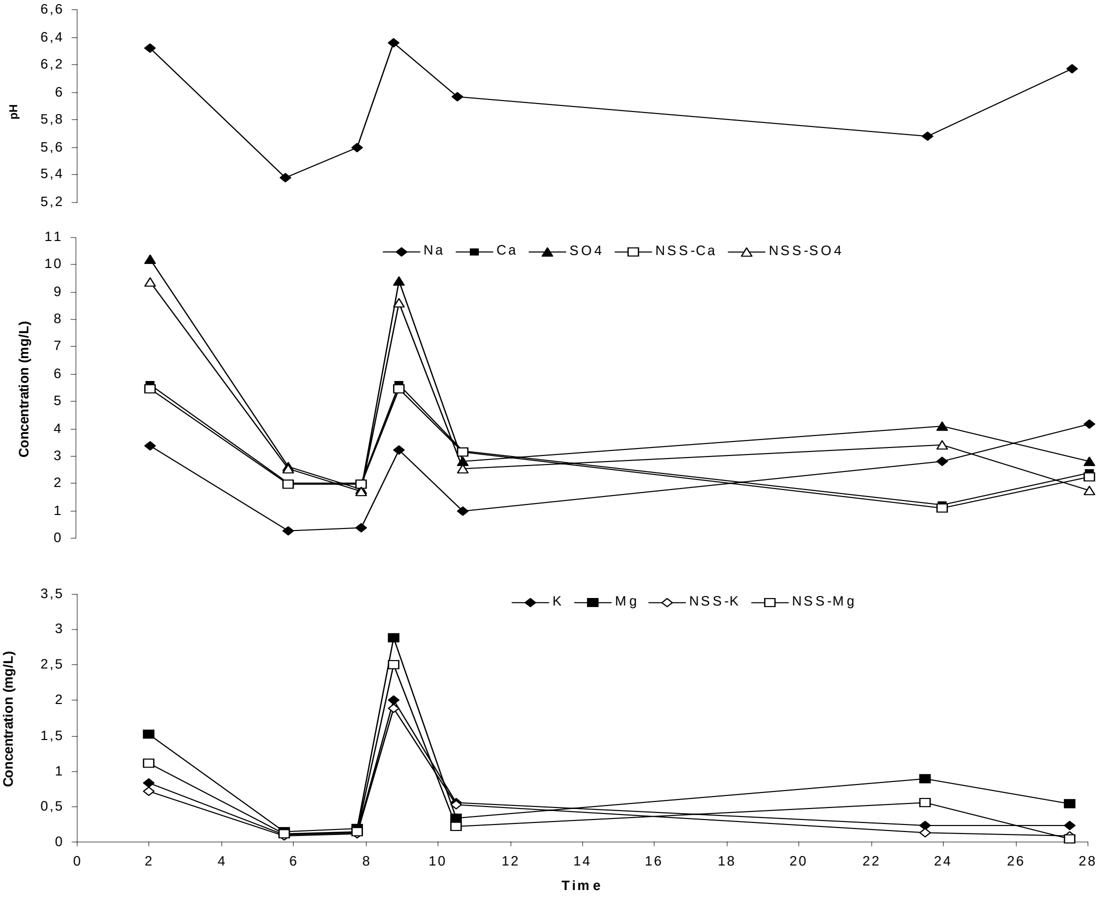

Figure 3. Variability of some ionic components and pH in sub-events as a function of time sampled on February 12 – 13, 2004.

Third Storm

On February 12 – 13, 2004, İstanbul was under the effect of a strong snow storm. It lasted 27.5 hours and 7 samples collected. Significant cold front passage was detected during the storm and snowing had been started after the two sub-event samplings and continued until the end of the storm. This storm was characterized by a slightly lower sea level pressure, 1009 mb, than the standart atmospheric value and very low temperatures, -7°C in İstanbul.

First and second sub-events that were sampled after 2 and 5.7 hours from the initiation of precipitation includes only rain (Figure 3). The first sampling resulted in a high value of pH and high concentration of ions. Especially very high SO_4^{2-} and NSS SO_4^{2-} concentrations were measured as 10.2 and 9.36 mg/L, respectively. Second and third sampling resulted in a lower concentration for these ions. Third sub-event has rain event together with snow. Precipitation lasted as snow after 4th sub-event. At this sub-event, 8.7 hour from the initiation precipitation, concentrations of ions increased dramatically. In third sample, which included only snow, concentrations of SO_4^{2-}, Ca^{2+}, Na^+, $Mg^{2+}$and K^+ were found as 9.4, 5.6, 3.21, 2.89 and 2.00 mg/l and NSS concentrations of SO_4^{2-}, Ca^{2+}, $Mg^{2+}$and K^+ ions were calculated as 8.60, 5.48, 2.5 and 1.89, respectively.

Fourth storm

The last storm studied in this work took place on October 27 – 28, 2003 and it precipitated only rain. Only 4 sub-events were collected through the storm that lasted in 13.2 hour. This storm was characterized by a minimum sea level pressure value of 1008 mb and a decrease of temperature from 13°C to 8°C.

pH and ions concentrations were found to be high in the first sub-events except SO_4^{2-} . The concentration of this ion increased continuously during the precipitation period (Figure 4). The concentration of cations decreased in the last sub-event. Owing to this decrease, acidity increased in this sample. Contrary to other storms, low correlation coefficients was found between SO_4^{2-} and other ions. It is believed that emissions of SO_4^{2-} from nearby areas due to domestic heating especially between 4.1 and 13.2 hours during the storm contributed into SO_4^{2-} concentrations. Other ions have variability similar to each other, with high correlation coefficients ranging between 0.99 and 0.75. Because anions do not have extra emissions during cooling periods, these anion concentrations in rain can decrease with time through the washout process and this may be the reason of finding a decrease in the acidity for the last sub-event sample. Anions and pH showed similar variability with a high correlation coefficient between them, ranging from 0.53 to 0.71.

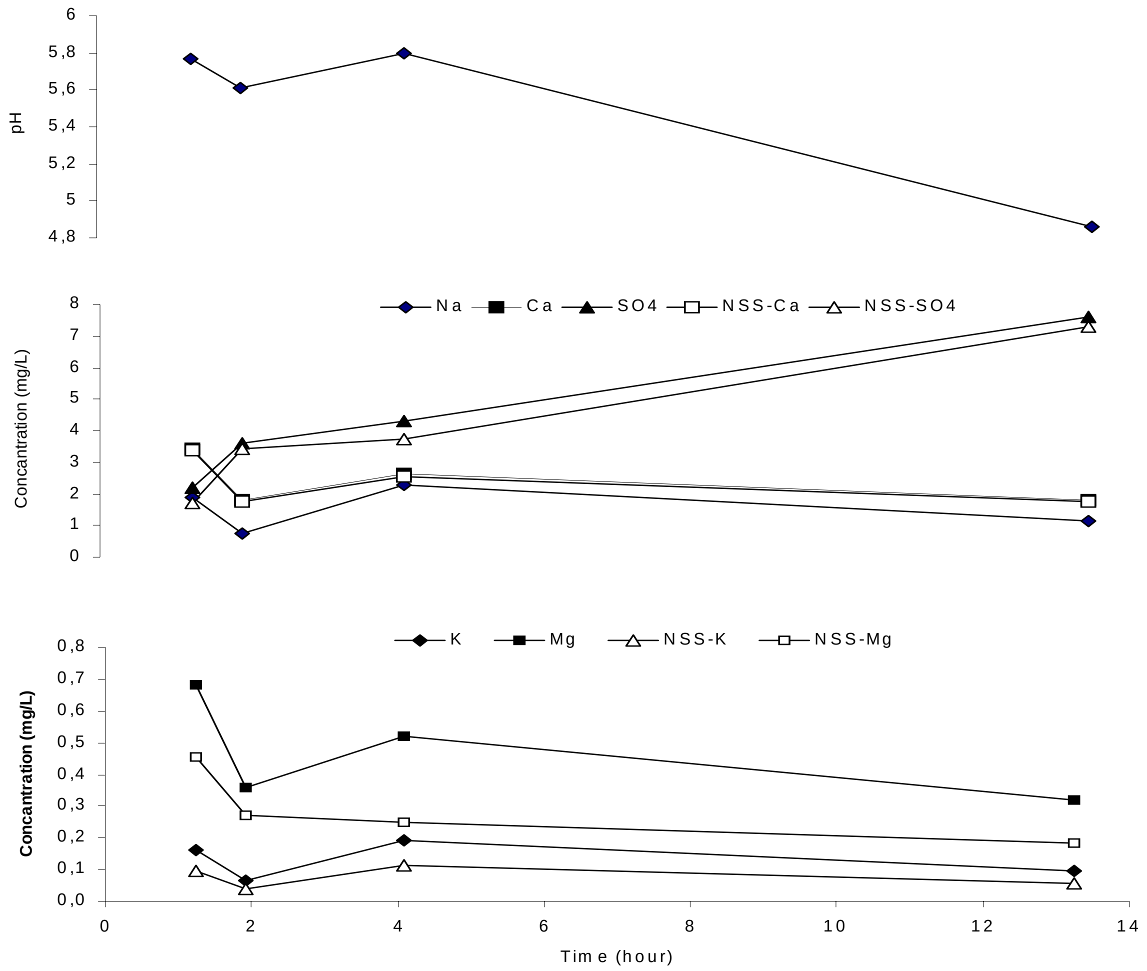

Figure 4. Variability of some ionic components and pH in sub-events as a function of time sampled on October 27 – 28, 2003.

Sources of the Ions

Mean concentrations and mean NSS concentrations of ions were depicted in Table 1. For the storms, mean NSS concentrations of SO_4^{2-}, Ca^{2+}, K^+, and Mg^{2+} were calculated as 3.37, 2.15, 0.37, 0.35 mg/L. Generally, SO_4^{2-} and Ca^{2+} were found to be the dominant ions. High sulfate concentration in samples was thought to be neutralized by the contribution of high concentrations of alkaline compounds. Results indicated that the ratio of the mean NSS concentration to the mean concentration of Ca^{2+} ranges between 0.91 and 0.98, suggesting that most of the calcium came from soil. Mg^{2+} seems to be diluted by sea and concentrated by soil. Average value of this ratio for Mg^{2+} was calculated as 0.55. This means that almost half amount of this ion came from non-sea sources. K^+ has a high ratio and main source of this ion can be expressed as soil. The ratio for SO_4^{2-} ranged between 0.75 and 0.92, leading to a possible conclusion that the industrial and domestic activities were the main source of this ion.

Table 1. Mean concentrations and mean NSS concentrations of ions (mg/L).

	Na^+	K^+	Ca^{2+}	SO_4^{2-}	Mg^{2+}	pH
January 21th - 23 th, 2004	1.82	0.58-0.52	1.95-1.88	3.23-2.78	0.40-0.19	5.80
November 9th – 11th, 2003	3.15	0.49-0.39	1.41-1.29	3.15-2.36	0.72-0.34	4.83
February 12th – 13th, 2004	2.17	0.58-0.51	3.14-3.06	4.81-4.27	0.93-0.67	5.93
October 27th – 28th, 2004	1.51	0.16-0.06	2.41-2.36	4.43-4.08	0.45-0.18	5.51
Average	2.16	0.45-0.37	2.23-2.15	3.90-3.37	0.63-0.35	5.52

4. CONCLUSIONS

This study presents the variation in the chemical composition and pH in four precipitation events that was sampled in İstanbul. These events lasted 53.3, 47.9, 27.5 and 13.2 hours and the number of collected samples for each event was 22, 14, 7 and 4. Sub-event samplings were carried out for each precipitation event in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps.

All ions showed similar variability during all storms with high correlation coefficients, except for rain event sampled on October 27 – 28, 2003. SO_4^{2-} gave negative correlations with other ions during this storm. It is believed that emissions of SO_2 from nearby areas contributed into SO_4^{2-} concentrations.

Generally values of pH and concentrations of ions belonging to the first samples of all four cases were found higher than those of other sub-event samples taken in sequence. It is clearly observed that the concentration of ions and pH decreased until third and fourth samples. Coarse particles existing in the atmosphere, close to the surface, can contain high amounts of cations and these type of particles are more efficiently scavenged by precipitation than fine particles. On the other hand, fine particles are considered as important sources of the precipitation acidity. They can be found in low atmosphere as well as in high troposphere and can be removed from atmosphere by rainout and washout processes. With progressing time during a storm, concentration of large particles in the atmosphere was decreased by scavenging, thus leading to less and less concentration of suspended large particles in comparison with small acidic particles. Consequently, less amount of large particles transferred into droplets, leading to the decrease in the levels of cations and to the development of more acidic wet deposition.

The variation of concentration of ions depends on the meteorological conditions and precipitation types. Two precipitation events included rain and snow together where precipitation started as rain and continued as snow. In this study, it was shown that snow flakes are efficient scavenging agents, more efficient than the rain drops, and lead to an increase in the concentration of ions and pH in the samples just after the snowing starts.

For 4 storms, SO_4^{2-} and Ca^{2+} were found to be the dominant ions. There was high correlation between the total concentration and NSS concentration of ions. The main source of SO_4^{2-} was believed to be the industrial and domestic emissions. For all precipitation events, results indicated that most of the Ca^{2+} and K^+ came from soil and half of the Mg^{2+} came from sea.

5. ACKNOWLEDGEMENTS

This work is financially supported by DPT with project FEN 2002K120450, by TÜBİTAK with project 104I025 and 103Y109.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

PERFORMANCE COMPARISON OF DIFFERENT BRANDS OF PASSIVE SAMPLING TUBES FOR THE DETERMINATION NO_2 AND O_3 IN URBAN ATMOSPHERE

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ABSTRACT

The efficiency of passive sampling tubes for simultaneous measurements NO_2 and O_3 in ambient air were evaluated. Results obtained from passive sampling tubes were compared with continuous monitoring device results. NO_2 is chemiadsorbed onto TEA as nitrite ions and determined with UV-VIS spectrophotometry. For Brand I and Brand II passive sampling, ozone reacts with DPE to form 4-pyridylaldehyde and measured with UV-VIS spectrophotometry. Brand III diffusion tubes contain stainless steel wire coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography. Precisions of the method as Standard Deviation are between 4- 20 $\mu g/m^3$ for NO_2 and 0.35 – 19 $\mu g/m^3$ for O_3. When results were compared with continuous monitors, deviations were ranged from +26% to -28% for NO_2. For O_3 differences between passive samplers and active monitors ranged between -50% and +30%. Some brands did produce results that are fairly comparable with the average concentrations obtained from continuous monitoring instruments. Further tests, such as effect of exposure periods on accuracy and reproducibility, reproducibility and accuracy tests at successive periods, effect of storage time will be performed using these brands.

Key Words: passive sampling, nitrogen dioxide, ozone

1. INTRODUCTION

Nitrogen dioxide is secondary pollutant in the atmosphere which converted from NO. As a result of reaction nitrogen dioxide with the VOCs which are abundantly present in the urban atmosphere, it contributes ozone formation and other photochemical oxidants. It has direct impact on the environment and human health through the formation of ozone, other photochemical oxidants and the deposition of acidity. Ozone is a strong oxidant and has adverse effects on human health and on materials.

Some 100 years after the first deployment of a 300- station passive monitoring network to determine relative atmospheric ozone concentrations (Fox, 1873), during some past two decades, there has been increasing interest to improve and use passive samplers to collect a number of gaseous air pollutants (Namiesnik et al., 1984; Cao and Hewitt, 1991). Today a number of passive samplers are commercially available and have been used to determine air quality in workplace, indoor living environment and ambient air. Passive samplers have found wide use for routine monitoring of air pollutants, because they are cheap, small in size, light, silent and do not require power and skilled people. However, passive samplers may be subject to biases caused by alteration in sampling rate due to variation in atmosphere turbulence, or caused by chemical interference (Ayers et al., 1998). So some evaluations are required by performing the tubes under real condition, before passive absorption samplers can be used to collect data on ambient pollutant concentrations.

A number of studies which has compared measurements of NO_2 and O_3 in parallel trials between passive samplers and real-time continues techniques. For example Atkins et al., 1986; Moscheandras et al., 1990; Campbell et al., 1994 used chemiluminescence techniques and Bernard et al., 1999 and Manning et al., 1996 used UV ozone monitors to compare results. Unfortunately results show variation. Campbell et al. (1994) found that NO_2 concentrations were overestimated, by up to 40%, by diffusion tubes in exposed positions. Atkins et al. (1986) observed no significant difference for NO_2 concentrations measured during validation trials in the field. Moschandreas et al. (1990) reported that low temperatures in the range 251-283 K resulted in underestimation of NO_2. Bernard et al. (1999) found satisfactory reproducibility and precision results for O_3 measurements. The correlation coefficient for forty measurements was r= 0.9, p <10-3, and the regression coefficient was close to 1. Manning et al. (1996) found that monitor/sampler ratios were between 0.78- 1.17. The authors concluded that any differences in the results between ozone passive sampling and continuous monitoring were solely due to their experimental error.

In the present work, three different commercially available passive sampling tubes were used to measure NO_2 and O_3 at point where close to cross section of the crowded roads in urban area (Sıhhiye) and results were evaluated with continuous monitoring system. The passive tubes used in this study have been widely in scientific researches and monitoring studies through the world.

We are planning to use passive samplers to determine spatial distribution of organic and inorganic pollutants at Bursa, to be able to evaluate distribution of health risk caused by these pollutants. Variety of passive samplers is available in the market. A small experiment was performed to test their performances and select the brand that will be used at Bursa. The experiment involved comparison of NO_2 and O_3 passive samplers. Although SO_2 was also initially included in the exercise, it is later not included in the experiment because some of the SO_2 samplers were contaminated in our laboratory.

Since sampling duration was very short and considerable small amount of sample was collected during this period of time, it is difficult to interpret the possible interferences arising from chemicals used to coat the filters. Hence aim of the study is compare efficiency of commercially available passive sampling tubes in real condition with the continuously monitoring devices.

2. EXPERIMENTAL

Three different commercially available passive sampling tubes were evaluated after one week sampling period. Since we don't want to declare brands of passive tubes used in the present work when evaluating the performance of tubes with continuous monitoring devices, cylindrical badge tube with tubular diffusion membrane was called as Brand I, open ended diffusion tube with protective shelter and without protective shelter were called as Brand II and Brand III, respectively. In Brand I cylindrical badge tube within microporous sintered polyethylene diffusive barrier; NO_2 is collected onto triethanolamine (TEA) mycroporous polyethylene cartridge. Brand II passive samplers comprise 7.4 cm long polypropylene tubes with 9.5 mm internal diameter, which contains glass fiber filter coated with TEA. Brand III passive samplers consist of a 7.1 cm length acrylic tube with 1.1 cm internal diameter which have stainless steel wire impregnated with TEA. And 7.4 cm long and 9.5 mm diameter polypropylene tubes, which contain glass fiber filter coated with TEA, were designed and improved extraction and analyzing procedure for determination NO_2, which was called as custom-made. For all passive sampling brands, nitrogen dioxide is chemiadsorbed onto TEA as nitrite ions.

For ozone measurement, Brand I badge cartridge is formed by a micropore olyethylene tube filled with slica gel coated with 4, 4'dipyridylrhylene (DPE). Brand II diffusion tubes consist of 4.9 cm long polypropylene tube with 9.5 mm diameter which contain glass fiber filter soaked in an acetic acid DPE solutions. For Brand I and Brand II passive sampling, ozone reacts with DPE to form 4-pyridylaldehyde. Brand III diffusion tube is acrylic tube which contain stainless steel wire coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography.

On site, Brand I and Brand II passive samplers were used with protective shelter to eliminate sun light and bad weather conditions. In addition, for Brand II and III tubes was opened on one end placed vertically inside a shed, with the opened side downwards, in order to avoid possible influence of meteorological parameters such as insolation, rainfall on the sampling. Since Brand cylindrical adsorbing cartridge is housed inside in a cylindrical diffusion body, there is no need to protect the cartridge from bad condition by placing vertically. These cartridges were placed parallel during sampling. All the samplers were hanged onto the bodies of trees, which were < 2m away from the inlets of continuous monitors. Three unused tubes were analyzed as blanks for each brand and. To evaluate precise of the tubes, more than three tubes were used for each brand. After 1 week sampling period, tubes were taken from the field and brought to the laboratory. After exposure the samplers were stored dark and cold condition. And they were analyzed within a week. Exposed and unexposed sample filters and cartridge were extracted in deionized water in sealed plastic bags.

Nitrite ions were determined calorimetrically with Griess Saltzman method. Extracted solutions for each brand were colored with NEDA (N- (1 naphtyl) ethylendiamine dihydrochloride) and sulphanilamide solution. PH of the colored solutions were adjusted with phosphoric acid for Brand II and Brand II and hydrochloric acid for Brand I and Hand-made sample. To determine concentration of colored sample solution, five point calibration curve was prepared from stock sodium nitrite solution (250 mg/L expressed as NO_2^{2-}). Nitrite ions were quantified by The Bausch&Lomb U.V. Visible Spectronic 20 D Spectrophotometry at 537 nm for Brand I and hand-made and 540 nm for Brand II and Brand III, respectively.

To quantify ozone ions, extracted solutions were colored with MBTH (3-methyl-2-benzothiazolinone hydrazone hydrochloride) solution to obtain the corresponding azide, yellow coloured for Brand I&II and hand made tubes. Standard stock solution was prepared from 4-pyridyaldehyde by using of the relationship between O_3 and pyridyaldehyde (1µg pyridyaldehyde=0.224 µg ozone) and colored with MBTH. Colored extraction solutions and standards were measured with spectrophotometry Brand III diffusion tube is acrylic tube which contain stainless steel wire coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography Varian Model 2010 HPLC coupled with VYDAC 302 IC anion exchange column. Standard solutions were prepared from stock sodium nitrate solution.

The atmospheric concentrations of NO_2 and O_3 in the measuring period were calculated by using the equation which based on Fick's First Law and obtained from manufactures. Although theory of the equations is same, each manufacture improved the equation by taking their tube shapes and meteorological conditions into consideration. Specific equations improved by manufactures were corrected with respect to temperature values daily recorded by Turkish State Meteorological Service. Hence, atmospheric concentrations of O_3 and NO_2 were calculated via these equations.

3. RESULTS AND DISCUSSION

Results were compared with the average concentrations measured by the automated monitors. Mean concentrations and percent error values for all NO_2 and O_3 passive sampling tubes are depicted in Table 1 and Table 2, respectively.

Table 1. Mean NO2 concentration results for all Brand passive sampling after 1 week period

Analyzing Brand	Mean NO_2 concentration (µg/m^3)	Percent Relative Error
Chemiluminescence Analyzer	53.6	
Brand 1 Passive Sampling	38.0 ± 4.0 (n=3)	- 27.8
Brand 2 Passive Sampling	67.0 ± 7.9 (n=4)	+25.7
Brand 3 Passive Sampling	59.2 ± 2.4 (n=6)	+10.4
Brand 4 Custom- made	39.7±20.0 (n=7)	-25.9

Table 2. Mean O3 concentration results for all Brand passive sampling at 1 week periods

Analyzing Brand	Mean O_3 concentration (µg/m^3)	Percent Relative Error
UV Fluorescence Analyzer	19,75	
Brand 1 Passive Sampling	9.6±0.35 (n=3)	-51.1
Brand 2 Passive Sampling	16.6±1.80 (n=4)	-15.8
Brand 3 Passive Sampling	26.2±19.0 (n=5)	+32.7

The limited exercise performed in this study demonstrated that there are differences in performances of different brands of passive samplers in the field for NO_2 and O_3 sampling. Generally, parallel samplers used from each brand generated comparable data indicating that reproducibility of are reasonably good for all brands tested. However, data generated from each brand deviated from average concentrations obtained from freshly calibrated continuous monitors for the same time period. For NO_2, deviations ranged from +26% to -28%. For O_3 differences between passive samplers and active monitors ranged between -50% and +30%.

Results showed that a general feeling for the levels of pollutants can be obtained with all brands of passive samplers. However, use of passive samplers beyond this, such as compliance with regulations, is not warranted.

Some brands did produce results that are fairly comparable with the average concentrations obtained from continuous monitoring instruments. Further tests, such as effect of exposure periods on accuracy and reproducibility, reproducibility and accuracy tests at successive periods, effect of storage time will be performed using these brands. They will be deployed to the field if satisfactory results are obtained from all those tests.

4. ACKNOWLEDGEMENTS

The authors are thankful to Refik Saydam Hygiene Center to help in deploying the passive sampler tubes and also sharing the continues monitoring results of pollutants of concern.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

MASS CONCENTRATIONS OF TSP, PM_{10} AND $PM_{2.5}$ IN ERZURUM URBAN CENTER, TURKEY

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ABSTRACT

Impact of atmospheric particles on human health and visibility degradation in urban areas is well documented in the literature. We have initiated a program in Erzurum to measure Total Suspended Particles (TSP), PM_{10} and $PM_{2.5}$, simultaneously at one point for one year period. Sampling was started in February 1, 2005 and will continue to the end of January 2006. Data generated in the first six months of the study were presented.

Average TSP, PM_{10} and $PM_{2.5}$ concentrations measured during sampling period (February to July 2005) are 114.7 ± 103, 31.4 ± 24 and 14.2 ± 14 µg m^{-3}, respectively. The ratios of $PM_{2,5}/TSP$, PM_{10}/TSP, $PM_{10-2.5}/TSP$, $PM_{2.5}/PM_{10}$ and $PM_{10-2.5}/PM_{10}$ are 0.13, 0.29, 0.16, 0.42 and 0.58 respectively. With the 0.13 value, $PM_{2.5}/TSP$ ratio is the lowest one and also the lowest value of the literature. When attributing the correlations of PM values measured during sampling period (February to July 2005), the correlations between TSP and PM_{10} and $PM_{10-2.5}$ are observed higher and the moderate correlation is found between TSP and $PM_{2.5}$ ($p<0.01$). This higher correlation is mostly seen between soil-sourced coarse particles and shows the same source of origination, however fine fraction ($PM_{2.5}$) has different source and therefore found as a moderate correlation ($p<0.01$).

Key Words: Air pollution, atmospheric particle, Total suspended particle, PM-10 fraction, PM-2.5 fraction, Erzurum

1. INTRODUCTION

Anthropogenic emissions leading to atmospheric aerosols which have been synonymous of modern industrial and technological development, have been implicated in human health effects; visibility reduction; acid deposition and in altering the Earth's radiation balance (Morawska, et.al., 1998).

Airborne particles vary in size form and chemical composition. They range in size from a few nanometers (10^{-9}m) up to tens of micrometers (10^{-6}m). The size of particles can be described by means of their aerodynamical diameter. The aerodynamical diameter is the diameter of a spherical particle with a density of 1 g/cm³, which moves in relation to atmospheric air in a gravitational field at the same speed as the particle in question (Arya, 1999).

Generally, particles found in the air range in size from 0.001 µm to 100 µm. The size of the particles is of decisive importance to their physical behavior. Particles of less than 0.2 µm in diameter are normally called ultra fine particles. They consist of combustion products, sea salt nuclei, and end products from chemical reactions in the atmosphere involving ozone and VOCs. The smallest particles approach the size of large gas molecules. Particles that range from 0.2 µm to 2.5 µm in diameter and consist of fumes and dust are normally called fine particles. Particles larger than 2.5 µm are generally called coarse particles. They mainly consist of fungal spores, pollen and particles generated through natural processes such as wind erosion and volcanic activities. In principle, particles with an aerodynamic diameter below 5 µm follow the motion of the air and may remain suspended for days in ambient air.

Larger particles, with an aerodynamic diameter of over 10 µm, are removed within a matter of hours either by settling or by rain. Particles may be measured based on weight, numbers or chemical content. Total suspended particles (TSP - µg/m^3) is the total weight of particles per volume of air and $PM_{2.5}$ and PM_{10} (particles with a diameter less than 2.5 µm and 10 µm, respectively) are the total weight of particles with diameters less than indicated by the subscripts per volume of air (EPA, 1996).

Given that PM is emitted into the atmosphere by a number of anthropogenic and natural sources, the physical and chemical patterns may vary considerably. Both natural and anthropogenic emissions supply primary (direct emission of PM) and secondary (formed from gaseous precursors) PM. On a global scale, PM emissions reach 3400 million tones/yr. Anthropogenic sources account for only 10% of total PM emissions, whereas the natural primary PM emissions reach 85% (2900 million tones/yr).

Although these figures change drastically on a local scale, natural emissions may interfere considerably in the PM monitoring around large natural PM emission sources (mainly arid and semiarid regions) such as the Mediterranean basin (Querol et.al., 2001).

Airborne particulate matter influences Earth's radiative balance, visibility, and human health. A number of epidemiological studies (Schwartz et al., 1996) have demonstrated that atmospheric particulate matter (PM) in urban areas has a clear correlation with the number of daily deaths and hospitalizations as a consequence of pulmonary and cardiac disease responses.

These studies show that measurements of thoracic and alveolar particles (PM<10 and <2.5 mm, respectively) correlate better with morbidity and mortality than total suspended PM (TSP). Recent establishment of $PM_{2.5}$ standards in the US have attracted everyone's attention to these fine fraction particles. If the new $PM_{2.5}$

standards prove themselves worthy, EU and other countries around the world will probably switch from PM_{10} to $PM_{2.5}$ standards in the near future.

Turkey, in the process of accession to EU will have to adopt and enforce EU air quality directives. Fair amount of information on the levels of PM_{10} and $PM_{2.5}$ in Turkish cities is necessary to be able to foresee the problems that will arise when new standards are adopted. However, such data is extremely scarce in most Turkish cities.

2. EXPERIMENTAL

2.1. Sampling site and period

Erzurum is located in the eastern part of Turkey and is one of the most important winter tourism centers in the country. It is surrounded by high mountains: the Gavur-Dumlu mountains (3200 m) to the north, Dumanlı-Palandöken (3125 m) to the south and Eğerlidağ (2974 m) to the east. The latitude of the city is 1950 m and it has a population of 402570 inhabitants. Since Erzurum is one of the coldest cities of Turkey, residential heating continues for at least six months in a year. With limited industrial activity, the main sources of air pollution are domestic heating and urban traffic. Average wind speed decreases from 3.3 m s^{-1} in summer to 2.2 m s^{-1} in winter.

Unfavorable topographical and meteorological conditions result in frequent inversions and subsequent pollution episodes in Erzurum, particularly during long and cold winter season.

In this study, 354 daily PM samples of TSP, fine (<2.5 µm) and coarse (2.5-10 µm) particles were collected at the garden of Erzurum Regional Directorate of Highways (see Figure 1), according to a new approach for sampling location, during February to July 2005 (Bayraktar et.al., 2005).

The sampling site is appropriate for the EPA criteria, and referred as the point reflecting the profile of the city pollution, because of its homogenous structure similar to the basic pollution sources of the city, such as the exhausted gases and the emissions of the fossil fuels used in domestic heating; and its distances far enough away from both local pollution sources and more than 150 m from main roads at north. It has also 1955 m altitude closer to the average city altitude (1950 m).

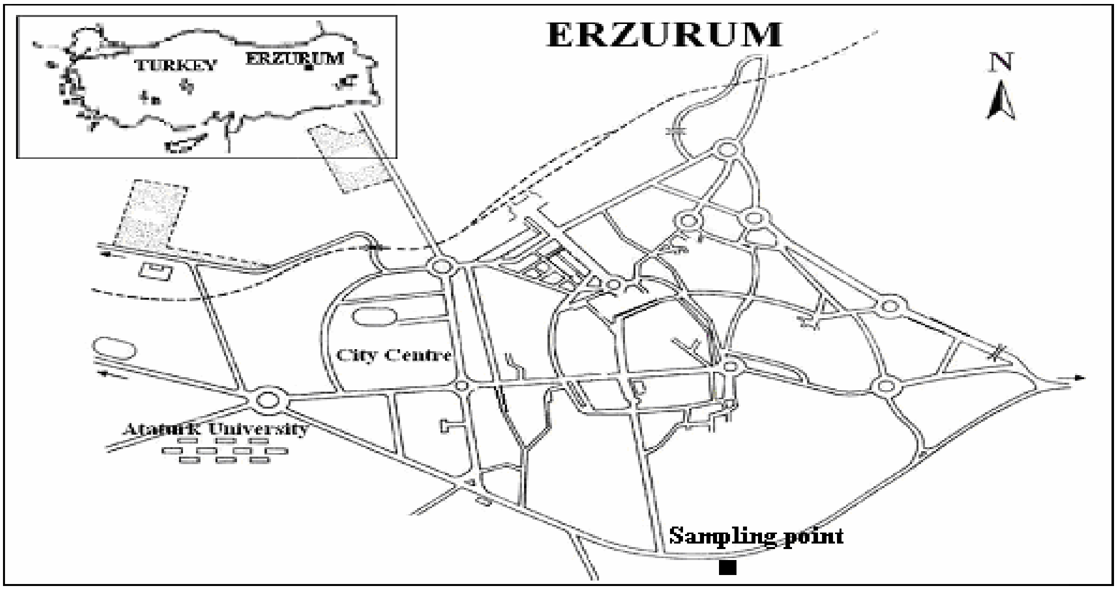

Figure 1. Study area

2.2. Sampling Method

A dichotomous 244 sampler (Anderson sampler) and low-volume sampler (Tecora TCR PM sampler) were used to collect three ranges of PM samples (TSP, PM_{10}, $PM_{2.5}$). Dichotomous sampler has an inlet with PM_{10} cut-off, which collects only particles smaller than 10 µm. The particles are then size-segregated by means of virtual impaction, into fine particles smaller than 2.5 µm and coarse particles between 2.5 and 10 µm ($PM_{2.5–10}$). The particles are collected on Ø37 mm Teflon membrane filters with a 2 µm pore size, which are recommended for gravimetric determination of particulate matter. The sampling flow rate used was 1 m^3/h. Before sampling, the Teflon membrane filters were placed into a desiccator at room temperature in open plastic Petri dishes for at least 24 h to reach a constant humidity. Afterwards, they were weighed with a five digit sensitive balance. The sample collection period was 24 h for all collected samples. After sampling, the filters were transferred to the laboratory. They were placed in the desiccator again for 24 h, and then weighted under exactly the same conditions as the empty filters. For each sample, three repeated weight determinations were performed and the average was reported.

3. RESULTS AND DISCUSSION

3.1. Mass Concentrations of $PM_{2.5}$, $PM_{2.5\text{-}10}$, PM_{10}, TSP

In the sampling period (from February to July 2005), the average concentrations of TSP, PM_{10} and $PM_{2.5}$ were 114.7, 31.4, 14.2 and standard deviations were 102.6, 24, and 13.8, respectively. Descriptive statistics of PMs measured in all sampling period are shown in Table 1.

Table 1. Descriptive statistics of PMs measured in sampling period

	N	Max	Min	Mean	Standard Dev.
TSP ($\mu g/m^3$)	102	435	16	114,7	102,6
PM$_{10}$ ($\mu g/m^3$)	115	93	4,7	31,4	24
PM$_{10-2.5}$ ($\mu g/m^3$)	115	73	0,4	17,2	16
PM$_{2.5}$ ($\mu g/m^3$)	115	65	1	14,2	13,8

The descriptive statistic results of measured PM data at the heating period, between February and April, and at the non-heating period from April to July are also given at Table 2. As can be seen, all of the maximum values and maximum standard deviations of parameters are observed in winter months, however all minimum PM values and minimum standard deviations are seen in summer months. Some meteorological parameters (wind speed, temperature, precipitation etc.) are more effective during winter season, and so the standard deviations of PM values become higher at this season.

Table 2. The descriptive statistic results of measured PM data at the heating period and at the non-heating period

	N		Max		Min		Mean		Standard Dev.	
	Feb-Ap	Ap-July	Feb-Ap	Ap-July	Feb-Ap	Ap-July	Feb-Ap	Ap-July	Feb-Ap	Ap-July
TSP ($\mu g/m^3$)	67	35	435	334	26	16	134,7	76,5	115,3	56,1
PM$_{10}$ ($\mu g/m^3$)	79	36	93	70	5,4	4,7	37,8	17,5	25,4	12
PM$_{10-2.5}$ ($\mu g/m^3$)	79	36	73	61	0,4	1,4	19,2	13	17,8	10,3
PM$_{2.5}$ ($\mu g/m^3$)	79	36	65	21,1	3	1	18,6	4,5	14,4	3,7

PM correlations which are measured during sampling period are given in Table 3. When attributing the correlations of PM values during sampling period, the correlations between TSP and PM$_{10}$ and PM$_{10-2.5}$ are observed higher and the moderate correlation is found between TSP and PM$_{2.5}$ ($p<0,01$). This higher correlation is mostly seen between soil-sourced coarse particles and shows the same source of origination, however fine fraction ($PM_{2.5}$) has different source and therefore found as a moderate correlation.

Table 3. PM correlations measured during sampling period

	TSP	PM_{10}	$PM_{10-2.5}$	$PM_{2.5}$
TSP	1			
PM_{10}	0,938	1		
$PM_{10-2.5}$	0,906	0,837	1	
$PM_{2.5}$	0,583	0,769	0,293	1

On the other hand, in order to seen seasonal (heating period and non-heating period) correlations between TSP, PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$, Table 4 is created. It was observed that although the correlations during winter season are generally higher and that during summer season is lower.

Table 4. The seasonal correlations of PMs

	TSP		PM_{10}		$PM_{10-2.5}$		$PM_{2.5}$	
	Feb- Ap	Ap-July	Feb- Ap	Ap-July	Feb- Ap	Ap-July	Feb- Ap	Ap-July
TSP	1	1						
PM_{10}	0,956	0,870	1	1				
$PM_{10-2.5}$	0,918	0,937	0,869	0,963	1	1		
$PM_{2.5}$	0,567	0,394	0,735	0,737	0,304	0,527	1	1

3.2. Ratios between $PM_{2.5}$, $PM_{2.5-10}$, PM_{10} and TSP

Table 5 shows the maximum, minimum and mean ratio of PMs measured during sampling period. $PM_{2,5}$/TSP, PM_{10}/TSP, $PM_{10-2.5}$/TSP, $PM_{2.5}/PM_{10}$ and $PM_{10-2.5}/PM_{10}$ ratios are 0.13, 0.29, 0.16, 0.42 and 0.58 respectively. With the 0.13 value, $PM_{2.5}$/TSP ratio is the lowest one and also the lowest value of the literature

Table 5. Maximum, minimum and mean ratio of PMs measured during sampling period

	Mean	Max	Min
$PM_{2,5}$/TSP	0,13	0,45	0,01
PM_{10}/TSP	0,29	0,87	0,13
$PM_{10-2.5}$/TSP	0,16	0,55	0,01
$PM_{2.5}/PM_{10}$	0,45	0,93	0,07
$PM_{10-2.5}/PM_{10}$	0,58	0,93	0,07

The seasonal ratios of PMs are also given at Table 6. The ratio of the coarse fraction ($PM_{10-2.5}$) inside the PM_{10} is 0.49 in winter months, and increases to 0.68 in the summer period, while soil is uncovered from snow. $PM_{2.5}/PM_{10}$ ratio is averagely 0.51 and maximally 0.93 in winter months and this ratio is averagely 0.32 and maximally 0.70 in summer season. These ratios show that the main source of $PM_{2.5}$ is heating and there is only a small effect of traffic on $PM_{2.5}$. $PM_{2.5}$ which is commonly emitted by burning during winter season constitutes maximally 0.45 of TSP, whereas this value drops to 0.01 during summer periods. $PM_{10-2.5}$ and PM_{10} ratios inside TSP observed during winter season are 0.14 and 0.29, respectively. These values confirm that the main source of coarse fractions is not burning. The dominant size of atmospheric particles in Erzurum is in coarse mode (PM_{10}/TSP=0.29) and the ratio of fine fraction inside the total atmospheric particles only is15 %.

Table 6. The seasonal ratios of PMs

	Mean		Max		Min	
	Feb- Ap	Ap-July	Feb- Ap	Ap-July	Feb- Ap	Ap-July
$PM_{2,5}$/TSP	0,15	0,11	0,45	0,32	0,03	0,01
PM_{10}/TSP	0,29	0,29	0,87	0,85	0,17	0,13
$PM_{10-2.5}$/TSP	0,14	0,18	0,55	0,41	0,01	0,08
$PM_{2.5}/PM_{10}$	0,51	0,32	0,93	0,70	0,18	0,07
$PM_{10-2.5}/PM_{10}$	0,49	0,68	0,82	0,93	0,07	0,30

Furthermore, when comparing the mean values of the literature and this study, the ratio of $PM_{2.5}/PM_{10}$ in Erzurum is averagely 0.45 and this ratio is 0.71 in Duisburg, Germany in 2001 and 0.47 at the same city in 1999. Another study done in Hong Kong in 2003 has found $PM_{2.5}/PM_{10}$ ratio as 0.61 averagely. The comparison of the observed values in this study with data in the literature are given at Table 7.

Table 7. The comparison of this study with the literature values

Study Area	$PM_{2.5}$ (µg/m^3)	PM_{10} (µg/m^3)	TSP (µg/m^3)	$PM_{2.5}/PM_{10}$	$PM_{2.5}$/TSP
This study	14	31	114,7	0,45	0,13
Duisburg, Almanya (John et al. 2001)	32	45		0,71	
Duisburg, Almanya (Kuhlbusch, et al. 1999)	8	17		0,47	
Hong Kong, (Ho et al. 2003)	51	84		0,61	
Qalabotjha, Güney Afrika (Engelbrecht et al. 2001)	84	90		0,93	
Raahe, Finlandiya (Oravisjarvi et al. 2003)	10	17		0,59	
Buenos Aires, Arjantin (Bogo et al. 2003)	37	48		0,77	
Yellow Sea, South Korea (Lee et.al., 2002)	18,7		37,2		0,50
İstanbul, Turkey (Karaca et.al. 2005)	21	47		0,45	

As seen in Table 7, this study and other studies done in Istanbul and Europe have closer values, however, the values measured in Argentina and South Africa are different than Erzurum. This can be attributable to the selection of sampling location, green parks, contents of fossil fuels, exposure to the industrialization and traffic pollutions.

4. CONCLUSIONS

The arithmetic mean of PM_{10} (31.4 µg m^{-3}) in sampling period was found to be lower than Turkish air quality standard of 60 µg m^{-3}. On the other hand, this value was also found to be lower than the European Union air quality annual PM_{10} standard of 40µgm^{-3}. But the mean concentration of $PM_{2.5}$ in this study is higher than United States EPA annual $PM_{2.5}$ standard of 15 µg m^{-3}.

There are statistically significant relationship between $PM_{2.5}$, PM_{10} and TSP at the 99% confidence level. The correlations between TSP and PM_{10} and $PM_{10-2.5}$ are 0.938 and 0.906 respectively and the correlation between TSP and $PM_{2.5}$ is found as 0.583. This shows the dominant mode of Erzurum atmosphere as coarse mode. However, fine fraction ($PM_{2.5}$) emitted by burning during winter months are also important in Erzurum atmosphere. Other way, the ratios of $PM_{2.5}$/TSP and PM_{10}/TSP in heating season (February-April) are 0.15 and 0.29 and, in un-heating season (April-July) are 0.11 and 0.29 respectively.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

PROPOSE OF SUITABLE HOSPITAL WASTE INCINERATORS IN I.R. IRAN

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ABSTRACT

Although, hospital wastes are considered as hazardous wastes, but unfortunately there was no suitable and proper consideration in collection, transportation and disposal procedures in the Islamic Republic of Iran (I.R.Iran). Large amount of hospital wastes are produced in the main cities of Iran, especially in populated ones and the capital cities of the big provinces with over 2 millions populations such as Tehran and Meshad. The estimated average weight of hospital solid wastes in Tehran and Meshad were 2.954 and 1.67 kilograms for each bed in 2001, respectively.

Some hospitals in Iran have incinerators with low efficiency and air pollution problems. Since much of the hospital wastes including hypodermic needles, body parts and fluids, diapers, laboratory cultures, etc., is infectious and potentially dangerous, many hospitals' managers feel safer to burn their waste, rendering it harmless, rather than to dispose it in landfills. Burning hospital waste and medical/infectious waste resulted in emission of various air pollutants, including hydrochloric acid, dioxin/furan, and toxic metals.

The main purpose of this study is to describe a suitable designed incinerator characteristic for hospital wastes by considering air pollution standards in Iran.

1. INTRODUCTION

One of the most common dangers in the countries is medical and health care waste. Hospital waste includes all the waste generated by health care establishments, research facilities and laboratories. The main generations of hazardous waste from hospital & health care facilities are infectious, pathological, sharps, pharmaceutical, chemical, high content of heavy metals, pressurized containers and radioactive wastes. Although, hospital wastes are considered as hazardous wastes, but unfortunately there is no suitable and proper consideration in production, collection, transportation and disposal steps in Iran.

There are many hospitals, clinics and health institutes in Iran. For example, 30, 88, 87, 74 and 71 hospital, clinic, laboratory, radiology and other centers are active in Meshad (6146 beds in witch 5238 are active ones). Statistics indicate that the average density and moisture content of hospital wastes are 0.28 gr/cm^3 and 60.7%, respectively. In two studies, it has been shown that the amount of waste produced per day for each bed was 2.954 and 1.67 kg in Tehran and Meshad, respectively (Ayati & Ganjidoust, 2001, Ganjidoust, 2000, Sadeghi, 2002).

From over 6400 different types of health institutions located in Tehran, only few of them have incinerators for waste treatment (Razian, 1995). No emission control has been observed in the cases. Smaller hospitals and clinics and health institutes collect their waste in plastic bags and dispose them with semi-municipal household waste in the street. The wastes are then collected by municipality staff in ordinary way and do have the possibility of health problems for them, too (Ganjidoust, 2000). These conditions may be seen in other main cities such as Meshad.

An important task in any enterprise dealing with hazardous waste is proper handling, storage and transportation. Improper handling of hazardous materials, in any quantity, can result in injury, environmental contamination, and fines. The key elements for a successful Hazardous Waste Management (HWM) program are effective regulatory system and adequate treatment and disposal facilities. Waste Minimization (WM) means any effort to reduce or recycle the quantity of waste generated and, when feasible, to reduce or eliminate toxicity. WM does not include treatment unless the treatment is part of the recycling process. There are several works that can be done in order to reduce the amount of solid waste consist of source reduction, reuse, recycle and recovery that is known as 4Rs. Source reduction, reuse and recycle are three ways that are being gradually applied in most industries in Iran. It is obvious that because of infectious waste from hospitals, more attentions should be considered in applying 4Rs in HWM.

In this paper suitable designed incinerator characteristic for hospital wastes by considering air pollution standards for two main cities of Tehran and Meshad are discussed.

2.METHODS

First two cities were chosen for research. Tehran is the capital city and Meshad is attractive for religious tourists with the population of over 10 and 2 millions, respectively. Totally, in both cities, 14 hospitals were examined. A questionnaire was prepared and filled by the investigated hospitals. These questions were consisting of production, temporary conservation, transportation, treatment and disposal of the waste.

3.RESULTS AND DISSCUSSION

Hospital waste analysis of Meshad indicated that more than 31 percent of the produced wastes are food ones. About 60, 4 and 4 percent are mix waste, bread and boxes, respectively. Figure 1 indicates percent distribution of waste in different areas of the hospitals. The information of hospitals waste characteristics for Tehran were given in the previous papers by the authors (Ganjidoust et. al, 2003 & 2004).

Treatment means any method, technique, or process designed to change the physical, chemical, or biological characteristics or composition of any waste to neutralize, recover energy or material resources, reduce the volume, and etc. Thermal methods, a mature technology, especially incineration is one the most popular kind of treatment. Incineration is a dry oxidation method in high temperature for volume and weight reduction. Choose of suitable system to control pathogens and all kind of hazardous and non-hazardous pollutants is very important. For this reason, in the first step, advantages and disadvantages of incinerator should be considered. Volume reduction, detoxification, high efficiency and energy recovery are the main advantages of thermal treatment. Disadvantages are high construction fee, complex operation and secondary pollution such as carbon dioxide, nitrogen oxides, toxic and poisonous, furan, tiny solids and low molecular weight organic compounds such as metals, halogenated acids and dioxins and that should consider standard conditions. Table 1 shows the incinerator standard in Iran (Sadeghi, 2002).

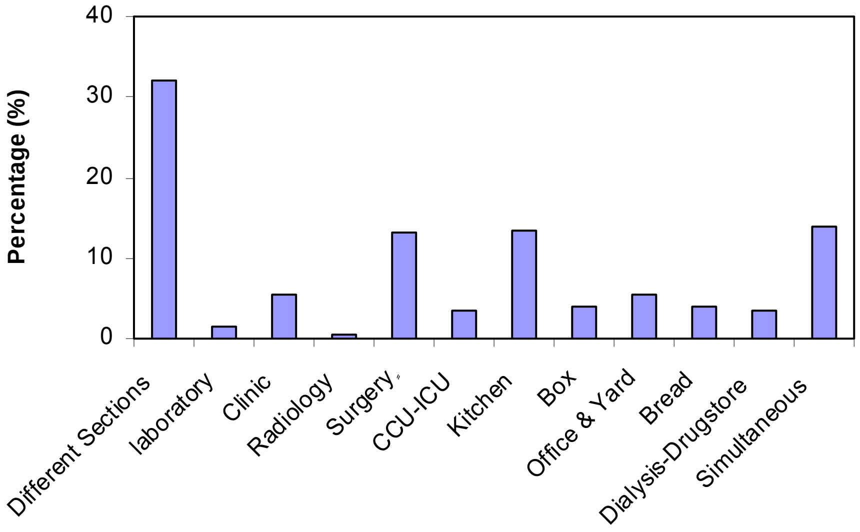

Figure 1. Characteristics of Hospital Waste in Meshad

Table 1. Incinerators Standard in Iran

Parameter	Type 1	Type 2
Dust (mg/m^3)	150	250
Turbidity (%)	20	30
SO_2 (ppm)	800	800
H_2S	10	25
CO (mg/m^3)	350	500
F_2 (mg/m^3)	10	25
NO_x (mg/m^3)	350	500
NH_3 (mg/m^3)	5	5

For incineration the following conditions should be considered:

- The least heat value for normal and Infectious wastes: 2000 and 4000 kcal/kg, respectively.
- combustible materials: 60%
- non-combustible materials: less than 5%
- non-combustible solids: less than 20%
- humidity: less than 30 %
- temperature (the first chamber 800-900 ^{o}C and the second chamber 900-1200^{o}C)

- Prohibited items: pressurized containers, reactive chemical, silver, photography, radiography, halogenated plastics such as PVC, high concentrated mercury and cadmium like broken thermometer and used materials.

In many developing countries high-temperature incineration, are available, entailed higher costs and different regulations. The view was expressed that, for a developing country, the main question in considering the construction of a new facility for disposal was the capacity for utilization, since only full capacity utilization over a number of years would make a plant cost-effective. Also for that reason, a new destruction facility should not be too specialized, but should be able to handle various types of material. It was noted that non-combustion technologies were not automatically a good solution. It was necessary to look at the data to see whether such technologies were cost-effective, safe, free from toxic by-products, and did the right job. In the final analysis, it was clear that, on the basis of the knowledge it had gained about its own situation, and taking all the other factors into account, each country had to find its own solution to the question of technology choice.

The followings are three main technologies to destruct hospital wastes in Iran regarding. Based on the type of waste, the available land and other conditions one of them is suggested.

1. Two-chamber pyrolytic (thermal destruction) incineration is the most common system for hospital and clinical wastes. This system is proper for infectious waste.
2. One-chamber furnace with constant temperature oven is suggested if pyrolytic incinerator couldn’t be used.
3. Rotary furnace with high temperature oven to destruct poisonous and chemical wastes.

4. CONCLUSION

1. Some hospitals in Iran have incinerators with low efficiency and air pollution problems. Since much of the hospital wastes including hypodermic needles, body parts and fluids, diapers, laboratory cultures, etc., is infectious and potentially dangerous, many hospitals’ managers feel safer to burn their waste, rendering it harmless, rather than to dispose it in landfills. Burning hospital waste and medical/infectious waste resulted in emission of various air pollutants, including hydrochloric acid, dioxin/furan, and toxic metals.
2. The most common way of disposing hospital waste is through high-temperature incinerators, which are expensive to run. Other methods also are being developed. Two-chamber pyrolytic, one-chamber furnace with constant temperature oven are proposed by considering hospital, kind of waste… conditions.

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UPDATE AND REVISION of TURKISH AIR QUALITY REGULATION

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ABSTRACT

In order to control pollution in accordance with the current Turkish Constitution of 1982, an environmental law was passed in 1983 which aimed at the control and improvement of the environment; preservation of land and natural resources; prevention of water, land and air pollution; preservation of the animal habitat, historical and natural values; improving present and future health civillisation and living conditions; and establishing themes plus realistic economic and social plans to fullfill these aims.

Based on the fundamentals of the Turkish Environmental Law of 1983, The Air Quality Assurance Regulation was issued on October 1986. This regulation was basically a direct translation of the German TA-Luft of 1984. The main thrust of The Air Quality Assurance Regulation was to effect industry, domestic heating and ambient air quality and traffic which previously had not been represented according to the weight of their emission contributions.

Two new regulations, “Industry Related Air Pollution Control Regulation” and “Heating Related Air Pollution Control Regulation”, presented by the Turkish Ministry of Environment and Forest, came into force on 7 October, 2004 and 13 January 2005, respectively. The Turkish Ministry of Environment and Forest is planning to publish two more regulations, on traffic-related air pollution control and ambient air quality.

In this study, we have critised industrial and heating-related air pollution control regulations on legal, technical, administrative, practical and global bases. A comparison of these two new regulations with EU Directives has also been made.

Key Words: Air Quality, Regulation, Emission Limits, Industrial Pollution, Heating

1. INTRODUCTION

In a previous paper we reported a fundemental weaknesses of the Turkish Air Quality Assurance Regulation (AQAR): its misapplication to the actual conditions in the country (Okutan et al., 1997) A contradiction between the characteristics of the fuels produced and emissions limits imposed to these fuels, and classification of the industrial sectors not reflecting the structure of the industry, are given as two examples. The reason given for the weakness of the Regulation was the fact that it was mostly a translation of it from German regulation in 1986 (Official Gazette, 1986). AQAR was issued as a continued enviromental legal structuring in Turkey based on the 1982 Constitution and the Enviroment Law of 1983. AQAR generally deals with ambient air quality, industrial installations, and the utilisation of fuels for heating. The restrictions on the ambient air-quality limiting values are imposed differently for general, heavy industrial and special conserved areas on long and short term bases. On the other hand, bases for target limiting values, clean air plans and modelling are established. The industrial installations are categorised in three groups: high-polluting installations (HPI); installations subject to permit (ISP); and installations not subject to permit (INSP) The fuel utilisation for heating purposes is given under "combustion installations "title and in high polluting installations and installation subject to permit categories. Vehicles are not dealt with in AQAR..

AQAR had limited success in the establishment of sound air-quality assurance in the country due to many reasons: lack of implementation structure and resources; inadequate fuel supply to the country; contradictions between authority and responsibility; slow responce in the bureaucratic structure; failure to include representatives of industrial stakeholders; regulation falling behind the fast developments in some industrial sectors; and inspection and economic deficiencies. However, it should be noted here that acute air pollution problems experinced in some of the populated cities in Turkey were resolved to a significant degree thanks to utilisation control of the quality of fuel. Due to the massive harmonisation efforts of the legal system with the EU, new regulations are being issued to replace the AQAR. The Industry Related Air Pollution Control Regulation (IRAPCR) (Official Gazette, 2004) and Heating Related Air Pollution Control Regulation (HRAPCR) (Official Gazette, 2005) were issued 7 July 2004 and 13 January 2005, respectively. And two more regulations, on ambient air quality assurance and control of vehicle emissions, are also being prepared. Regarding air quality, preperation of "The Air Framework Draft Law " is planned for the harmonisation with EU Directive (2001/80/EC), concerning large combustion installations and "Air Quality Framework Directive". There are ongoing preperations for "Large Heating Installations" (LHI) which have thermal power output higher than 50 MW, and for the creation of "emissions trading." Completion of all these preperations will meet most of the harmonisation program of Turkish Air Quality System with the EU.

2. COMPARISON of INDUSTRY RELATED AIR POLLUTION CONTROL REGULATION and AIR QUALITY ASSURANCE REGULATION

AQAR consists of 8 sections, 64 articles, 1 temprorary article and 10 adet appendices. The Prime Ministry's General Directory and Ministery of Health were the primary responsible authority and Ministry of Energy and Natural Resources, Ministry of Industry and Trade and Municipalities are the other related institutions.

As explained above, the installions were grouped into ISP, INSP and and HPI according to AQAR. Furthermore, ISP had 10 main groups and 136 subgroups and HPI had 18 main groups and 43 subgroups.

The weakness of AQAR in many areas is attributed to the fact that it was not based on facts and information on the sources of polluting sources. Even today there is not a sound emission inventory in various sectors. The only complete emission factors for conventional and micro pollutants which has been realised is for the cement production plant, by the Quality and Environmental Council (Ekinci et al., 1998 and Canpolat et al., 2002) During the course of application of AQAR, sharing control of the emission permit procedure by the municipalities and the mayor's offices weakened the overall controlling operation and prevented the accumulation of emission information in one common pool. For this reason, even after 18 years a healthy emission inventory could not be established. The public and private emission measuring institutions did not use common and internationally accepted standards and equipment, and this shortcoming makes it difficult to have confidence in the accuracy of the comparable measurements after 18 years of AQAR application. Clean air plans could not be realised. The legal limits on the ambient air quality were kept at higher levels than is the case in the EU and some other countries. The renewable energy resources were not included into the provisions of AQAR. The liquid fuels produced at the refineries had sulfur contents which had no relevence to the limits imposed on SO2 emissions.

Installations classified under HPI and ISP did not represent the state of the industrial structure in the country and caused problems in application.The limiting excess oxygen for the case of inefficient and variable small scale and mostly heating installations had 13% excess oxygen limitations. On the other hand, for gas turbines operating under high excess air rates of %13-15 were restricted to 3 % excess oxygen. For the “old aged” installations having an operation life of less than 20.000 hours, the limit values were diluted and thus caused serious confusion in application.The dust emission limitation for the combustion appliances were kept high due to insufficient control technologies and resources of the country. In the chimney control issues, like flue gas discharge velocity and chimney height, there have been difficulties in application. Even though stone and sand quarries were sources of high dust emissions, the controlling capability of the AQAR was very limitted.

One of the main new concepts ushered in by the new Industry Related Air Pollution Control Regulation (IRAPCR) relates to the level of technology used in installations. Clean technologies are accepted as the priority goal. For this purpose it is accepted that for the plants in continuous operation and which have realized a successful consolidation and control (due to comparable methods, setups and operational modes), the emission limitation precautions become practical and usable, advanced and suitable to the national conditions and cleaning methods which constitute the essence of “technological level” and which comprise the foundation of the Regulation. This level dictates which waste free or minimum waste and clean production technologies should be considered before the treatment option.

In the new Industry Related Air Pollution Control Regulation (IRAPCR), ISP and HPI classifications of the industries the number of sections increased and new industries were introduced. For example, under the ISP heading 10 main groups and 138 subgroups were defined, whereas for HPI 26 main groups and 61 subgroups were defined. In particular the combustion installation which was referred as Group I in HPI is branched into 8 subgroups. The extensive use of internal combustion engines in co-generation and combined cycle installations, given as disel engines and gas engines and gas turbines, are also included as new combustion installations. In this group, apart from the known fuels, petroleum coke and biomass are included as well. And others also became subject to regulation for the first time: cote, barn, slaughterhouses, and fat melting related to recovery of wastes from these operations, meat smoking, animal dung drying, plant protection and pesticise production plants, metal painting, automobile and house appliance painting, storage of petroleum and liquid fuels, yeast production, vegetable oil production and sugar and sugar molasses drying plants. This approach is generally in accordance with the structure of industry at present day Turkey. In the new Regulation, the "old plant" concept has been dismissed altogether.

IRAPCR also introduces for the first time an "efficiency concept" in air quality assurance regulation. According to this new provision, if a plant is operated at a higher efficiency than the set value, the restrictions are then calculated by multiplying with a correction factor calculated as: efficiency realised/efficiency set. Accordingly the emission limits of efficiency combustion plants may be increased, which will in the long run prevent the operation of low efficiency combustion plants.

Comparison of IRAPCR and AQAR in Terms of Emission Restrictions

For the case of ISP, the emission limits for dust, special dusts, organic gases and vapours, carcinogenic substances, flue gas velocities, chimney height and excessively dangerous substances for both regulations are compiled in Table 1. The changes are indicated in bold characters.

Table 1. Emission Limits for IRAPCR and AQAR

Emission Parameters		AQAR	IRAPCR
Soot	Solid Fuel	< 2 Ringelman scale	≤ 3 Ringelman Scale
	Liquid fuel, Diesel oil	< 2 Bacharach scale	≤2 Bacharach scale
	Liquid fuel, Fuel oil number 4 and 5	< 3 Bacharach scale	≤ 3 Bacharach scale
	Liquid fuel,, Fuel oilnumber 6	< 4 Bacharach Scale	-
Dust (Diagram 1)	Chimneys	Max. 500 mg/m^3	Max. 325 mg/m^3
	Loading, Handling etc.	<3 kg/h 300 mg/m^3	<1,5 kg/h 200 mg/m^3
	Loading, Handling etc.	>3 kg/h 150 mg/m^3	1,5<total dust <2,5 150 mg/m^3
	Loading, Handling etc.	-	>2,5 kg/h 100 mg/m^3
Special Dusts		Same	Same
Organic Gases and Vapors		Same	Same
Carcinogenic Substances		Same	Same
Flue Gas Velocities	TP>300 kW	>6 m/s	
	TP<300 kW		≤2 m/s
	200< TP<500 kW		≥2 m/s
	TP> 500 kW		velocity ≥4 m/s (compulsory conditions, may be ≥3 m/s).
Chimney Height	TP<300 kW	1m above the roof	
	300 kW<I TP <1 MW	1m above the roof	
	TP>1,2 MW	At least 19 m from the ground and 3 m above the roof	At least 10 m from the ground and 3 m above the roof
	TP <500 kW		1m above the roof
	500 kW < TP<1 MW		2m above the roof
Exceedingly Hazardous Substances*	PCB,PCDD,PCDF	-	<0,01 ng/Nm^3

*Instead of the 0,01 ng/Nm^3 limit value cited in the regulation **0,1 ng/Nm^3** value is being used.

The changes in Table 1 show that in soot control similar limits are emposed to the other fuels and the dust emission limitations are based on the load and concentration. An important change has been made on the flue gas velocities and chimney heights which had substantial application difficulties under AQAR.

Monitoring of the Ambient Air Quality at the Impact Area of the Installations

In the new approach for the installations having emmisions above a defined value, the effect of emmissons on the surrounding air quality does not need to be determined by direct measurements. The polluting substances discharged from chimneys and the other ways are reported as the mass flowrate. The related values to the mass flowrates are given in Appendix 3 in AQAR and in article 40 and Table 14-1 in IRAPCR. The differences between the two regulations are listed in Table 2.

Table 2. The Emmission Value Changes Made in the Two Regulations for Installations' Contributions to Air Polution

Emmitted Hazordous Substaneces	The mass flowrates under normal working conditions and working days (kg/hr)			
	AQAR		IRAPCR	
	From chimney	From other sources	From chimney	From other sources
Hydrogen fluoride and Gaseous Inorganic flouride compounds	1	0.1	2	0.2
Hydrogen sulphide	-	-	4	0.4
Carbon Monoxide	1000	100	500	50
Total Volatile Organic Compounds	-	-	30	3

For the ambient air quality mesurement around the plant for the gaseous and dust polluters, the period was specified as not less than 6 months in AQAR, but this period is specified as one month for at least two stations. A passive sampling system is accepted, and for this purpose the measurement period is determined as two months for a measurement points of at least 8 different places. For the settling dust measurements, a period of two months from two stations is required.

Evaluation of the changes between the two regulations from Table 2 show that hydrogen sulphide and total volatile substances are included in IRAPCR and the carbon monoxide and flouride compounds limit values are reduced by 50% and 100 %.

Continuous Measurements

The changes in the continuous measurement of emissions in large plants are given in Table 3, which compares Appendix 2 of AQAR, and article 41 of IRAPCR.

Table 3. Comparision of the Continues Emissions Required by the Two Regulations

		AQAR	IRAPCR	
Pollutant	Fuel Type	Capacity	Capacity	Parameter to be measured
Combustion Control (Combustion Installation)	Solid and Liquid	TP*>15 GJ/h (4,167MW)	36 GJ/h (10 MW)	CO_2 or O_2 and CO
Sulfur dioxide		100 kg/h	60 kg/h	SO_2
Carbon monoxide (For other installations)			50 kg/h	CO

From the table it is clear that, for the purpose of combustion control, the continuous monitoring limit of the plants was increased from 4.167 MW to 10 MW for carbon dioxide or oxygen and carbon dioxide, and the mass emission of sulphur dioxide is reduced to 60 kg/h. Carbon monoxide emission limitations are imposed for other installations for the first time, due to the issuing of IRAPCR.

The POP's group parameters are reduced, under the title of "excessive hazardous substances" in IRAPCR, for the first time.

In AQAR, the oxygen ratio in the flue gas for the small capacity heating solid fuel installations, which are usually inefficient and fluctuating, are set at very high value of 13%. On the other hand, the gas turbines which on technological reasons operate at high oxygen ratios of 13-15% were given a limiting value of 3%, which caused considerable problems in the past years.

In IRAPCR, for the solid burning installations the oxygen excess ratio is set as 6% and for internal combustion engines and for gas turbines it is set as 15%. The petroleum coke and biofuels are included in the air quality regulations for the first time. The dust emissions limit values are reduced and for the liquid fuels sulphur dioxide limiting values are increased considering the refinery capacities in the country up to 100 MW capacity. For the installations having thermal capacities up to 100 MW using liquid or multiple fuels, provided that one of the fuels is liquid and taking 3% excess oxygen as the base the sulphur dioxide limit was increased from 1700 mg/Nm^3 to 2400 mg/Nm^3. For the liquid fired combustion installations for 1.5% sulphur content fuels in a similar manner sulphur dioxide limit has been increased to 2400 mg/Nm^3 and in case of unavailability of the proper fuel provided that it does not exceed 6 months the limit can be 3000 mg/Nm^3. By this way provided that the emissions are monitored by continuous measurement at the trasient stage fuel oil and gaseous fuels may be burnt together.

Emission of of Specific Pollutants

According to AQAR the specific pollutants are classified as special dusts (SD), organic gas and vapors (OGV) and carcinogenic substances (CS). In the SD list (Appendix 3) 49 inorganic substances, in the OGV list (Appendix 4) 121 organic compounds, and in the CS list (Appendix 5) 15 special substances are included. These substances are sub divided in to 3 different classes and for each of them different volumetric and mass emission limits are listed.

In IRAPCR, SD is listed as Table 39.1, OGV as Table 39.2 and CS as Table 39.3 but there is no change in the number of pollutants and in the emission limitations. However, it is planned to bring reductions in the emission limits starting from 1.1.2007. The changes related to these polluters are given in Appendix 3 for SD group under 3 new groups in IRAPCR. These are Special Substances in Inorganic Dust Emissions (SSIDE), Table 1.1 containing a list of 21 Inorganic Vapour and Gases (IVG) containing a list of 29 pollutants totaling 96 pollutants.

238 OVG substances are listed in Table 1.2. The volumetric and mass based emission limits for these kind of polluters are reduced at an appreciable level. In order to provide the necessary backup and planning the facilities in the laboratories to improved in order to be able to perform the necessary detailed analysis required by the new Regulation. This ofcourse need to be backed up with substantial financial backing and intense accreditation efforts of the laboratories.

Measurement Frequency

In air quality control policies usually it is desired that the emission measurements should be done as frequently as posible. However this approach may cause the increase of the measurement needs to excessive levels which may result in a drop in the quality of services and raise querries on the dependabilityof the services. In AQAR in the emission permits measurements were necessary for every year (Article 36) or once every two years (Article 22). Whereas in IRAPCR the measurement frequency (Article 15) is widened for the plants in List A'da as 2 years and for the plantas listed in List B as 3 years.

3. HEATING RELATED AIR POLLUTION CONTROL REGULATION (HRAPCR) AND EMISSION RESTRICTIONS

HRAPCR is consisted of 35 articles and 10 Appendices. In majority of the residential regions the most dominant air pollution source during the past 10 years or so has been the fuel used for heating. For this reason both the combustion appliances and stadardisation of the has to be considered for proper polution manegement. IRAPCR generally prepared with this view and therefore favours the use of natural gas for heating purposes. The combustion installations starting with TP <15 kW are to be evaluated according to Turkish Standarts TS and EC norms to standardize them in terms of technological level and efficiency. The principal intention was to reduce the harmful effect of combustion of different quality fuels in a variety of combustors..

Fuels are defined in Article 5 as follows.

a) Coal.

1) Bituminous coal, bituminous coal briquettes, bituminous coal coke
2) Lignite, lignite briquette,
3) Peat briquette, peat,
4) Anthrasite,
5) Asfaltite.

b) Wood, Wood Derived Fuels and Other Biomass Fuels

In this section wood and wood derived fuels are defined in seven categories.

c) Liquid Fuels

Imported fuel oil with a maşximum sulfur content of %1,0 and indegeneous fuel oil with maximum sulfur content 1,5 % and after 1/1/2007 indegeneous fuel oil with maximum sulfur content of 1 % also diesel gasoline, kerosene etanol and similar fuels.

d) Gaseous Fuels

City gas,natural gas, liqufied petroleum gas (LPG), hidrojen, biogas, treatment gas, coke oven gas, coal bed methane, blast furnace gas, refinery gas andsynthetic gas are in this list. The sulfur content of the gaseous fuels is limitted to %0.1.

Forbidden Substances

A those subtances not referred to in (a), (b), (c) and (d) of this section are forbidden to burn for heating purposes. This forfidden substances include: as petroleum coke, used mineral oil, pieces of vehicle tire, dung, solid wastes and textile wastes, cables, wet wood, painted wood, plastics, household goods excluding newspapers and food

wastes and other household wastes, special wastes, medical wastes, asphalt and asphalt products, paint and paint products and fuel-oil containers.
The restrictions related to the fuels defined above are given in Table 4.

Table 4. Heating Related Air Pollution Control Regulation (HRAPCR)

CI	Thermal Power (TP) kW	Fuel Types	O2, %	Soot	Emission Limitations,mg/Nm^3				Heat Loss with flue gas (%)
					Dust mg/Nm^3	CO mg/Nm^3	NOx mg/kWh	HC as CH4 ppm	
SF	TP≤15	Coal Wood	13	<1RS	150				
SF	15 <TP<1000	Coal Wood	8	<1 RS	150				
SF	15<TP≤50	Wood	13	1RS	150	4000			
SF	50<TP≤150	Wood	13	1RS	150	2000			
SF	150< TP< 500	Wood	13	1RS	150	1000			
SF	500<TP≤1000	Wood	13	1RS	150	500			
SF	15 -1000	Wood	13	1RS	150	4000			
SF	15<TP≤100	Wood	13	1RS	150	800			
SF	100<TP≤500	Wood	13	1RS	150	500			
SF	500<TP≤1000	Wood	13	1RS	150	300			
L&GS		Fuel oil					250		
L&GS	TP<120	Diesel oil					120		
L&GS	TP<120	Natural gas					80		
PBLFCI	70<TP≤1000	Liquid Fuel				110 mg/kWh	250	20	11
PBLFCI	15<TP≤70 (1. class)*	Liquid Fuel		1RS	2-4 BS	110 mg/kWh	185	10	11
PBLFCI	15<TP≤70 (2. class)*	Liquid Fuel		1RS	70-150	80 mg/kWh	120	10	11
PBLFCI	15<TP≤70 (3. class)*	Liquid Fuel		1RS		60 mg/kWh	120	10	11
PBLFCI	70<TP≤1000	Gas fuel		1	-	1070	260	20	9
GFCI	30<TP≤70 (1. class)*	Gas fuel		1	-	-	260	20	9
GFCI	30<TP≤70 (2. class)*	Gas fuel		1	-	-	200	20	9
GFCI	30<TP≤70 (3. class)*	Gas fuel		1	-	-	150	20	9
GFCI	30<TP≤70 (4. class)*	Gas fuel		1	-	-	100	20	9

CI: Combustion Installations **SF: Solid Fuel, L&GS:** Liquid and Gas Oil,
PBLFCI: Pulverized Boiler- Liquid Fuel Combustion Installations
PB: Pulverized Boiler, GFCI: Gas Fuel Combustion Installation

In Table 4, no limits have been imposed on the SO_2 pollutant. This control is achieved by the control of fuel specifications. In actual practice, depending on the frequency of exceeding the air quality limit, the values specification of the fuels are announced by the authoritories. In the provinces where the limiting values are exceeded the maximum sulfur content of the fuel is 2 %, whereas in provinces where the limit values are not exceeded the sulfur content limit is 2.3%. Similarly the 20%

ash limit is also increased. On the other hand, the limits imposed on the coal supply by the new regulation resulted in shortages for both national and imported coal supplies. Therfore a circular has been issued to solve the problem which has arisen from the application of HRAPCR on 26/05/2005, in which the limits are loosened especially as moisture and ash limit values are increased (Table 5).

Table 5. Properties of the Fuels Used for Heating

Coal Name	Properties	Limitations-Regulation	Limitations-Circular
The Properties of thel coal that will be used in cities and towns where the air quality limitations are exceeded	Total Sulfur (on dry basis)	% 2 (max.)	
	Lower Calorific Value (original)	4000 (-200 tolerated) Kcal/kg (min.)	
	Total Moisture (original)	%20 (max.)	max. %25
	Ash (on dry basis)	%18 (max.)	max. %25
	Swelling Index	1 (max.)	
	Dimension*	18-150 mm (Until 18 mm max. %10 is tolerated, above 150 mm max. % 10 is tolerated)	
The Properties of the coal that will be used in cities and towns where the air quality limitations are not exceeded	Total Sulfur (on dry basis)	% 2,3 (max.)	
	Lower Calorific Value (original)	3500 (-200 tolerated) Kcal/kg (min.)	
	Total Moisture (original)	%20 (max.)	max. %30
	Ash (on dry basis)	%20 (max.)	max. %30
	Swelling Index	1 (max.)	
	Dimension*	18-150 mm (Until 18 mm max. %10 is tolerated, above 150 mm max. % 10 is tolerated)	
The properties of the coals used in the residence areas outside of the cities and towns which are pollution rated (villages etc.)	Total Sulfur (on dry basis)	-	max. % 2,5 :
	Lower Calorific Value (original)	-	Min 3000 kcal/kg (-200 tolerated) :
	Dimension*	-	18-150 mm (Until 18 mm max. %10 is tolerated, above 150 mm max. % 10 is tolerated)
The properties of the coals imported for heating use	Total Sulfur (on dry basis)	% 0,9 (max.)	
	Lower Calorific Value (original)	6200 kcal/kg (min.)	min 6200 kcal/kg (- 400 tolerated)
	Volatile matter (on dry basis)	% 12-28 (+1 tolerated)	
	Total Moisture (original)	% 10 (max.)	
	Ash (on dry basis)	%14 (max.) (+1 tolerated)	
	Swelling Index	1 (max.)	
	Dimension*	18-150 mm (Until 18 mm max. %10 is tolerated, above 150 mm max. % 10 is tolerated)	
The properties of the coals imported for industrial use	Lower Calorific Value (original)	-	min 6000 kcal/kg (-500 kcal/kg tolerated)
	Total Sulfur (on dry basis)	-	max. % 1
	Volatile matter (on dry basis)	-	max. % 36
	Dimension*	-	0-50 mm

HRAPCR introduced a swelling index concept, which is a measure of cokability and fast volatile release. The swelling behaviour of Turkish coals is not well documented, and this shortcoming may cause further bottlenecks and other possible problems in the future. Efforts to increase coal quality prior to use could not be strengthened. The practical results of the applications will be obtained during the winter of 2005/2006.

4. CONCLUSION

In this paper copmparison of the AQAR of 1986 and replacing two regulations IRAPCR and HRAPCR is made. Evaluation of two new regulations especially in view of the failures of the former is also offered. AQAR was useful in producing a manegement concept and dicipline to Turkey, and as well as by crystalising the missing points and national realities. Together with the other two regulations that are in the preparation stage, a set of four regulations are expected to provide harmonisation of Turkish air quality assurance system with EU regulations. Past experience should demonstrate that these regulations can only serve their purpose efficiently if they are sufficiently dynamic to respond to the changes in the country and in the world. Corrective developments after the issuing of HRAPCR of the coal characteristics for heating purposes, may be interpreted to mean that the new concept will be more responsive to needs and problems. This on the other hand points to weakness to the new regulations in that they are not based on relevant data. Furthermore there are also impertinent sections, and these may be direct translations, as in the case of the “Wood, Wood Derived Fuels and Other Biomass Fuels”section of HRAPCR. For the purposes of implementation, the regulations must be supported with research, data collection, allocating resources, and technical and service back-ups.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

THE ASSESSMENT OF PERSONAL EXPOSURE: WHAT FOR?

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The number of surveys relating to the direct measurement of personal exposure has multiplied in recent years. However, carrying out these studies is costly, not only from a financial point of view, but also in social terms, as the constraints of a rigorous scientific protocol must be imposed on large groups of individuals with highly varied lifestyles and habits. What do these studies contribute and, conversely, what are their limitations? By examining the issue of personal exposure measurement and the question of air pollution in general, we can see the shaping of a social framework for air quality, incorporated in a subtle dialectic between the individual and the community. When the results of these studies rest upon the acceptance of individual constraints, they serve paradoxically to draw overall conclusions that are more useful when managing a community than when seeking to learn lessons about individual situations. Indeed, beyond the question of the contribution of individual efforts to a collective cause we must also examine the relationship between knowledge and action. Air pollution, like all other environmental issues, rests on a pragmatic and sensitive relationship between man and his surrounding environment (L.Charles 2004). This relationship cannot be of a solely intellectual nature. It must also rely on practical experience, which in turn interacts with and questions knowledge. Participating in such measurements allows volunteers to improve their awareness of the research that can be carried out on their environment.

I The contributions of personal exposure measurement

The studies undertaken have made it possible to restore the air to the same state as that of the surrounding area, which individuals breathe all day regardless of their activities. Knowledge of personal exposure, when combined with detailed information about the activities of individuals and the environments they pass through, makes it possible to provide an indication of the factors governing this exposure.

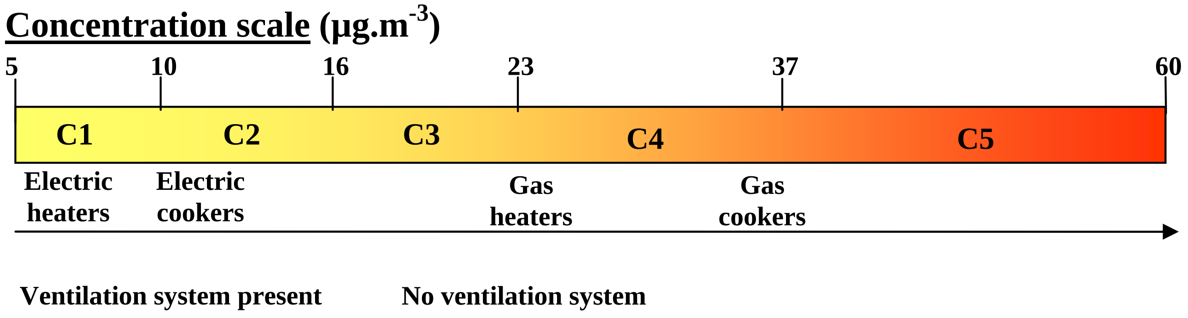
These studies can be used as alerts when particularly high levels are detected in the homes of sentinels, as was the case in Dunkerque. Table 5.6 presents the “abnormal” values measured by these two sentinels during a measurement campaign.

Table 1. Benzene and toluene levels (indoor and personal) measured by two sentinels in Dunkerque (g/m^3)

PERSONAL BZ	PERSONAL TOL	INDOOR BZ	INDOOR TOL
36,45	277,83	42,83	304,33
31,21	225,24	40,77	304,33

Despite the low representativeness of the sample, these studies must be used in the development of effective exposure models, in order to improve the results of epidemiological studies. Indeed, all the studies relating to the measurement of personal exposure report personal exposure levels that are higher than the pollution levels recorded in the surrounding air outside. Also, given the sanitary importance of living conditions in the home, the environmental variables of epidemiological studies need to be linked to the personal exposure of individuals rather than the background noise of urban air pollution.

Knowledge of personal exposure, when combined with detailed information on the activities of individuals and the environments they pass through, makes it possible to provide an indication of the origin of this exposure. These determining factors must be considered from a dynamic perspective and weighted according to the duration of the activities observed. However, as in all statistical surveys, the results obtained must be interpreted with caution. On one hand, these are only valid if examined as a whole, for the entire sample studied, and can only be individualised if special precautions are taken. On the other, the relationships highlighted are not necessarily causal and must be considered within a complex context. Numerous factors come into play in determining exposure, and it is therefore difficult to reduce the relationship with these factors even to one that is simply of statistical significance. However, the results obtained can provide certain general indications to decision makers and allow metrologists to refine exposure models. Thus, Y. Le Moullec () has been able to highlight certain pollution factors in order of gravity.



The low representativeness of the sample is not the only limitation to be taken into consideration when using this type of survey.

II Limitations of personal exposure measurements

The measurements carried out do not take into account the synergy between pollutants. As is the case for most of the air pollution measurements carried out, pollutants are identified separately in spite of the fact that when mixed they can be more harmful than it would appear.

These field measurements cannot be territorialized. Despite the progress made by GIS, which can introduce a diachronic dimension, the measurement of personal exposure runs counter to the territorialization of risks and of the environment. Which are most vulnerable: individuals or territories? No standards have been set up to identify individual risks. Yet, the territorialization of the risks relating to air pollution is now common practice in planning documents, in particular those required by the LAURE (Law on Air and the Rational Use of Energy) in France. By using pollution maps in conjunction with population density maps, we can obtain an index of the population that could potentially be exposed, which allows risks to be ranked according to the number of people exposed. For the sake of accuracy, this index should be different in the day and at night, to take into account the difference between residential and industrial areas.

Modelling exposure based on an indirect assessment of concentrations, which depend on the environments that individuals pass through, requires a certain number of assumptions to be made which limit the possible uses of the document. Indeed, the time devoted to different activities varies greatly from one individual to the next, and uncertainty over localised pollution is considerable because of the variability of the phenomenon. Uncertainty is a component of the collective processes associated with air pollution and is directly linked to the constraints of proximity. It is fundamentally linked to the multiplicity and heterogeneity of knowledge and information systems and to the forms of action available, between which it is impossible to achieve formal consistency. This uncertainty is catered for on the scientific front by so-called deterministic models, which combine the complexity of meteorological phenomena (temporal variations) with the unpredictability of the spatio-temporal variations of emissions and the spatial heterogeneity of immissions. Real-time knowledge of personal exposure and, crucially, of the related health risk will remain a dream.

III Air pollution: building a dialectic framework between the individual and the community

The experiments used in this type of study highlight the importance of personal experience of air pollution, but this experience cannot serve as the basis for an assessment of personal risk, despite the magic of numbers. The volunteers involved in the study are therefore “used” as vessels of knowledge in order to obtain collective results. However, beyond the one-off alert situations mentioned previously, volunteers benefit from their participation in this type of study only insofar as it provides them with a personal assessment, since it does not offer practical and immediate access to the results obtained individually (study by the AFSSE – the French Agency for Environmental Health and Safety).

To better understand the expectations, motivations and benefits required by volunteers involved in the two studies of this type, the APPA (Air Pollution Prevention Association) and the CSTB (Scientific and Technical Building Centre) launched a specific survey of the total population of 240 people who volunteered to take part in a study to measure their individual and/or domestic exposure. 127 questionnaires were filled in, 76% of which were completed by people who took part in the study on exposure entitled *"the air sentinels"* and 24% by OQAI (Indoor Air Quality Observatory) homes. These volunteers live in the Nord Pas de Calais region, the "Grenoble Alpe Métropole" area and the Aix-Marseille region. We can assume that this sample population is comprised of people who are particularly aware of air pollution issues. Yet, the vast majority of the volunteers appear to have been unaware of indoor pollution up until now and confuse pollutants with their sources.

Even when people are interested in the issue of air pollution, the knowledge gap is fairly wide. According to the answers provided by the volunteers, participating in the study gives them the opportunity to improve their knowledge of the subject and, more generally, to help science progress (91%) while participating in the battle against air pollution (91%). Many wanted to be able to inform their friends and family (77%) and to some, the study's appeal stemmed from its innovative approach (68%). 63% of those questioned accepted to take part in the study simply through curiosity. The sentinels were motivated by other, more personal reasons, and for them, the relationship between health and pollution is a close one. A third of the people questioned volunteered because of the health problems suffered by a member of their immediately family. With regard to this point, the sentinels seek information that is of particular relevance to them, and they wonder whether they are particularly exposed to air pollution (67%). In most cases, they wish to convert their knowledge into action by improving the quality of the air in their environment (87%), or they want more information on methods of combating air pollution (87%).

To what extent did the results of these studies meet their expectations? The volunteers were supplied with the results of their exposure measurements, but also of their situation compared to all the other volunteers in the study. 44% believe that these results do not point to high concentrations of pollutants. Conversely, 33% are of the opinion that the measurements taken indicate high concentrations. We should also point out that 23% were unable to answer the question. The figures are spectacular, but also slightly disconcerting. They are as much a cause for worry as they are reassuring, and in any case they remain difficult to interpret and translate concretely.

Table 2: Distribution of the agreement of sentinels regarding the presentation of results

	Agree	
	N	**%**
the results were comprehensive	70	83
it was clear	57	68
it lacked graphics and diagrams	37	44
there were too many numbers	37	43
the figures could not be interpreted	36	42
there was no practical advice on how to act	27	33
it was vague	20	24

33% of those questioned would have liked more practical advice on what action to take, while 44% were disappointed at the lack of graphics and diagrams. Some also thought that there wee too many numbers (43%) or that the figures were impossible to interpret (42%). These failings demonstrate how difficult it is, in the field of air quality, to make the shift from knowledge to action.

Table 3: Distribution of the agreement of sentinels regarding the knowledge provided by the study

	Agree	
	N	**%**
I increased my knowledge of the issue of air quality	77	90
I learnt that there can be many sources of indoor pollution	77	90
it is hard to remember the names of pollutants	65	76
I learnt that you can be exposed without knowing it	61	71
I learnt that there is pollution inside homes	59	69
this reassured me	49	57
this worried me	41	48
it was impossible to determine my situation in relation to standards	33	39

Looking at the comments gathered, it can be said that the volunteers now view air pollution in a more sophisticated way, as 71% realise that one can be exposed without knowing it. Indeed, it is essential to acquire knowledge that makes it possible to go beyond the notion of perceived pollution.

However, it is impossible for the sentinels to assess individual risk. This limitation stems from the ambiguous nature of air quality, which leads to an experience of the environment that is individual, but to a set of solutions that are collective. With respect to the size of the challenges presented (climate change, nuclear, renewable energy, etc.), even the most enthusiastic volunteers feel completely powerless in the face of a phenomenon they are helping to understand, but which they can do nothing about.

CONCLUSION

Can we not detect, through this dialectic, the effects of the change in the paradigm described by A.Touraine, in a society in which the actions of the individual become more relevant than those of society?

These studies demonstrate the importance of the context and of the environment in which individuals live, while highlighting the fact that an individual’s health depends on their habits, their home, the climate, the season, etc. However, this dependence is not univocal and it would be pointless to search for an obvious linear causal relationship. The different factors examined interact in many complex and varied ways. From a health perspective, the assessments conducted show the symbolic importance of health when discussing environmental issues, while pointing out that the notion of health cannot be likened to a pathology, and that it must evolve, as the WHO suggests, in order to take into account quality of life and the dynamics of individuals. Is it always possible for people to choose a high-quality environment? Is environmental injustice not linked to social injustice? The measurement of personal exposure can therefore be used for applications other than the assessment of a health risk. The ability to identify the factors governing exposure can provide a number of admittedly tenuous, but nevertheless realistic indications of the possible routes to promoting prevention.

By emphasising the importance of individual contexts, the exposure studies were able to highlight the responsibility of individuals, and of the choices they make on a daily basis, vis-à-vis pollution. Air quality is no longer considered simply as an outdoor phenomenon, linked to industry and towns. It has now entered the scope of individual responsibility and behavioural choice. At the same time, the challenge for industry has shifted from atmospheric emissions to its products, with the consumer becoming a key player in environmental quality.

The measurements taken contribute to refining the sentinels’ understanding of air pollution, while fulfilling the need for knowledge that is so clearly expressed by populations. Although the reference standards do not deal with personal exposure, populations view the types of measurement discussed here as being more concrete and closer to the reality experienced than the figures produced by measurement networks. These experiments bring into play the homes of individuals, and therefore their most private choices, but they also examine the impact of the seasons and the relationship between pollution and climate. This type of experiment is also crucial if we wish to understand the links between the different scales of pollution. But we must not consider that knowledge of exposure is more representative of the way people perceive this exposure simply because the subject is of more immediate concern to them than the measurement of background pollution. Analyses have shown that perceived pollution always differs greatly from the pollution levels actually measured for a number of reasons, but most of all because the most toxic pollutants are often imperceptible, invisible and odourless.

The approach put forward in this paper is based essentially on an environmental vision of personal exposure, but a more health-related approach can be developed through the use of biomarkers. And more than ever, work on personal exposure rests upon “current scientific knowledge”.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

AN OVERALL MODEL FOR AIR QUALITY MONITORING WITHIN TURKEY FOR IMPLEMENTATION OF EUROPEAN AIR QUALITY FRAMEWORK, DAUGHTERS AND RELATED DIRECTIVES

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ABSTRACT

The objective of this paper is to provide a model to establish the basis for an overall model for air quality monitoring within Turkey for implementation of Air Quality Framework, first, second and third Daughter Directive, as well as the EoI Directives.

Current situation in air quality monitoring in Turkey is discussed.

It is concluded that Turkey stands at the starting point for preliminary assessment.

The network for preliminary assessment under the provincial structure of the MoEF implies every province to be taken as a zone in monitoring air quality. This assumption is not critical, because assignment of zones have no effect on the number of sampling points. However the zone concept is very important from manageability point of view.

The assumptions that need to be made for setting up a national air quality monitoring network are discussed.

Number of sampling points for comprehensive air quality monitoring is calculated to be slightly more than 200 sites.

Key Words: air quality monitoring, air quality

INTRODUCTION

Followings are the directives under considereation:

Air Quality Framework Directive (Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management)

First Daughter Directive (Council Directive 1999/30/EC of 22 April 1999 relating to Limit Values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air)

Second Daughter Directive (Council Directive 2000/69/EC of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air)

Third Daughter Directive (Council Directive 2002/3/EC of 12 February 2002 relating to ozone in ambient air).

The related Directives, are:

First EoI Directive (Council Directive 97/101/EC of 27 January 1997 establishing a reciprocal exchange of information and data from networks and individual stations measuring ambient air pollution)

Amendment of EoI Directive (Council Directive 2001/752/EC of 17 October 2001 amending Annexes of EoI Directive to adopt the list of pollutants covered to changes and requirements on additional information, validation and aggregation.

ASSUMPTIONS

- The monitoring system establishment related scenarios are based on the assumption that transposing EU directives to Turkish legislation is completed and enforced during the next years, up till the year 2010. It is assumed further that efficient enforcement of strict air quality management legislation will encourage private sector to assume responsibility for compliance with the requirements.

- Deadlines and limit values set in the AQF and daughter directives have been taken into account.

- Even though some measurements are taken by various stations in Turkey, the data quality, technical compliance with the reference methods, sampling point compliance are highly questionable and the parameters do not fall into the ones required. Therefore it is safe to assume that Turkey stands at the starting point for preliminary assessment.

- MoEF is responsible for setting limits and thresholds, performing measurements and doing assessment. The network for preliminary assessment under the provincial structure of the MoEF implies every province to be taken as a zone in monitoring air quality. This assumption is not critical, because assignment of zones have no effect on the number of sampling points. However, the zone concept is very important from manageability point of view. Even if the structure of the competent authority changes in the future, this will have no effect on the estimation, made herewith.

- Stations for preliminary assessment should be placed and designed in such a way that they can be used for continuous monitoring after completion of the preliminary assessment period.

- Based on the comments in the Guidance on Assessment under the EU Air Quality Directives, and the Annexes in the Air Framework Daughter directives the minimum number of sampling points for fixed measurement of pollutant concentrations is assigned as shown in Annex 9.

- In Annex 9 are shown the minimum number of sampling points in cases where the Upper Assessment Threshold (UAT) is exceeded or in cases where pollutants concentrations are below the Lower Assessment Threshold (LAT). Number of sampling points are assigned on the basis of pollutant concentrations exceeding the upper assessment threshold (UAT), set by the directive 99/30/EC.

- Urban areas having a population more than 250 000 are assumed to be an agglomeration.

- One sampling point is assigned per 20 000km^2 in the rural areas.

- Additionally, rural areas holding a population density more than 260 people per square kilometre (based on the fact that, average urban population density in the provinces, where population is more than 250 000 inhabitants, is 260 persons per square kilometre) are also assumed to be agglomerations.

- Some of the provinces have high industrial activity, therefore are assumed as Industrial Hot Spots for monitoring.

- Some of the provinces have heavy traffic load because of their transit position on high ways, therefore traffic hot spots are assumed for monitoring.

These assumptions allow us to be on the safe side in terms of considering all the densely populated parts of the country.

Different compound coverage is assumed for stations situated at sites with different characteristics (population, traffic, industrial, rural).

The features of a typical monitoring station, applicable for all kind of stations are suggested to be as follows:

generate data on levels of pollutant concentration in ambient air (SO_2, NO_2, PM_{10}, $PM_{2.5}$, Pb, O_3, Benzene, CO, PAHs, Cd, As, Ni, Hg, 30 VOCs and nm-HC) by means of either continuous measurement at fixed sampling points or periodic measurement techniques based on sample collection followed by analysis in a laboratory / modelling / objective estimation techniques,

generate data for SO_2 , NO_2 and NO_x and O_3 on hourly basis, for CO on 8-hourly basis, for PM_{10} and likely for $PM_{2.5}$ on 24-hourly basis, for Pb and Benzene on annual basis, at the sampling points where continuous measurement is imposed, comply with requirements on the number of sampling points for fixed measurements in zones and agglomerations,

comply with zoning and agglomerations criteria,

The legal minimum number of stations is chosen as the basis for cost calculation, based on the comments in the EC Guidance on Assessment document (EC, 2003).

CONCLUSIONS

Explanation on how and where all monitoring stations for preliminary assessment are proposed is presented in the Table 3.

Population data are obtained from SIS. Total, urban and rural population figures are given in Table 3.

Province areas are obtained from the web site of the Ministry of Interior. Total province areas add up to 549292 square km.

Urban population is assumed to stay in 30% of the province area, therefore rural population is assumed to stay in the remaining 70% of the province area.

Rural population density is calculated by dividing the rural population by the rural area. This figure came out to be 260 people per square km.

Urban areas, where the population density is greater than the average rural population density, are assigned as population agglomerations. Three sites came out to be urban population sites as dense as average rural character.

Total rural area of Turkey is assumed to be 80% of the total area of Turkey, and calculated to be 610027 square km.

Average urban population density is calculated by dividing total urban population by 30% of the total province area.

Sampling points in the urban agglomerations are calculated alternatively, on the basis of pollutant concentrations to be higher than the upper assessment threshold (UAT) and lower than the lower assessment threshold (LAT). The total number of sampling points are given on the assumption that the pollutant concentrations will be higher than UAT.

Total area of Turkey is given to be 774815 square km in the web site of Ministry of Interior

It should be noted that there is only a macro planning for preliminary assessment of air quality management requirements. There is a need for further study on micro siting of monitoring stations as well as specifying the pollutants to be monitored at each station.

Setting up quality assurance system is another significant component to be handled separately.

The next steps after preliminary assessment should be identifying the points of continuous sampling and areas, where air quality to be objectively estimated.

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Web Site of Ministry of Internal Affairs: www.icisleri.gov.trWeb Site of State Institute of Statictics: www.die.gov.tr
ETC/ACC (2004): European Exchange of Air Quality Monitoring Meta Information in 2002; by E.Buijsman and others; ETC/ACC Technical Paper 2004/1, June 2004

TABLE 1: Number of stations per pollutant and station type in Europe 2002

	Daughter Directive							
	1	1	1	1	1	2	2	3
	Sulphur dioxide	**Nitrogen dioxide**	**Particulate matter (<10 µm)**	**Particulate matter (< 2.5 µm)**	**Lead**	**Carbon monoxide**	**Benzene**	**Ozone**
Reporting EU countries	14	14	14	5	4	13	8	14
Total number of stations	1678	1815	1164	37	85	834	179	1524
Of which								
Traffic	394	527	363	8	49	419	97	312
Urban background	598	679	457	20	16	303	58	610
Industrial	333	233	140	0	11	48	7	129
Regional background	256	263	127	1	6	35	7	342
Other 1)	98	113	77	8	3	29	10	131
Reporting non-EU countries	15	14	11	2	2	9	2	13
Total number of stations	249	231	142	5	27	80	5	147
Of which								
Traffic	35	35	26	2		2 0	2	20
Urban background	151	136	82	2	23	44	2	60
Industrial	15	12	7	1	3	6	0	9
Regional background	48	48	27	0	1	10	1	58
Other 1)	0	0	0	0	0	0	0	
All countries	29	28	25	7	6	22	10	27
Total number of stations	1927	2046	1306	42	112	914	184	1671

1) Primarily unknown.

Source: page 12 of 52 ETC/ACC Technical paper 2004/1, Table 3 (10)

TABLE 2: Number of stations in the EU and other countries

	SO2		NO2		PM10		PM2.5		Pb	CO	Benzene		O3
EoI Code	1		2		3		4		6	9	8		7
Time Resolution	H	D	H	D	H	D	H	D	D	H	H	D	H
Austria	*138*		*144*			*74*	*1*			*47*			*113*
Albania 4)													
Belgium	*67*		*47*			*23*	*3*		*28*	*18*		*5*	*33*
Bosnia Herzegovina	*1*		*1*							*1*			
Denmark	*2*	*2*	*12*			*8*				*6*	*1*		*8*
Bulgaria	*38*		*38*			*7*			*19*				
Finland	*9*	*4*	*4*		*26*		*3*			*4*			*12*
Cyprus 4) . .													
France	*477*		*491*			*269*	*28*			*103*			*399*
Czech Republic	*55*		*55*		*53*					*27*	*4*		*35*
Germany	*417*		*476*		*264*	*116*				*297*	*77*		*377*
Estonia	*7*		*7*			*4*				*5*			*7*
Greece	*23*		*26*		*15*					*15*			*26*
FYROM		*25*											
Ireland	*6*		*6*			*8*					*1*		*7*
Hungary	*1*	*1*	*1*	*1*	*1*					*1*			*2*
Italy	*94*		*117*		*46*	*4*				*84*	*32*		*99*
Iceland	*1*		*2*		*2*		*2*			*1*	*1*		*3*
Luxembourg 4)													
Latvia	*6*	*2*	*6*	*2*		*1*							*6*
Netherlands	*38*	*45*		*20*					*4*	*22*		*4*	*38*
Liechtenstein 4)													
Portugal	*30*		*32*		*21*	*1*	*2*		*1*	*26*			*26*
Lithuania		*1*		*1*									*3*
Spain	*22*	*10*	*272*		*140*	*55*			*52*	*130*	*18*		*299*

	SO2		NO2		PM10		PM2.5		Pb	CO	Benzene		O3
EoI Code	1		2		3		4		6	9	8		7
Malta													*1*
Sweden	*4*	*5*	*7*	*14*	*4*					*3*			*8*
Norway	*1*	*7*	*1*	*6*	*3*								*10*
United Kingdom	*79*		*102*		*65*	*5*				*79*	*6*	*35*	*79*
Poland	*17*	*31*	*28*	*20*		*33*	*3*			*24*			*21*
Romania 2		*23*		*18*					*8*				*2*
Slovak Republic	*8*		*8*		*8*					*5*			*17*
Slovenia	*8*		*6*		*7*					*4*			*10*
Switzerland 31	*16*		*30*			*23*				*12*			*30*
Turkey 4) . .													
TOTAL	*159*	*90*	*183*	*48*	*74*	*68*	*5*	*0*	*27*	*80*	*5*		*147*

Source: ETC/ACC Technical paper 2004/1 page 19 of 52 (10)
Table 4-5 Number of stations in the EU countries for which data for components of the daughter directives were available in AirBase, 2002

TABLE 3: Identification of Monitoring Stations for Turkey

Provinces	Population				Province area	Agglomeration Sampling Points		Additional Sampling Points		
								For Dense Pop.	For Hot Spots	
	Total	Urban	Rural	Rural pop. density		Total if <LAT	Total if >UAT	RPD>260	Industrial	Traffic
Adana	1 849 478	1 397 853	451 625	46	14 030	2	4		2	1
Adıyaman	623 811	338 939	284 872	53	7 614	1	2			
Afyon	812 416	371 868	440 548	44	14 230	1	2			1
Ağrı	528 744	252 309	276 435	35	11 376	1	2			
Amasya	365 231	196 621	168 610	44	5520					
Ankara	4 007 860	3 540 522	467 338	26	25 706	2	7		2	1
Antalya	1 719 751	936 330	783 421	54	20 591	1	3			1
Artvin	191 934	84 198	107 736	21	7436					
Aydın	950 757	493 114	457 643	82	8 007	1	2		2	1
Balıkesir	1 076 347	577 595	498 752	50	14 292	1	2			1
Bilecik	194 326	124 380	69 946	23	4307				2	
Bingöl	253 739	123 470	130 269	23	8125					
Bitlis	388 678	219 511	169 167	36	6707					
Bolu	270 654	142 685	127 969	25	7410				1	1
Burdur	256 803	139 897	116 906	24	6887					
Bursa	2 125 140	1 630 940	494 200	64	11 043	1	5		2	1
Çanakkale	464 975	215 571	249 404	37	9737				1	
Çankırı	270 355	141 186	129 169	25	7388					
Çorum	597 065	311 897	285 168	32	12 820	1	2			

Provinces	Population					Agglomeration Sampling Points		Additional Sampling Points		
								For Dense Pop.	For Hot Spots	
	Total	Urban	Rural	Rural pop. density	Province area	Total if <LAT	Total if >UAT	RPD>260	Industrial	Traffic
Denizli	850 029	413 914	436 115	52	11 868	1	2		2	
Diyarbakır	1 362 708	817 692	545 016	51	15 355	1	3			
Edirne	402 606	230 908	171 698	39	6279					
Elazığ	569 616	364 274	205 342	32	9 153	1	2			
Erzincan	316 841	172 206	144 635	17	11903					
Erzurum	937 389	560 551	376 838	21	25 066	1	2			
Eskişehir	706 009	557 028	148 981	16	13 652	1	2		1	
Gaziantep	1 285 249	1 009 126	276 123	66	6 000	1	4		2	1
Giresun	523 819	283 316	240 503	50	6 934	1	2			
Gümüşhane	186 953	77 570	109 383	24	6575					
Hakkari	236 581	139 455	97 126	19	7121					
Hatay	1 253 726	581 341	672 385	178	5 403	1	2			
Isparta	513 681	301 561	212 120	34	8 993	1	2			
İçel	1 651 400	999 220	652 180	59	15 853	1	3		1	
İstanbul	10 018 735	9 085 599	933 136	257	5 196	3	10	1	5	2
İzmir	3 370 866	2 732 669	638 197	76	11 973	2	6		3	
Kars	325 016	142 145	182 871	27	9587					
Kastamonu	375 476	174 020	201 456	22	13108					
Kayseri	1 060 432	732 354	328 078	28	16 917	1	2		1	
Kırklareli	328 461	189 202	139 259	30	6 550				1	
Kırşehir	253 239	147 412	105 827	23	6 570					

Provinces	Population				Province area	Agglomeration Sampling Points		Additional Sampling Points		
								For Dense Pop.	For Hot Spots	
	Total	Urban	Rural	Rural pop. density		Total if <LAT	Total if >UAT	RPD>260	Industrial	Traffic
Kocaeli	1 206 085	722 905	483 180	190	3 626	1	2		2	
Konya	2 192 166	1 294 817	897 349	34	38 257	1	4		2	
Kütahya	656 903	318 869	338 034	41	11 889	1	2		1	
Malatya	853 658	499 713	353 945	41	12 313	1	2			
Manisa	1 260 169	714 760	545 409	56	13 810	1	2		1	
K.Maraş	1 002 384	536 007	466 377	47	14 327	1	2			
Mardin	705 098	391 249	313 849	50	8 891	1	2			
Muğla	715 328	268 341	446 987	48	13 338	1	2		1	
Muş	453 654	159 503	294 151	51	8 196					
Nevşehir	309 914	136 523	173 391	45	5 467					
Niğde	348 081	126 812	221 269	43	7 312					
Ordu	887 765	416 631	471 134	112	6 001	1	2			
Rize	365 938	205 245	160 693	59	3 920					
Sakarya	756 168	459 824	296 344	88	4 817	1	2		1	
Samsun	1 209 137	635 254	573 883	86	9 579	1	2		1	
Siirt	263 676	153 522	110 154	29	5 406					
Sinop	225 574	101 285	124 289	30	5 862					
Sivas	755 091	421 804	333 287	17	28 488	1	2			
Tekirdağ	623 591	395 377	228 214	52	6 218	1	2			
Tokat	828 027	401 762	426 265	61	9 959	1	2			
Trabzon	975 137	478 954	496 183	106	6 685	1	2			1
Tunceli	93 584	54 476	39 108	7	7 774					

Provinces	Population				Province area	Agglomeration Sampling Points		Additional Sampling Points		
								For Dense Pop.	For Hot Spots	
	Total	Urban	Rural	Rural pop. density		Total if <LAT	Total if >UAT	RPD>260	Industrial	Traffic
Şanlıurfa	1 443 422	842 129	601 293	46	18 584	1	3			
Uşak	322 313	182 040	140 273	38	5 341					
Van	877 524	446 976	430 548	32	19 069	1	2			
Yozgat	682 919	315 156	367 763	37	14 123	1	2			
Zonguldak	615 599	250 282	365 317	118	4 420	1	2			
Aksaray	396 084	200 216	195 868	37	7 626					
Bayburt	97 358	41 356	56 002	22	3 652					
Karaman	243 210	139 912	103 298	16	9 163					
Kırıkkale	383 508	285 294	98 214	32	4 365	1	2		1	
Batman	456 734	304 166	152 568	46	4 694	1	2			
Şırnak	353 197	211 328	141 869	28	7 172					
Bartın	184 178	48 002	136 176	92	2 120					
Ardahan	133 756	39 725	94 031	24	5 661					
Iğdır	168 634	81 582	87 052	35	3 593					
Yalova	168 593	98 661	69 932	471	212			2	1	
Karabük	225 102	157 756	67 346	40	2 420				1	
Kilis	114 724	74 985	39 739	35	1 642					
Osmaniye	458 782	311 994	146 788	56	3 767	1	2			
Düzce	314 266	130 632	183 634	72	3 641					

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

DIURNAL VARIATIONS OF PARTICLE SIZE DISTRIBUTION AND MASS CONCENTRATION IN THE KOREAN COAST

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ABSTRACT

To investigate mass concentrations of PM-10, PM-2.5 and PM-1 and the distribution of particle size from 300 nanometer to 20 micrometer diameters, two aerosol samplers were equipped at Kangnung Meteorological Administration, Kangnung city in the coast from February 14 through 16, 2005. The concentrations of PM10, PM2.5 and PM1 showed a typical pattern such as high concentration near 0900 LST (beginning time of office hour) and 1700 LST (ending time of office hour) and their low concentration near noon. PM10, PM2.5 and PM1 had the first maximum concentrations of 145.12 /m^3 of PM10 and 88.93 /m^3 of PM2.5 and 44.71 /m^3 of PM1 at 2000 LST (three hours later after sunset), respectively. The secondary maximum concentration is detected with a magnitude of 93.06 /m^3 at 0100 LST, February 15. The distribution of CO and NO_x concentrations showed a similar tendency of PM10, PM2.5 and PM1 concentrations, except for concentrations in the morning on February 14. When PM10, PM2.5 and PM1 had the first maximum concentrations at 2000 LST and their second maximum at 0100 LST, February 15, NO_x had the first and secondary maximum concentrations at the same times. It implies that the increases of emitted gases like NO_x and CO from vehicles on the street and combustion gases from boilers in the resident area for nighttime heating could make a great contribution to the increase of PM concentration. After sunset, much shrunken surface inversion layer than daytime convective atmospheric boundary layer could also increase the concentrations of particle matters, but after midnight, the concentration gradually decreased due to the reduction of vehicle number on the street. Under westerly wind, the particles transported from the city into the mountain side in the west for daytime returned again to the city and some amount of particles from an upwind side city toward the coastal city could also make a great contribution to the occurrence of secondary maximum. The number densities of particle size distributions, regardless of particle diameters were much lower in the early morning than both afternoon and night. Particle size distribution at 1800 LST to 2350 had bigger number densities in the diameters of 1.2 to 20 .

Key Words : Particle Size Distribution, Nanometer Particulate, PM10, PM2.5, PM1

1. INTRODUCTION

In recent years, many research papers relating to particle size distribution have been published as findrmantal aspect of serosol science (Xu et al., 2004, Kim et al, 2003). Gao and Anderson (2001) investigated characteristics of Chinese aerosols determined by individual particle analysis, where most of measurement of aerosol size is based upon laser sizing on the particles. Adby and Demster (1974) developed powell algorithm as a dependent method and Hansen (1992) and Hansen and O'Leary (1993) utilized L-curve as an independent one. Goldberg (1989), Michelewicz (1996) and Xu et al. (2004) applied genetic algorithm to treat the optimization problem in a quite different way in the particle size distribution fromdata of multispectral wxtinction measurements.

During the Asian Dust period in 2001, the factors of TSP, PM10 and PM2.5 affecting the cycle of aerosols and their chemical properties and compositions was investigated in the Seoul district, Korea (Kim and Kim; 2003) and comprehensive researches on particulates and gases at many measurement points in China, Korea and Japan from 2001 to nowadays have been carried out (Carmichael et al, 1997; Xuan and Soklik, 2002). In Korea, persistent measurement of aerosols have been established Gosan, Jechu island and Taean pensininsula in the west of Korea by Korean Meteorological Administration, but their measurement have been focussed on mass concentration of total suspended particulate and PM 10 and their chemical component and heavy metals, except for PM1. In addition, thier researches do not include partical size distribution of aerosol and the relation between mass concentration and partical size distribution.

Thus, the objective of this study is to explain diurnal variation of aerosol concentration such as PM10, PM2.5 and PM1, which greatly influences upon local pollution state and particle size distribution on human health condition, considering especially time band of their high concentrations.

2. MEASUREMENT OF AEROSOL AND TOPOGRAPHY

2.1. Instrument and experiment

Two aerosol samplers called GRIMM aerosol samplers – Model 1107 and Model 1108 were fixed at Kangnung Meteorological Administration (KMA; $37^0$45'N, $128^0$54'E) in Kangnung coastal city, which is in the eastern mountainous coastla region of Korean peninsula. Particle size distribution of aerosol from 300 nano to 20um and collection of all three PM fractions of PM10, PM2.5 and PM1 were investigated by GRIMM aerosol samplers from February 13 through 17, 2005, which included dust storm and non-dust storm periods of China and Korea in spring.

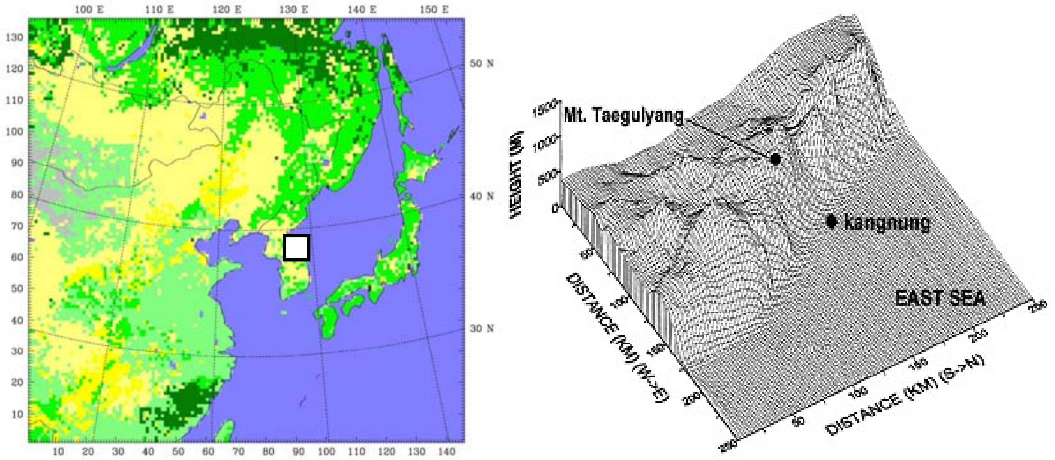
The Model 1107 is specifically designed for PM-10, PM-2.5 and PM-1 environmental ambient air analysis using the laser light scattering technology. This technology enables the Model 1107 to make very precise "cut points" for all three PM size classifications and this system allows the user to collect all three PM fractions simultaneously without changing sampling heads or weighing filters. However, the Model 1107 is the only PM monitor to offer dual technology consisting of both optical and gravimetrical analysis. The Model incorporates a removable 47 mm PTFE filter, which allows the user to verify the optical analysis gravimetrically, as well as providing the option for other chemical analysis on the collected residue.

The 1107 model is devised for particulate measurements via 900 laser light scattering and air with multiply particle sizes passes through a flat laser beam produced by an precisely focused laser and several collimator lenses. The scattered light are detected by a 15-channel pulse height analyzer for size classification. The counts from each size classification are converted to mass by a well established equation. The data are presented in the P.S. EPA conventions for PM-10, PM-2.5 and PM-1. Its complete system consists of 165 fiberglass housing, drying temperature control system, 1107

PM dust monitor, sensors for humidity and temperature and 170M sampling system. Dislays real time data of PM-1 and PM-2.5 and even PM-1 is detected as quickly as every as every six seconds. Sensitivity is from 0.1 microgram/m^3 upwards and tand-alone system is able to be operated directly all times out in the field. The Model 1108 different from the Model 1107 is able to count the number of particles from 300 to 20 and collect all three PM fraction of PM10, PM2.5 and PM1.

2.2. Topography in study area

The study area is located in the eastern mountainous coastal region of Korean peninsula (Fig. 1). Two GRIMM aerosol samplers of Model 1107 and Model 1108 were equipped at Kangnung Meteorological Administration (KMA), Kangnung city adjacent to the East Sea in the east. 2.5^0 degree interval terrain date was used for the largest domain and then 1km interval data was used for fine mesh domain, respectively.



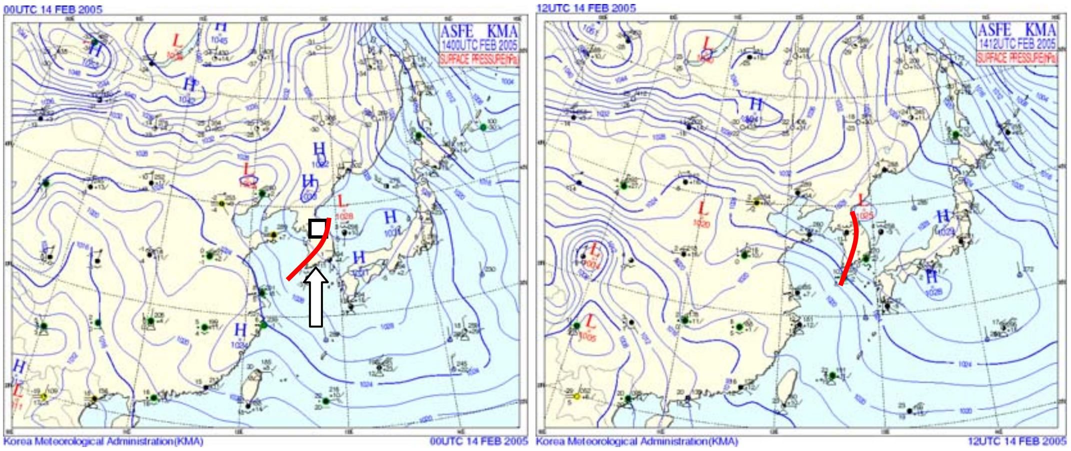
(a) (b)

Figure 1. (a) Land-use data for a coarse domain of a horizontal grid size 27 km. Box denotes the adjancent area of Kanunung city (Korea). (b) 3D (right) topography near Kangnung city (20m above mean sea level, 10 km width; box area shown in Fig. 1a) with 90^0 turning into the right with a horizontal grid size 5 km, and Mt. Taeguallyung (860 m), Korea.

3. RESULT AND DISCUSSION

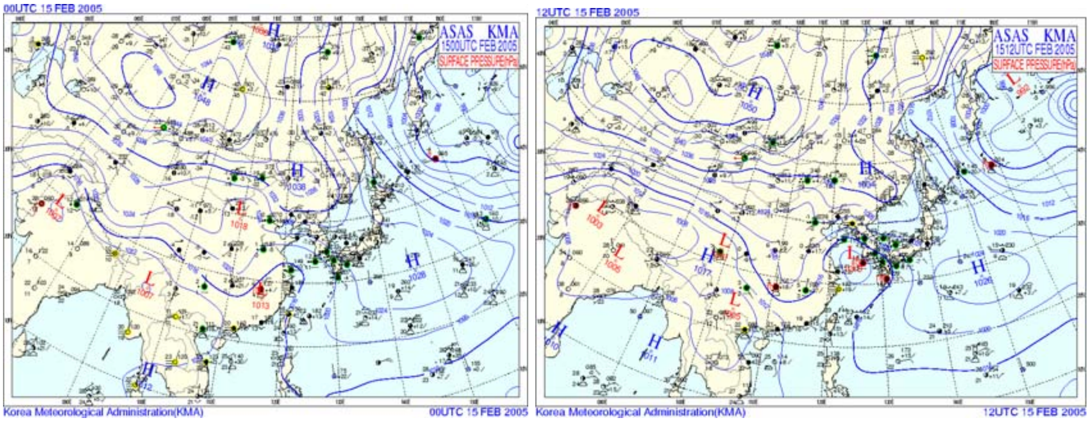
3.2 Weather condition

At 0900 LST (0000 UTC), February 14, 2005, the center of a high preesure of 1033 mb was located in the northern part of Korean peninsula and another high pressure of 1031 mb was located in the mid of Japan. On the other hand, between two high pressure systems, a low-pressure of 1028 mb is located in the west of a coastal city called Kangnung city of Korean peninsula, that is, the East Sea (Fig. 2a) and most of winds observed at Kangnung Meteorological Administartion were south-westerly under the influence of low pressure system, except for north-easterly during 1000 LST to 1700 LST.



(a) (b)

Figure 2. (a) Weather map at 0900 LST and (b) 2100 LST, February 14, 2005 near Korean peninsula. Arrow, box and red line indicate Korean peninsula, the area near Kangnung city and cold front, respectively.



(a) (b)

Figure 3. As shown in Fig. 2, except for (a) 0900 LST and (b) 2100 LST, February 15.

At 2100 LST (1200 UTC), the low pressure center became slightly enforced with a magnitude of 1025 mb and cold front moved anti-clockwisely, gradually showing its eastward movement. South-westerly wind still prevailed in the city until 0900 LST, the next day (Fig. 2b). From 0900 LST, February 15, both a high pressure system of 1038 mb located in Manchuria in China over the northen Korea and another low pressure center of 1013 mb located in the south-eastern part of China controlled synoptic weather pattern and local observed wind fileds until 1400 LST were north-easterly, inducing moisture advection from the sea into the inland area. After the time, winds were changed into south-westerly until 1800 LST (Fig. 3a).

At 2100 LST, February 15, the high and low pressure systems further moved toward the east, showing the locations of high pressure of 1043 mb in Vladivostok, Russia and the more strengthern low pressure of 1010 mb in the southern Yellow Sea near south-western side of Korean peninsula (Fig. 3b). This pressure pattern could strongly induce north-easterly wind and a great amount of moisture advection from the East Sea into the Kangnung city, showing 6.5 mm precipitation amount.

3.2 Mass concentration of aerosol

From Model 1107, the distribution of 10 minutes averaged mass concentration of PM10, PM2.5 and PM1 near the ground surface at KMA of Kangnung coastal city was given by Fig. 4. From 0000 LST to until 0000 LST, February 14, the mass concentration of PM10 was in the range of 50.62 /m^3 ~145.12 /m^3, especially showing its maximum concentration at 1420 LST, after passage of cold front. The concentratios of PM2.5 and PM10 had also similar patterns to the concentartion of PM10. Their concentrations were in the range of 15.14 /m^3 ~ 56.19 /m^3 for PM2.5 and 10.73 /m^3 ~ 44.71 /m^3. From 0000 LST, February 14, the concentrations of PM10, PM2.5 and PM1 were in the almost steady until 1700 LST, just before the end of office hour and near sunset.

After 1800 LST near the ending time of offcie hour, the concentration of aerosol rapidly increased up to 145.12 /m^3 of PM10 and 88.93 /m^3 of PM2.5 and 44.71 /m^3 of PM1 at 2000 LST (two hours later after sunset), respectively.

Then the concentraions decreased to 59.78 /m^3 at 2200 LST and increased again up to 93.06 /m^3 at 0100 LST, February 15. Thus two maximum concentartions of PM10, PM2.5 and PM1 were detected with their first maximum at 2000 LST and secondarly maximum at 0100 LST. After 0100 LST, the concenrations continuously decreased to 19.32 /m^3 at 0600 LST. Relatively moderate winds with speeds in the range of 2.9 m/s ~ 4.7 m/s were south-westerly at Kangnung city, until 1000 LST. Then winds became weak with speeds less than 2 m/s and wind directions was also changed into north-easterly from 1100 LST to 1700 LST, due to the turning of cold front anti-clockwisely and easterly sea breeze toward Kangnung city in the eastern coast of Korean peninsula. Relative humidity were still low less than 38 %.

The maximum concentration of aerosol at 2000 LST might be due to the increase of vechile number on the street near the ending time of office hour and resulted in the increase of aerosol concenrations. Another reason might be the much shrunken of atmospheric boundary layer (nocturnal surface inversion layer; NSIV) under the cooling of ground surface at night, comparing to the depth of daytime convective boundary layer at the city (Choi et al, 2004). Choi (2004) and Choi et al (2004) indicated that in general, particulate matters generated from the ground surface of the downtown were drifted under thermal convection from the surface into the lower atmospher and transported from Kangnung city near the coast toward Mt. Taeguallyung in the west of the city (downwind side) under easterly sea-breezee and valley wind until sunset, staying near the mounatin side.

After sunset, downslope wind like mountan wind and land-breeze droved the daytime transported particulate matters in mountain side along the eastern slope of Mt. Taeguallyung and land-breeze further induced those particulate matters toward the city, resulting in a high concentration of particulates near mid night. As nighttime went on, after the ending time of office hour, the number vehicles continuously reduced and PM concentraiuons also had to decrease. Thus secondary maximum of aerosol concentration could be generated by the shrunken atmospheric boundary layer (NSIV) and the returning of some amount of transported particulate matters from the mountain side toward the city at night.

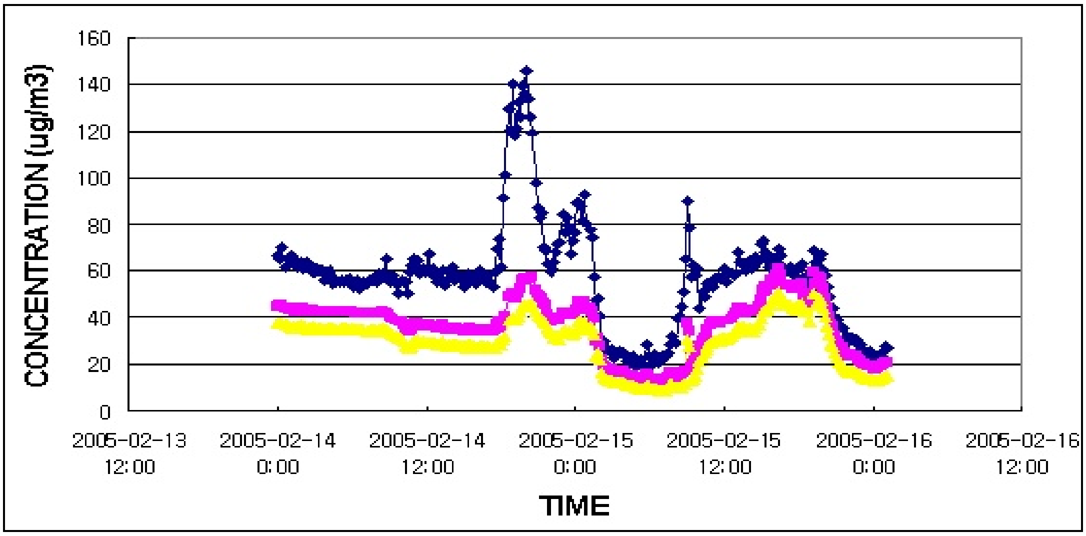


Figure 4. Hourly based concentration (/m^{3}) of PM10, PM2.5 and PM1 at an aerosol sampling point of Kangnung Meteorological Administration from February 14 to 16, 2005.

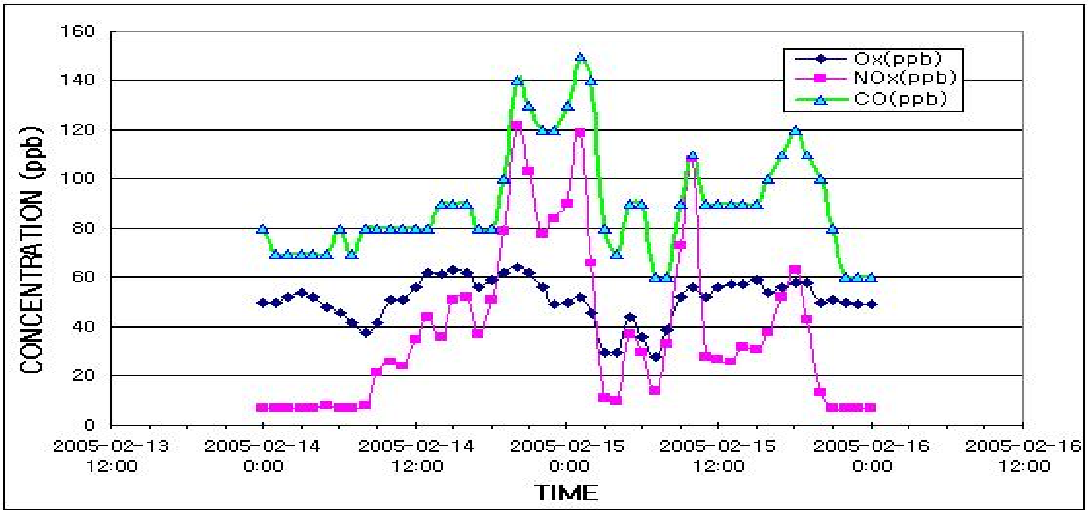


Figure 5.Hourly concentrations (ppb) of CO, NO_x(= NO_2 + NO), O_x(= O_3 + NO_2) at Kangnung Environmental Monitorinting Site, Monistry of Environment from February 14 to 16.

After mid night, PM concentrations rapidly decrease until 0900 LST, the next day morning, as most of particulate matters in Kangnung city were dispesed into the East Sea. Then Kangnung city was in a very clean atmospheric environmental condition less than 30 /m^{3}. The relatively high concentration of PM in the morning on

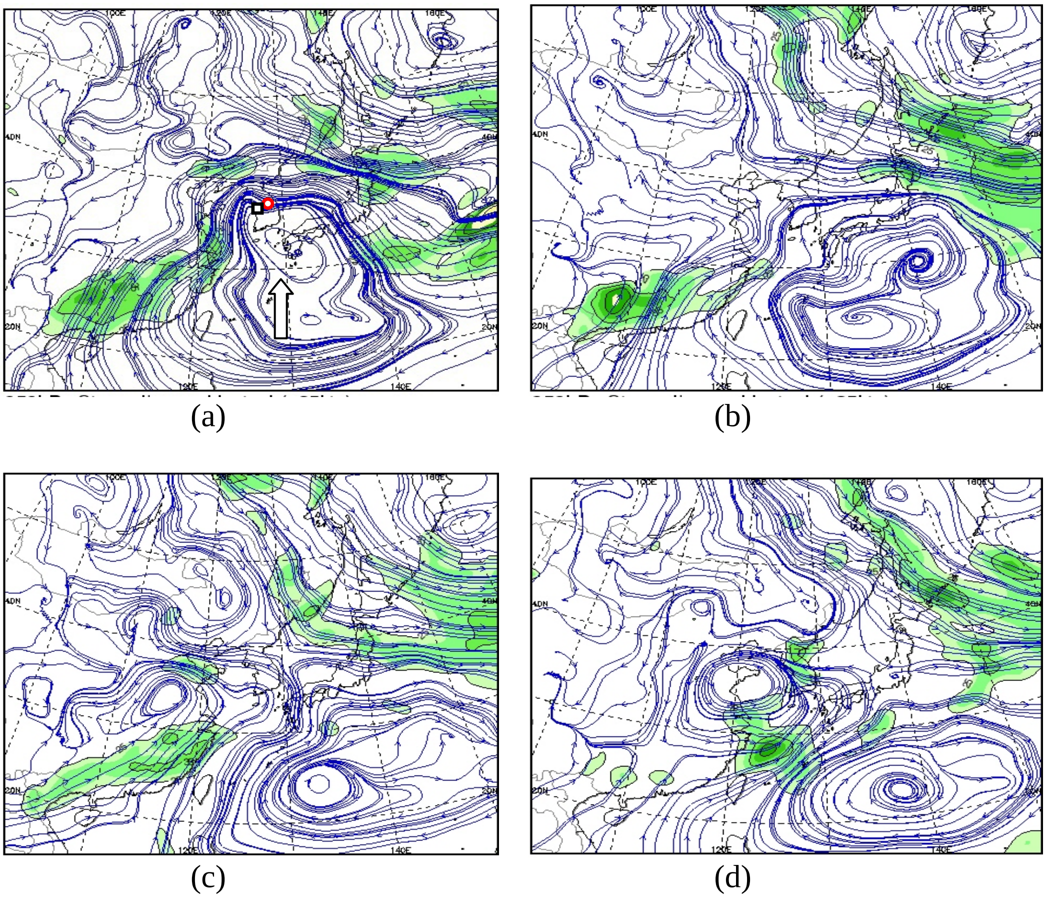
February 14 might be attributed to the transportation of some amount of paarticulate matters from upwind side area (Wonju city) toward Kangnung city. Under the maximum concenration of PM10 at 2000 LST on February 14, PM2.5 and PM1 also had maximum concenrations.

One may postulate that gases phases of PM 2.5 and PM1 made a great contribution to the increase of PM10 concentration. Therefore, it is necessary to compare the concentration of gases of CO, NO_x (= NO_2 + NO), O_x(= O_3 + NO_2) at Kangnung Environmental Monitorinting Site, Monistry of Environment from February 14 to 16, 2005. Tendency of CO concentration well matched the distribution of PM10, PM2.5 and PM1. The distribution of NO_x concentraion also showed a similar, except for concentrations in the morning on February 14. When PM10, PM2.5 and PM1 had the first and secondary maximum concentrations, NO_x concentration had the first and secondary maximum concentrations at 2000 LST on February 14 and 0100 LST on February 15. It implies that gases of NO_x and CO emitted from vehicles on the road due to fuel combustion and boilers in the resident area can make a great contribution to the increase of PM10 concentration. O_x is composed with $O_3 + NO_2$ and is assumed as permanent capacity of O_3. O_x concntrations were generally in the range from 39 ppb to 62 ppb, except for 30 ppb, when NO_x concentrations were very low on February 15. O_x distribution did not reflect the characteristics of CO and NO_x.

3.3 Effect of upwind side transporttion

Further consideration was given to the transportion of particulate matter and gases from Wonju city in the upwind side of Kangnung. Fig. 6 showed streamlines simulated by MM5 model, version 3.5, with horizontal interval of 2.5^0 from 0900 LST, February 14, 2005 to 2100 LST, February 15. Mass transportation was expected from Wonju city (box) toward Kangnung city (red circle) in the downwind side at 0900 LST and 2100 LST, February 14 (Fig. 6a and b), but it might be difficult to be on February 15, because Kangnung city was not in the downwind side on the streamline (Fig. 6c and d). PM10 concentration (here, only possible measurement of PM10 concentration) at Environmental Monitorinting Site, Wonju city was in the range of 92 /m^3 ~ 146 /m^3 from 0000 LST to 1900 LST, and the concentration at Kangnung city, about 200 km away from Wonju ciy was in the range more or less than 60 /m^3, showing a half concentration of Wonju city. As two cities were in westerly and southwesterly wind fields for this time period and on the streamline, the occurrence of high PM concentrations at Kangnung city in the downwind side should be affected by the transportation of some amount of particulate matters from Wonju city, resulting in more or less than 60 /m^3.

Further consideration was given to the contribution of CO, NO_x and O_x concentrations at Wonju Environmental Monitorinting Site (Fig. 8). NO_x concentration at Wonju city in the upwind side on February 14, which could influcence upon NO_x concentration at Kangnung city was generally higher than ones at Kangnung city. At this city, NO_x concentration rapidly increase with a magnitude of 108 ppb and up to 163 ppb at 2100 LST. Even though the transportation of NO_x from Wonju toward Kangnung for this period could be expected, the transported amount of NO_x could not make a great contribution to the occcurrene of a maximum concentration of NO_x at the downwind side city at 2000 LST on February 14.


(a) (b)

(c) (d)

Figure 6. (a) Streamline simulated by MM5 model at 0900 LST, (b) 2100 LST, February 14, and (c) 0900 LST and (d) 2100 LST, February 15 in notheastern Asia. Arrow, box and red cicle indicate Korean peninsula, Wonju city (upwind side) and Kangnung city, respectively.

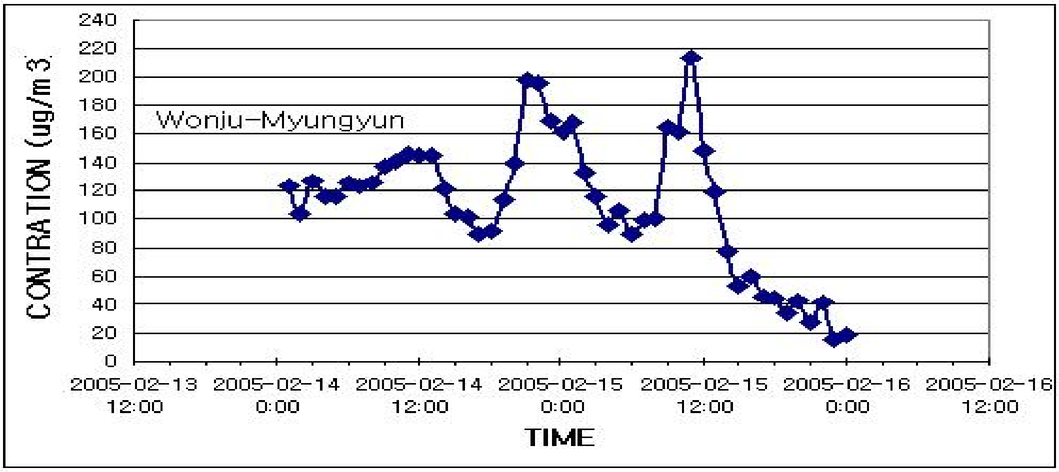
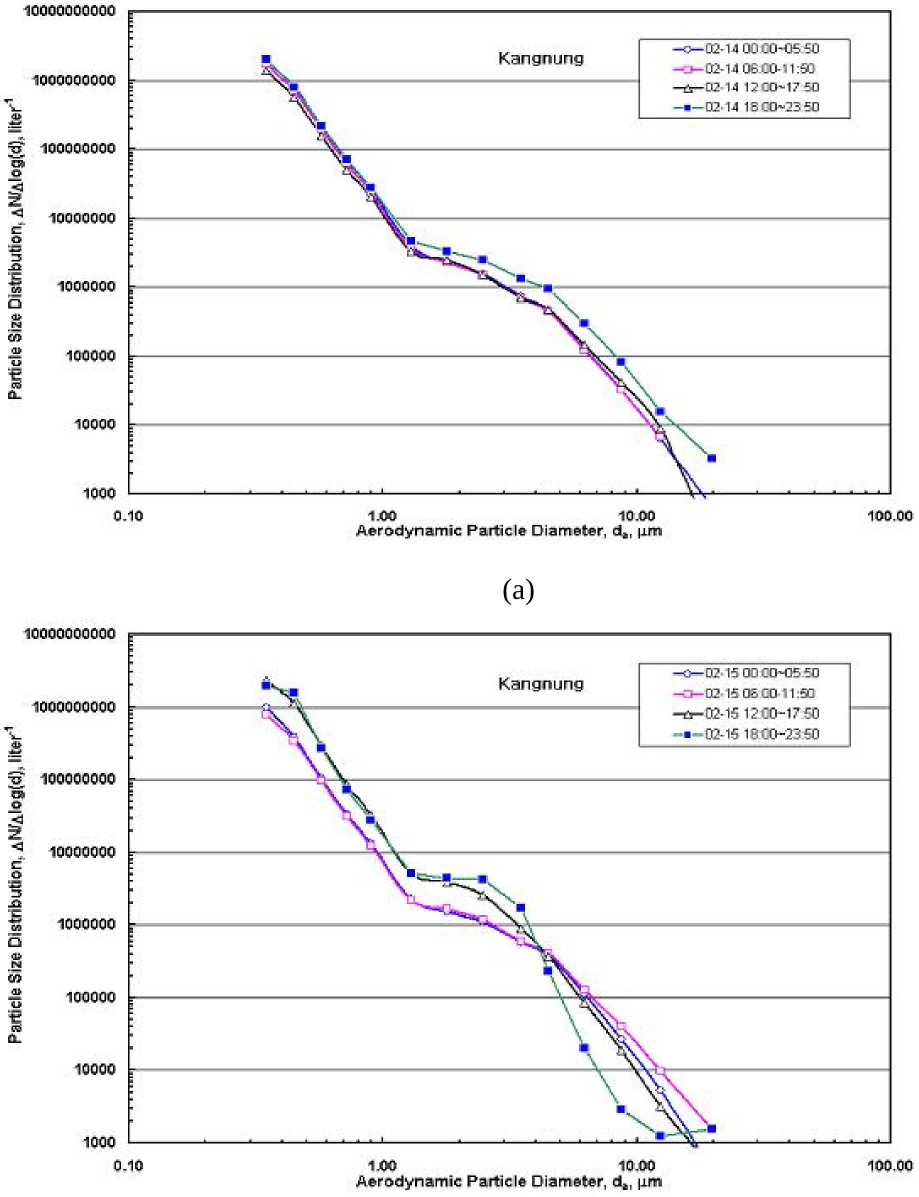


Figure 7. Hourly concentrations (ug/m^3) of PM10 at Environmental Monitorinting Site from February 14 to 16, 2005.

3.3 Particle size distribution

The number densities of particle size distributions from 300 to 10 of particle diameters were given in Fig. 8. The number densities of diameter smaller than 1.2 um rapidly increased, as the particle diameter decreased (Fig. 8a). On the other hand, the number densities of diameter greater than 1.2 um to 20 um gradually increased the diameter decreased.



(a)

(b)

Figure 8. Particle size distribution from 300 nm to 20 at KMA aerosol sampling point on February 14 and 15, 2005.

Especially particle size distribution at 1800 LST to 2350 had a different pattern from the others, showing slightly bigger number densities in the diameters of 1.2 to 20 . This result indicates that large size particles make better contribution to the occurrence of maximum concentrations of PM at 2000 LST and 0100 LST in the previous Fig. 4. On February 15, the number densities of particle size distributions from 300 to 4 were bigger from 1200 LST to 2350 LST than those from 0000 LST to 1150 LST, as the diameter decreased. The number densities of particle size greater than 4 to 13 were still increased, but they were much lower than the others. However, the number densities of particle size greater than 13 um to 20 um decreased, as particle size decreased.

4. CONCLUSION

The concentrations of PM10, PM2.5 and PM1 showed a typical pattern such as high concentration near 0900 LST (beginning time of office hour) and 1700 LST (ending time of office hour) and their low concentration near noon. PM10, PM2.5 and PM1 had the first maximum concentrations at 2000 LST (three hours later after sunset) and the secondary maximum concentration was detected at 0100 LST, near mid night. When PM10, PM2.5 and PM1 had the first and second maximum concentrations, NO_x had the first and secondary maximum concentrations at the same times.

The increases of NO_x and CO concentrations emitted from vehicles on the street and combustion gases from boilers in the resident area for nighttime could make a great contribution to the increase of PM concentration. Furthermore much shallower nocturnal surface inversion layer than daytime convective atmospheric boundary layer could also increase the concentrations of particle matters. In general, after midnight, the concentration particulate matters decreased due to the reduction of vehicle number, but under westerly wind, the particles transported from the city into the mountain side in the west for daytime returned again to the city and some amount of particles from an upwind side city toward the coastal city could also make a great contribution to the occurrence of secondary maximum. The number densities of particle size distributions, regardless of particle diameters, in general, were much lower in the early morning than in the afternoon and at night.

5. ACKNOWLEDGEMENTS

Author much thanks Gangwon Meteorological Administration (GMA) located in Gangnung city for the measement of aerosol from February 5 through April 5, 2005 and further thanks to Mr. Sang Kook Kim, GMA for setting aerosol samplers.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

SPATIAL ANALYSIS OF THE IONIC COMPONENTS OVER CENTRAL AND SOUTHEASTERN EUROPE, 1994-2002

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ABSTRACT

Central and Southeastern Europe are affected by the higher SO_2 and NO_x emissions. The annual and monthly average concentrations (1994-2002) of the major ionic components in precipitation are analyzed for 19 stations in central and southeastern Europe. In order to find the ion pattern of the region, Principal Component Analysis has been subjected. The annual pH varied between 4.40 and 6.07 throughout the region. Minimum pH values are found in the eastern part of the region including Poland, Czech Republic, Slovakia, and Austria with a mean 4.67 pH values. The lower Ca^{2+} concentrations in the limestone environment correspond to low pH values. However, The Mediterranean part of the Southeastern Europe including Italy, Croatia, Hungary, Serbia and Montenegro and Turkey have a mean 5.58 pH value. In order to evaluate the relative contribution of H_2SO_4 and HNO_3 to the acidity of precipitation the ratio of nitrate (NO_3^-) to sulfate (SO_4^{2-}) in precipitation have been examined. Furthermore, due to the acidity in rainwater which can be partially neutralized by base cations, the equivalence ratio of $H^+/(SO_4^{2-} + NO_3^-)$ has been examined to provide an information on the magnitude of such a neutralization.

At the coastal areas, Na^+ and Cl^- components contributed up to 61% for Na^+ and 36% for Cl^- of the total average ionic concentrations respectively. They had minimum for inland areas. In general they tend to be more elevated on the Adriatic coasts. This is mostly due to the high Ca^{2+} concentrations in these sites. NH_4^+ which comes mostly from agricultural activities is the most abundant cation in Croatia, northern Italy and northern Serbia and Montenegro.

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

SOLUBILITY OF DEPOSITED AIRBORNE HEAVY METALS

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ABSTRACT

Soluble fractions of the deposited air pollutants are important for the food chain mechanisms as they might cause ecotoxic impacts. In this study Cr, Cd, Pb, Cu, Zn and Ni were investigated in the deposition samples for total, dissolved and suspended fractions as collected in a surrogate water surface sampler in Izmir, Turkey during the October 2003-June 2004 period. To find the overall solubility of each metal in dry and wet deposition samples, concentrations in soluble and suspended phases in aqueous solutions were separately analyzed. Ratios between the total and dissolved forms and the metals in the same form were statistically analyzed and evaluated.

It was found that the deposited metals are strongly correlated in wet deposition with the highest correlation between Cd and Pb in the total form, and between Cd and Cu in the soluble part. Comparatively smaller correlations were found between these metals in dry deposition samples.

Key Words: Heavy Metals, Dry Deposition Flux, Wet Deposition Flux, Air Pollution in Izmir, Solubility of Heavy Metals.

1. INTRODUCTION

Transfer of metals into the water and soil from the atmosphere is a significant part of their biogeochemical cycles. Heavy metals are persistent for long periods of time, leading to a gradual increase in the environmental concentrations of these contaminants in polluted areas (Mowat, F.S., 2000). Metallic pollutants may be transported in the atmosphere over long distances with very small particles. Atmospheric deposition occurs when these particles are aggregated and settled down or washed out by rain. Dry deposition is by the settlement of the particles whilst aerosols and gases are either dissolved or suspended in water droplets or ice crystals and settle together with them in wet deposition (Azimi et al., 2003). Besides the long-range transport processes, significant dry and wet depositions also occur locally due to different sources with varying mineralogical composition and relative contributions. Also the leachability of heavy metals is expected to vary among sites (Voutsa and Samara, 2002).

The solubilities of heavy metals strongly depend upon their chemical speciation. Longer atmospheric residence times provide higher opportunities for contributions from several different emission sources and atmospheric reactions change the metal speciation for the dry depositing material ending in slightly lower correlations between suspended and soluble fractions in water (Voutsa and Samara, 2002).

Heavy metals in atmospheric precipitation may create ecotoxic effects in the receiving water and soil environments but they are bioavailable only if the metal is in soluble form. The percentage of dissolved metals in the deposited matter depends largely on the anions with which they are incorporated. Hydrolysis rates of the heavy metal salts in the water bodies or soil waters also depend on the anion and cation balance, redox potential and pH of these waters, as well as the size distribution and chemical nature of the depositing particles (Morselli et al., 2004).

For example pH is another most important factor determining the ratio of dissolved and suspended heavy metals. It is therefore important to know about the probability of acid rain to estimate the possibility of high hydrolysis rates of the metals. Gulsoy et al. (1999) indicated the frequency of acidic pH to be about one fifth of the total rain incidences in 1996 in Istanbul, Turkey. Akkoyunlu and Tayanc (2003) showed that although SO_4^{2-} concentration in precipitation was high, so was the Ca^{2+} as a neutralizing factor of the acidity in rain. Similar argument was reported by Al-Momani et al. (1995), based on the data indicating that the excessive alkaline materials in crustal aerosols in the Eastern Mediterranean areas have a strong neutralizing impact on the rainwater. Al-Momani et al. (1998) have concluded that the neutralizing capacity of aerosols of crustal origin in precipitation are high due to the excessive limestone coverage in the Izmir area where this research was conducted, too.

2. MATERIALS and METHODS

Deposition sampling was carried out on a platform 3 meters above the ground in the Dokuz Eylul University Kaynaklar Campus so that the re-entrainment from the soil surface is minimized. The site is located in a growing forest about 10 km south of the city center. A water surface sampler was used in the deposition sampling. Technical drawings and operating principles of the water surface sampler are designated in the literature (Shahin et al., 1999; Odabasi et al., 1999, Cakan, A., 1999; Tasdemir, Y., 1997; Yi et al., 1997).

Twelve dry deposition samples and thirteen rainwater samples were collected at random between October 2003 and June 2004. This covered rainy and dry seasons in this Mediterranean climate area. Dry deposition samples were collected when there was no rain. Sampling time was 24 h for dry deposition samples. Duration of rainwater sampling varied with the raining period. pH values were measured and recorded in this study in order to discuss the effect of pH on the solubility of the heavy metals in rainwater and receiving water of the dry deposition sampler.

Heavy metal concentrations were measured using a Perkin-Elmer Model 700 atomic absorption spectrophotometer equipped with a graphite furnace. For Zn analysis AAS with flame technique was used in the same instrument to avoid erratic results in the graphite furnace due to high concentrations in the samples. Background correction was applied using a deuterium lamp with the two-line method.

Soluble and insoluble metals in dry and wet deposition samples were determined, correlation analyzes were carried out by using STATLETS Statistical Program.

3. CONCLUSION

3.1. Dissolved and suspended fractions in dry and wet deposition

Dissolved and suspended fractions of dry and wet deposition samples were shown in Figure 1 and Figure 2 respectively. To discuss the solubility of the deposited heavy metal salts, the percentage mass ratio between the dissolved fraction and total heavy metals in dry and wet deposition were calculated. In dry deposition samples The soluble percentages of the Cr, Cd, Pb, Cu, Zn and Ni were 90.4, 5.4, 91.8, 87.5, 89.7 and 98.8 of the total, respectively. The soluble percentages of the Cr, Cd, Pb, Cu, Zn and Ni were 80.1, 87.2, 92.6, 92.7, 88.5 and 95.2 of the total respectively, in rainwater samples. The ratios of soluble fractions of heavy metals in the dry deposition and in the rainwater were in the order of 80-99 percent of the total metals in deposition except for one or two samples having somewhat less soluble Cd and Cr forms in deposition. Another exception to that is Ni which has a larger range of soluble fractions in dry deposition than in wet deposition. This result is in contradiction with the results of Morselli et al. (2003) who reported lower soluble fractions in dry deposition than in wet deposition in Bologna, Italy. In contrast Voutsa and Samara (2002) reported soluble fractions of the Cd, Pb, Cu, Zn and Ni as 80, 66, 90, 93 and 82 percent, respectively in the Greater Thessaloniki area of Greece. Significantly higher labile fractions of these metals were found suggesting the dominance of easily available metal forms in atmospheric particles.

Although the average figures in this study are in parallel with results in the international literature, the ratio of heavy metal concentrations in dissolved and suspended depositions showed strong fluctuations as may be noted from Figure 2. The ratio of insoluble to soluble fractions is quite high for the first three samples for all heavy metals but for Cd. It must be noted that the first three samples are taken during rain incidences following elongated dry periods.

3.2. Correlations between metals in dry and wet deposition samples

Statistical analysis for dry deposition samples showed no significant relationship between heavy metals concentrations. The level of the r^2 values were 0.594 ($p<0.01$) for the dissolved and 0.703 ($p<0.01$) for the total metal concentrations in dry deposition samples for Pb-Ni at the 95% confidence level. Correlations were between Cd-Cu ($r^2=0.366$, $p<0.05$) and Zn-Ni in dissolved forms ($r^2=0.633$, $p<0.01$) in rainwater samples at the 95% confidence level. In the total metal concentrations in rainwater samples correlation tests were carried out for Pb-Cu ($r^2=0.410$, $p<0.05$), Pb-Zn ($r^2=0.591$, $p<0.01$), Pb-Ni ($r^2=0.478$, $p<0.01$), Zn-Ni ($r^2=0.534$, $p<0.01$).

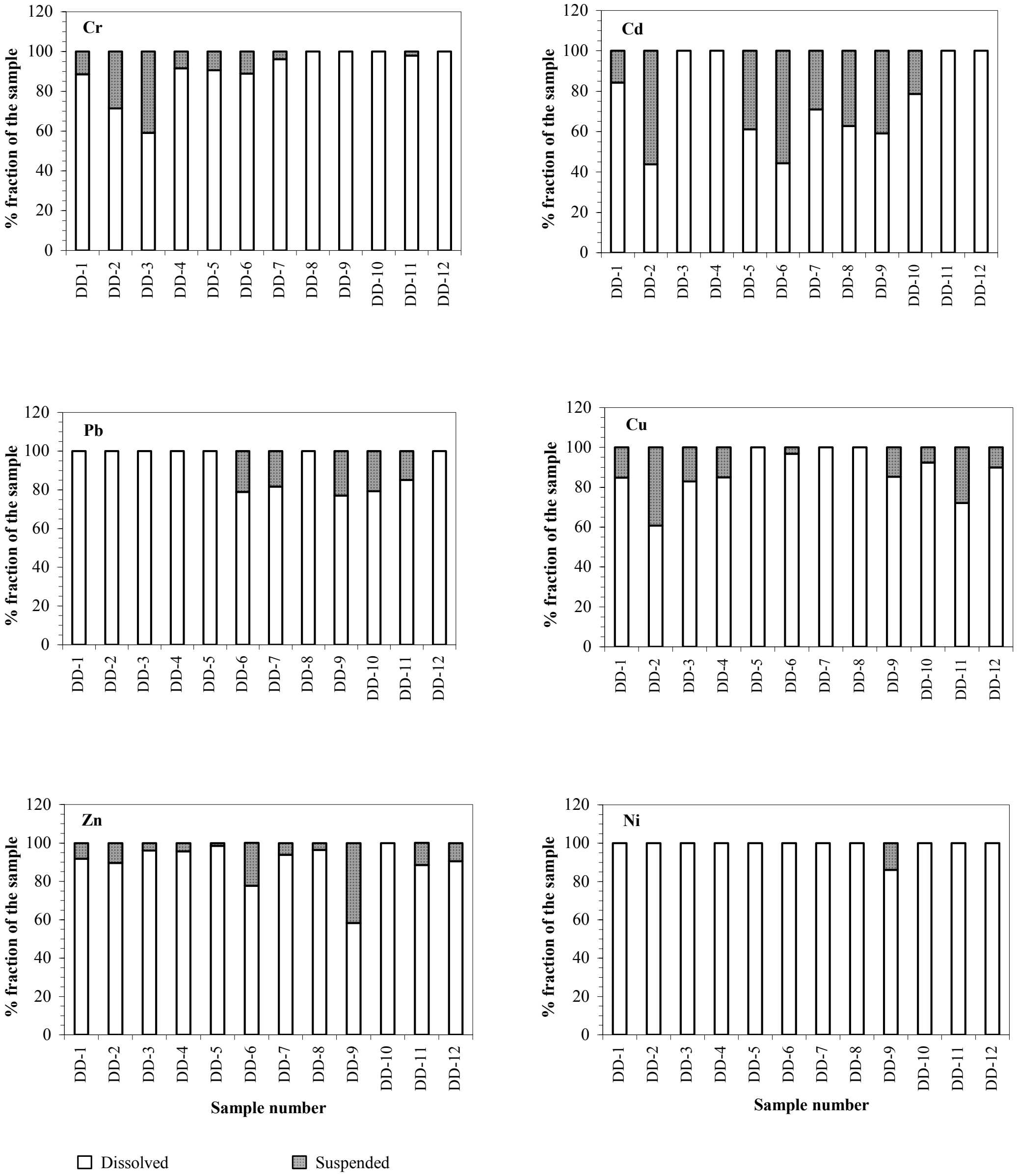


Figure 1. Dissolved and suspended fractions of heavy metals in dry deposition samples

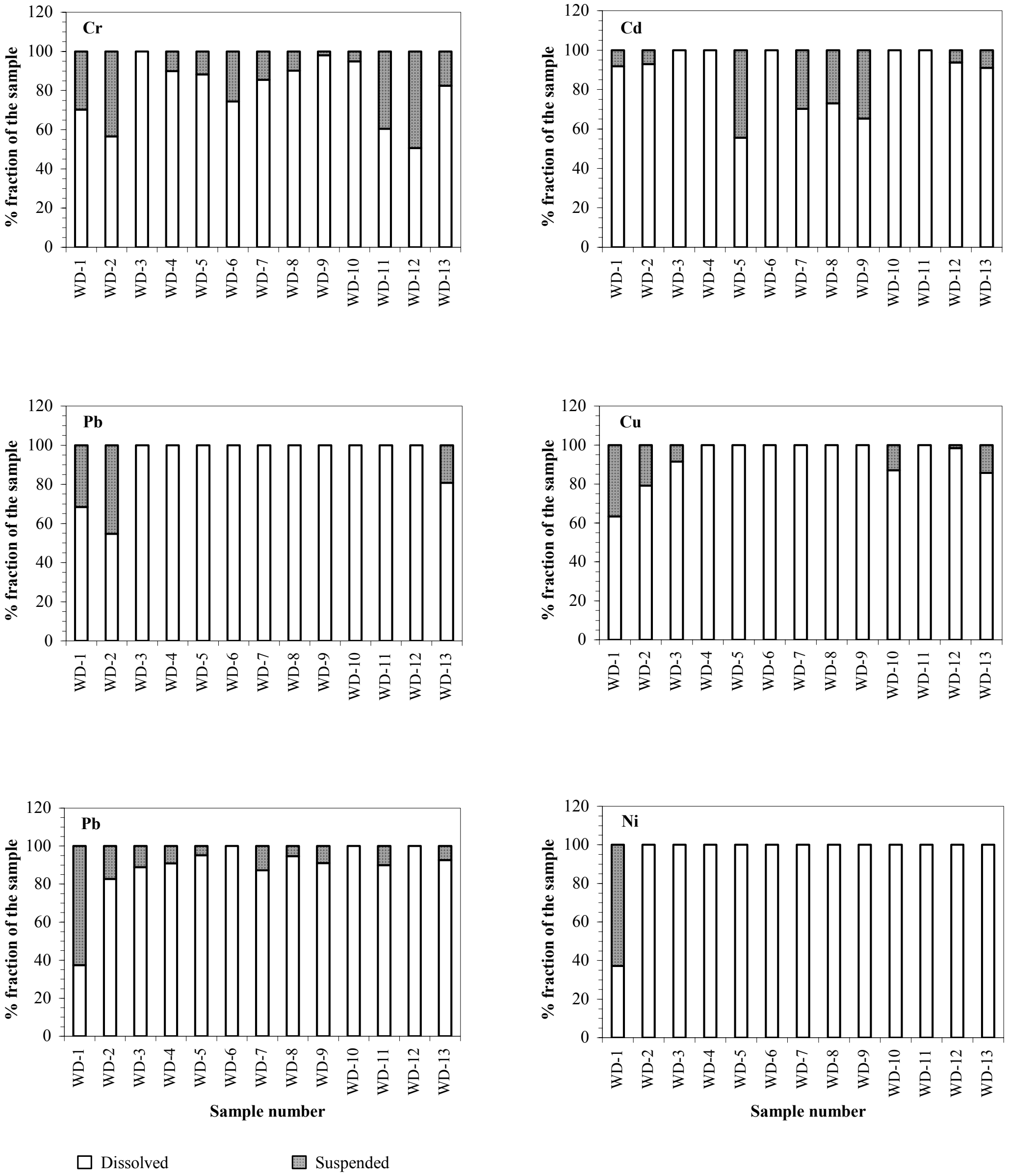


Figure 2. Dissolved and suspended fractions of heavy metals in rainwater samples

3.3. Correlations between fluxes of dry and wet deposition samples

Generally speaking the correlation coefficients among the fluxes of metals were much better in wet deposition than in dry deposition. This is in parallel with the findings of Maneux et al. (1999) who reported that the dissolved fraction of heavy metals in rain was greater than the particulate fraction.

Strong relationships were not found between heavy metals in dry deposition samples when total and soluble fractions were separately tested; highest correlations were for the Pb-Ni when total metals in the flux ($r^2 = 0.535$, $p<0.01$) and soluble metals in the flux ($r^2 = 0.538$, $p<0.01$) were studied.

In wet deposition, however, the deposition fluxes of different metals were correlated better (Fig.3 and 4). In the soluble form the best relationship was between Cd and Cu with an r^2 value of 0.945. In the total form highest correlation was between Cd and Pb with an r^2 value of 0.886. Strong relationships probably indicate that they come from the same emission sources and/or undergo similar reactions in the atmosphere before they were brought down by the raindrops.

3.4. Impact of pH on the solubility of heavy metals in the deposition samples

A significance test was applied to discuss the impact of pH on the solubility of the heavy metals. The pH of the dry deposition samples in the water surface sampler water were ranging between 5.56 and 7.68 with an average of 6.60. The pH of the collected rainwater samples were ranging between 5.06 and 7.72 with an average of 6.50. Acid rain (*i.e.* rain with $pH<5.6$) occurred during the sampling period three times, with the lowest pH value on January 31, 2004. Yet no significantly low pH was notable in any sample which would create changes in solubily of the metals. Neutral pH values were found in the dry deposition water samples before and after the daily sampling and also in the rainwater samples. This indicates that strongly acidic rain was not seen in Izmir during the study period. This is in contrast to the high quantity of SO_2 emissions in the area (Dincer et al., 2003), but can be explained by the findings of Al-Momani et al. (1995) who have described the impact of high quantities of limestone containing dust reentrained from the ground in the Izmir area.

Dissolved and total metal concentrations and pH values of rainwater samples at the 95% confidence level did not correlate well. The only notable correlations were found between the pH values and dissolved and total dry deposition concentrations of Pb and Ni at the 95% confidence level (Fig. 5). Highest correlation was found between Pb total concentrations and pH values ($r^2=0.552$, $p<0.01$). This low dependence might have been caused by the relatively narrow range of pH values in the rain in Izmir.

The results of this study showed the importance of metal pollution in the rainwater especially in regard to the ecotoxic properties of heavy metals rather than the dry deposition. It also showed that the pH is a relatively unimportant property in creating ecotoxic solubility effects.

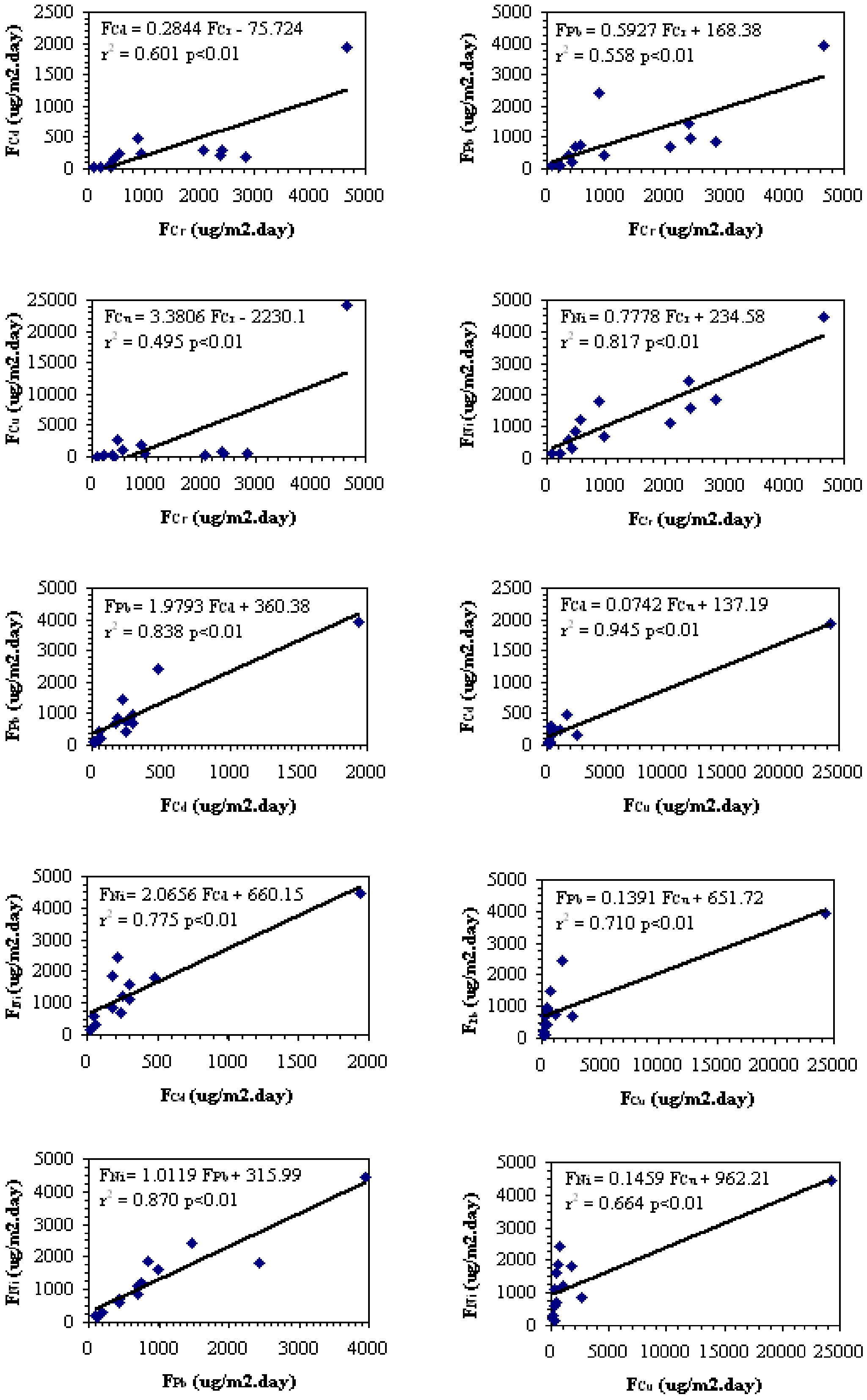


Figure 3. Correlations between dissolved metal fluxes in wet deposition samples

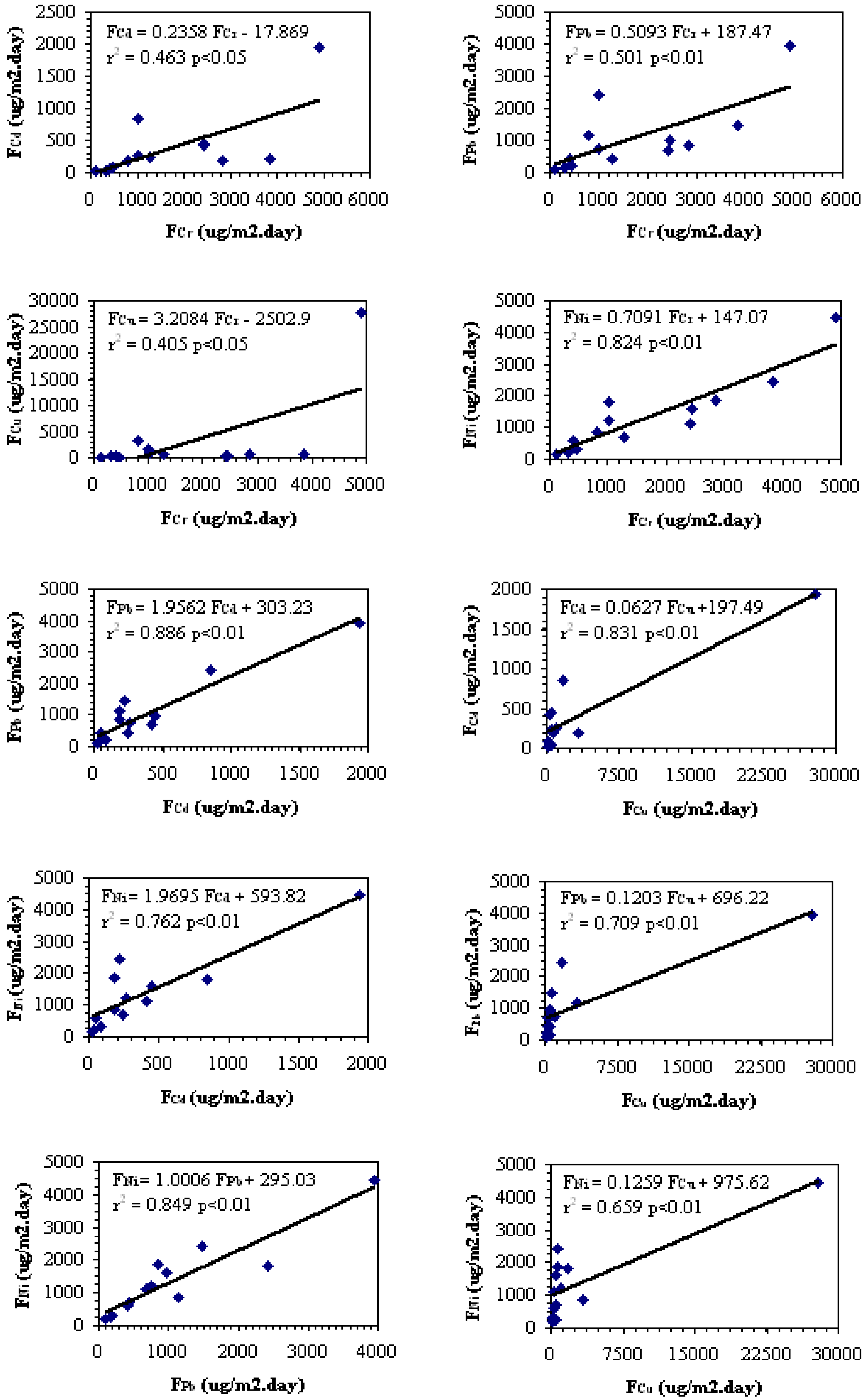
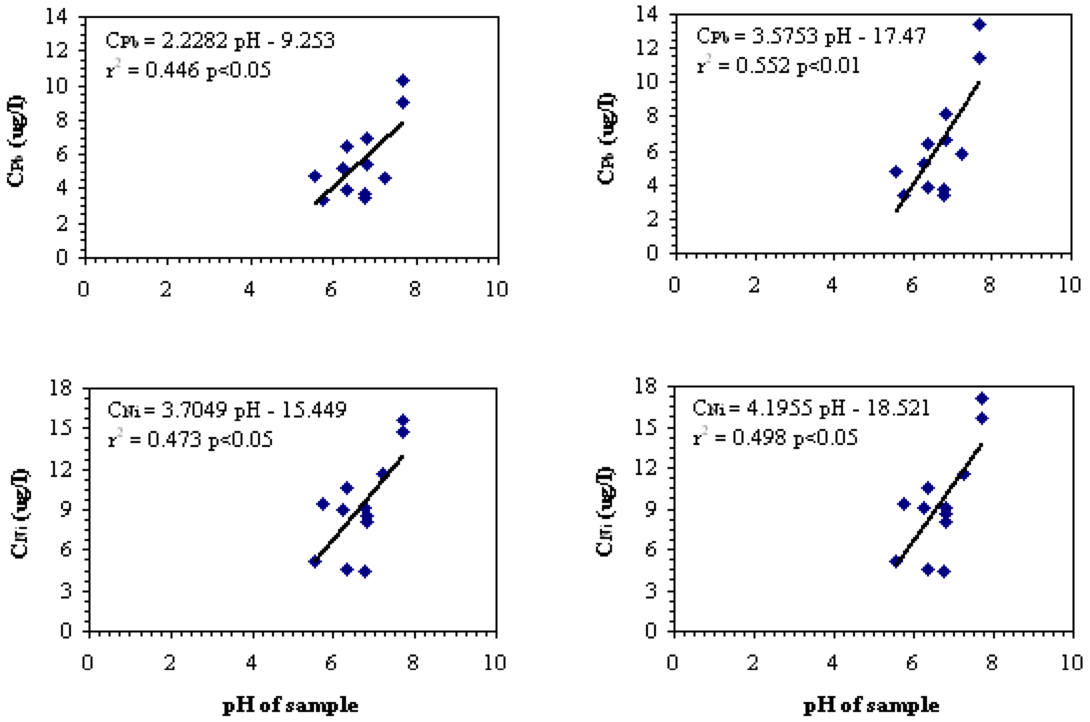


Figure 4. Correlations between total metal fluxes in wet deposition samples



(a) (b)

Figure 5. Relation between concentrations and pH values of dry deposition samples (a) soluble concentrations (b) total concentrations

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

PREDICTION OF MISSING SO_2 AND PM_{10} CONCENTRATIONS USING CELLULAR NEURAL NETWORK (CNN)

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ABSTRACT

Air pollutant, monitoring using continuous samplers are carried out in most major urban centers in the world and generally forms the basis for air quality assessments. Such assessment less reliable as the proportion of data missing due to equipment failure and periods of calibration increases. Missing data, i.e incomplete data matrices, are a problem that is repeatedly encountered in environmental research. In this paper, we predict missing concentrations of PM_{10} and SO_2 air pollutant from Istanbul Yenibosna and Ümraniye air pollution measurement stations with meteorological parameters: temperature, pressure, sunshine, cloudy, rainfall, wind speed and wind direction relative humidity etc.., from Istanbul Florya and Göztepe meteorological stations using CNN model. We consider one-neighborhood relation and guarantee stability of CNN by choosing symmetric feedback and feed-forward cloning matrices of A, B. Here, the total number of different assigned elements of matrices (A,B) and bias constant (I), are limited to only 11 and our air pollution problem is optimized by altering these 11 elements. Then, we correlate CNN outputs with actual measured values by using three statistical performance criteria. In this paper, we have measurement index of agreement (*d)* between 0.69 and 0.92 for all pollutant. CNN model for PM_{10} are producing considerably better predictions than SO_2. As a result, CNN-based approaches can be considered as a compromising approach in air pollutant prediction.

Key Words: Missing data, Air Quality, Particulate Matter (PM), Sulfur Dioxide (SO_2), Meteorology, Cellular Neural Network (CNN).

1. INTRODUCTION

Istanbul has the risk of air pollution, since it is the most industrialized city of Turkey with lots of factories. The main air pollutants of Istanbul are Particulate Matter (PM), Sulfur Dioxide (SO_2), which threaten human health and corrupt air quality. It is necessary that measured continuously these air pollutants for the regional authorities. As the incomplete data, missing data is occur, air quality assessment is less reliable. Missing data are a problem that is repeatedly encountered in environmental research. The situation may be the result of insufficient sampling, errors in measurements or faults in data acquisition. Whatever the reasons, discontinuities pose a significant obstacle for time-series prediction schemes, which generally require continuous data as a condition for their use.

The substitution of mean values for missing data is commonly suggested, and is still used in many statistical software packages (Junninen et al., 2004). A slightly better approach is to impute the missing elements from an ANOVA model or something similar. Another approach to the problem is to use a simplistic interpolation method such as assuming the season's average concentration for the particular time of day that is missing, or linearly interpolating between the previous and following day, in order to obtain continuous data sets. Neither of these methods is ideal since the meteorology on the missing day may have been significantly different from the days on which the interpolation was based, leading to unrealistic predictions (Dirks et al., 2002). Clearly, a complementary method is required.

There are many deterministic and stochastic approaches in modeling of the air pollutants. As a well-known stochastic approach, Artificial Neural Network (ANN) has been applied to various environmental problems since 1990 and some satisfactory results are obtained. In many studies, ANN is applied to predict SO_2 concentration (Boznar et al., 1993; Mok and Tam, 1998; Saral, 1999; Chelani et al., 2002). Perez et al. (2000) have compared the $PM_{2.5}$ predictions produced by three different methods: multi-layer neural networks, linear regression and persistence. Gardner and Dorling (1998) have examined all main studies and summarized the use of ANN in environmental air pollution. Kukkonen et al. (2003) have studied five neural network models, a linear statistical model and a deterministic modeling system for the prediction of urban NO_2 and PM_{10} concentrations. Sahin et al. (2004) have applied the multi-layer neural network model to predict daily CO concentrations using meteorological variables as predictors for the European part of Istanbul, Turkey. Junninen et al., (2004) have applied regression based imputation, nearest neighbor interpolation, self organizing map, multi-layer perceptron model and hybrid methods to simulate missing air quality data. In all study, it is reported that ANN could be used to develop efficient air-quality analysis and prediction models in future. But in ANN, the training process becomes more complex and needs long time durations as the number of weight coefficients of ANN rise up to millions due to the complexity of environmental study.

To reduce weight coefficients, Chua and Yang (1988) have introduced Cellular Neural Network (CNN) in 1988. Since each cell of the CNN is represented by a separate analog processor and since each cell is locally interconnected to its neighbors by matrix A and gets a feedback from them by matrix B, this configuration results in a very high-speed tool for parallel dynamic processing of 2-D structures (Cimagalli ,1993; Guzelis and Karamahmut, 1994; Uçan et al., 2001; Grassi, 2002).

In this study, we have applied CNN to predict the daily mean missing concentrations of PM_{10} and SO_2 pollutants in the Yenibosna and Ümraniye-Istanbul region of Turkey. PM_{10} and SO_2 pollutants and meteorological parameters are measured from Yenibosna and Ümraniye air pollution monitoring stations, and Istanbul-Florya and Göztepe meteorological stations.

2. MATERIALS AND METHODS

2.1. Study Area and Data

The study area is in Istanbul metropolitan city, which is located 41^{o}N and 29^{o}E. The Bosphorus channel separates this city into two parts, the European and the Asian side. The total area of the all parts of city is about 5700 km^{2}. More than 12 millions people are living and more than 40 % of the heavy industrial activities of Turkey are located in Istanbul. For this reason, air pollution problems are important in Istanbul. For this reason, air pollution problems are important for this city. Istanbul Greater Metropolitan Municipality, Directorate of Environmental Protection (IGMM-DEP) has made air pollution measurements in 10 stations placed in various points of Istanbul considering the topography of the city since 1992. In this study, the daily SO_2 and PM_{10} concentration data was measured by two stations located in Yenibosna and Ümraniye and the daily meteorological data was measured by two stations located in Florya and Göztepe as shown in Figure 1.

Figure 1. Location of the air quality measurement stations in Istanbul and study area (Y-AQMS: Yenibosna Air Quality Measurement Station, Ü-AQMS: Ümraniye Air Quality Measurement Station).

Air pollution measurement station, Yenibosna is in Bahcelievler County of the European side of Istanbul, and Ümraniye is in the Asian side of Istanbul. 5 % and 5.5 % of Istanbul population is lives in Bahçelievler and Ümraniye, respectively. In heating, 60 % natural gases and 40 % fossil fuel are used. Goncaloglu (2000) has investigated the overall industrial factories in Istanbul and emission inventory is listed. Our working area, Bahcelievler and Ümraniye has found to be the polluted county of Istanbul due to the emission ratios of SO_2 and PM_{10} and the usage of fuel oil 4 and coal.

In this study, the daily SO_2 and PM_{10} data were taken by IGMM-DEP and measured using AF 21 M and MP 101 M sensors, respectively, produced by the Environmental Inc. We have evaluated data measured during 2002 and 2003 years. The numbers of total data is 1460 per one air pollutant for Yenibosna and Ümraniye AQMS during 2002-2003. The monitoring data is designed to meet the requirements of training and testing CNN.

The climate of Istanbul is of Mediterranean type. The summers tend to be hot and winters are cold and wet. The Bosphorus, Marmara and Black Sea influence the climate of Istanbul. Here, the General Directorate of the Turkish State Meteorological Services (GDTSMS) in Istanbul provided the daily meteorological data. There are 17 meteorology stations in various points of Istanbul. We have used Florya in European side and Göztepe in Asian side Meteorological Stations data because of its being close to our working stations, Yenibosna and Ümraniye. To predict the missing air pollutant concentration, the meteorological parameters are used and their notations and daily statistical evaluation during 2002-2003 shown in Table 1.

Table 1. The minimum, mean and maximum values of meteorological model parameters during 2002 and 2003 years.

Parameters	Notations	Units	Minimum		Mean		Maximum	
			F-AQMS	G-AQMS	F-AQMS	G-AQMS	F-AQMS	G-AQMS
Temperature	T	°C	-2.2	-2.2	14.7	14.7	31.2	32
Wind Speed	WS	m/s	0.3	0.2	2.2	2.5	6.2	7.3
Sunshine	S	hour	0	0	6.7	6.3	13.8	12.9
Rel. Humidity	RH	%	43.3	38.7	72.2	74.8	95.7	96
Pressure	P	mbar	990.9	988.8	1012.5	1012.6	1031.4	1032.7
Cloudy	C	m	0	0	4.4	6.3	10	10
Wind Direction	WD	North (N), South (S), West (W), East (E)	WSW		-		NNW	
Rainfall	R	mm	0	0	1.5	1.7	31.8	61.9

F-AQMS: Florya Air Quality Measurement Stations, G-AQMS: Göztepe Air Quality Measurement Stations,

2.2. Cellular Neural Network (CNN)

Most neural Networks fall into two main classes: (1) Memoryless Neural Networks and (2) Dynamical Neural Networks. As in Hopfield Networks and Cellular Neural Network (CNN), Dynamical Neural Networks have usually been designed as dynamical systems where the inputs are set to some constant values and the path approach to a stable equilibrium point depends upon the initial state. A CNN is composed of large-scale nonlinear analog circuits, which processes signals in real time (Chua and Yang, 1988). Like cellular automata, the CNN is made of a massive aggregate of regularly spaced identical circuits, called cells, which communicate with each other directly only through their nearest neighbors (Figure 2 and 3).

Adjacent cells can, therefore, interact directly with each other. Cells not directly connected together affect each other indirectly because of the propagation effects of the continuous-time dynamics of CNN. An example of a two-dimensional (2-D) CNN is shown in Fig. 2. Now let us define the neighborhood of *C(i,j)*.

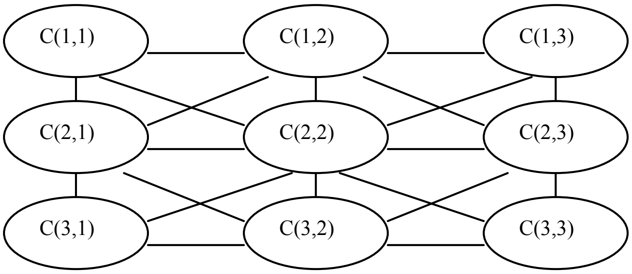

Figure 2. A 2-D cellular neural network. The circuits size 3x3. The link between cells (ellipse) indicates interactions between the linked cells.

We consider a cellular neural network, which consist of *M* line and *N* column (*MxN*). In this structure i^{th} line and j^{th} column are named (*i,j*) cell and explained as C*(i,j)*. Figure 3 shows the neighborhoods of the *C(i,j)* cell (located at the center and shaded) for neighborhood of first second and third (r=1,2,3). In addition, the neighborhood has the property of symmetry (if C*(k,l)* $\in N_r(i,j,$ C*(i,j)* $\in N_r(k,l)$). The r-neighborhood of a cell *C(i,j)* in a cellular neural network is defined by:

$$N_r(i,j) = \{C(k,l) / max (/i-k /, /j-l / \leq r, \qquad 1 \leq i \leq M ; 1 \leq j \leq N\} \quad (1)$$

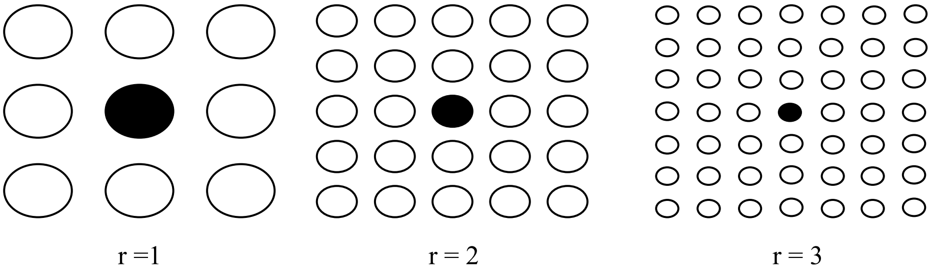

Figure 3. The neighborhood of cell *C(i,j)* for r = 1, r = 2 and r = 3, respectively.

Cells are multiple-input single-output nonlinear processors described by one, or one among several different, parametric functional. A cell is characterized by a state variable, which is generally not observable as such outside the cell itself. It contains linear and nonlinear circuit elements, such as linear resistors, capacitors and nonlinear controlled sources (Fig. 4). Every cell is connected to other cells within its neighborhood. In this scheme, information is only exchanged between neighboring neurons and this local information characteristic does not prevent the capability of obtaining global processing. The CNN is a dynamical system operating in continuous or discrete time.

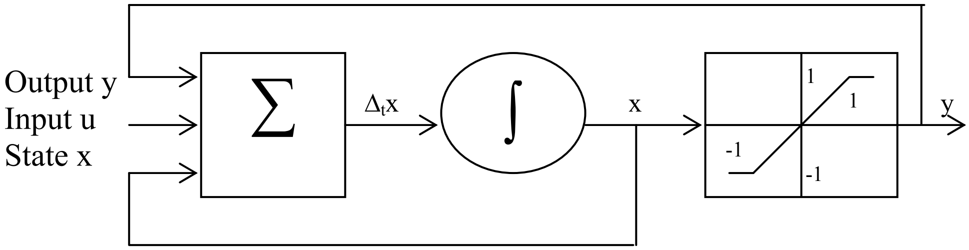

Figure 4. Functional block diagram of a CNN cell.

Cells can be characterized by a functional block diagram that is typical of neural network theory: Fig. 4 depicts a two-stage functional block diagram of a cell, composed of a generalized weighted sum (in general nonlinear with memory) integration, output nonlinear function / functional (Cimagalli, 1993; Albora et al., 2001). Data can be fed to the CNN through two different ports: initial conditions of the state and input *u*. Bias value *I* may be used as a third port.

A general form of the cell dynamical equations may be stated as follows:

$$\frac{dx_{ij}(t)}{dt} = -x_{ij}(t) + \sum_{C(k,l)\in N_r(i,j)} A(i,\ j;k,l)y_{kl}(t) + \sum_{C(k,l)\in N_r(i,j)} B(i,\ j;k,l)\,u_{kl}(t) + I$$

(2)

$$y_{ij}(t) = f\left[x_{ij}(t)\right] = \frac{1}{2}\left(\left|x_{ij}(t)+1\right| - \left|x_{ij}(t)-1\right|\right)$$

(3)

$$A=\begin{bmatrix} a_{-1,-1} & a_{-1,0} & a_{-1,1} \\ a_{0,-1} & a_{0,0} & a_{0,1} \\ a_{1,-1} & a_{1,0} & a_{1,1} \end{bmatrix},\ B=\begin{bmatrix} b_{-1,-1} & b_{-1,0} & b_{-1,1} \\ b_{0,-1} & b_{0,0} & b_{0,1} \\ b_{1,-1} & b_{1,0} & b_{1,1} \end{bmatrix},\ I$$

(4)

where; *x*, *y*, *u*, *I* denote respectively cell state, output, input, bias and *j* and *k* are cell indices. CNN parameter values are assumed to be space-invariant and nonlinear function is chosen as piece-wise linear (Fig. 4). *A*, *B* and *I*, the cloning matrices, are identically repeated in the neighborhood of every neuron.

The network behavior of a CNN depends on the initial state of the cells, namely the bias *I*, and the weights values of *A* and *B* matrices, which are associated with the connections inside the well-defined neighborhood of each cell. CNNs are arrays of locally and regularly interconnected neurons, or, cells, whose global functionality are defined by a small number of parameters (*A, B, I*) that specify the operation of the component cells as well as the connection weights between them. CNN can also be considered as a nonlinear convolution with the template. Since their introduction in 1988 by Chua, the CNN has attracted a lot of attention. Not only from a theoretical point of view these systems have a number of attractive properties, but also furthermore, there are many well-known applications like image processing, motion detection, pattern recognition, simulation. Albora et al., 2001 applied this contemporary approach for the separation of regional and residual magnetic anomalies, on synthetic and real data. Here, we have predicted air pollution parameters using CNN approach. To evaluate the prediction results of CNN, statistical performance indices have calculated and shown in Section 3.

2.3. Statistical Performance Indices

In this study, in order to objectively evaluate model prediction, three statistical performance indices are computed: the mean bias error (*Bias*), correlation coefficient (*R*), and the index of agreement (*d*). These are based on the deviations between predicted and original observation values. *Bias* is the degree of correspondence between the mean prediction and the mean observation. Lower numbers of *Bias* are the best and values of b*ias* <0 indicate under-forecasting. Evaluation can also be undertaken by considering measures of agreement, such as the Pearson product moment correlation coefficient (*R*) values. The index of agreement, bounded, relative measure that is capable to measure the degree of which predictions are error-free. The denominator accounts for the model's deviation from the mean of the observations as well as to the observations deviation from their mean. In a good model *d* and *R* should approach to one (Kukkonen et al., 2003). All these indices are formulated as follows;

$$Bias = \frac{1}{N}\sum_{i=1}^{N}(O_i - P_i) \quad (5) \qquad r = \sqrt{1 - \frac{\sum_{i=1}^{N}(P_i - O_i)^2}{\sum_{i=1}^{N}(O_i - \overline{O})^2}} \quad (6) \qquad d = 1 - \frac{\sum_{i=1}^{N}(P_i - O_i)^2}{\sum_{i=1}^{N}(|P_i - \overline{O}| + |O_i - \overline{O}|)^2}$$

(7)

where, O_i and P_i are the observed and predicted pollution values, respectively, in $i = 1., 2., ..., N$ days, $\overline{O}$ is the mean of the observed times series and *N* is the total observation number. In addition, σ_o, σ_p standard deviations of the observed time series (*O*) and predicted time series (*P*) have been calculated.

3. RESULTS AND DISCUSSION

In this paper, missing PM_{10} and SO_2 concentration values are predicted using Cellular Neural Networks in Istanbul–Yenibosna and Istanbul-Ümraniye air pollution station. We have estimated two data sets for SO_2 and PM_{10}. One of them, data set of PM_{10} and SO_2 is formed missing data percentage of 50, another them; it is formed missing data percentage of 20. %50 and %20 of daily mean observed SO_2 and PM_{10} concentrations are changed average concentration value of all SO_2 and PM_{10} data, respectively. These missing data is predicted using CNN model.

We have calculated correlations between meteorological and pollution parameters by statistical package program SPSS11.5. In our CNN model, the elements of input (*u*) and target (*T*) matrices are shown in Fig.5. The elements of input matrix consist of 20% and 50% missed data of SO_2 and PM_{10} to be predicted. We arrange *u* and *T* matrices' elements regarding to correlation coefficient information to improve prediction performance. After training CNN using *u* and *T* matrices, we have obtained A, B and I templates for each study as shown in equation 8-15.

$$u=\begin{bmatrix} RH_{t1} & RH_{t2} & RH_{t3} & \cdots & RH_{t730} \\ R_{t1} & R_{t2} & R_{t3} & \cdots & R_{t730} \\ C_{t1} & C_{t2} & C_{t3} & \cdots & C_{t730} \\ WS_{t1} & WS_{t2} & WS_{t3} & \cdots & WS_{t730} \\ MAP_{t1} & MAP_{t2} & MAP_{t3} & \cdots & MAP_{t730} \\ T_{t1} & T_{t2} & T_{t3} & \cdots & T_{t730} \\ P_{t1} & P_{t2} & P_{t3} & \cdots & P_{t730} \\ S_{t1} & S_{t2} & S_{t3} & \cdots & S_{t730} \\ WD_{t1} & WD_{t2} & WD_{t3} & \cdots & WD_{t730} \end{bmatrix} \quad T=\begin{bmatrix} RH_{t1} & RH_{t2} & RH_{t3} & \cdots & RH_{t730} \\ R_{t1} & R_{t2} & R_{t3} & \cdots & R_{t730} \\ C_{t1} & C_{t2} & C_{t3} & \cdots & C_{t730} \\ WS_{t1} & WS_{t2} & WS_{t3} & \cdots & WS_{t730} \\ AP_{t1} & AP_{t2} & AP_{t3} & \cdots & AP_{t730} \\ T_{t1} & T_{t2} & T_{t3} & \cdots & T_{t730} \\ P_{t1} & P_{t2} & P_{t3} & \cdots & P_{t730} \\ S_{t1} & S_{t2} & S_{t3} & \cdots & S_{t730} \\ WD_{t1} & WD_{t2} & WD_{t3} & \cdots & WD_{t730} \end{bmatrix}$$

Figure 5. Input (*u*) and target (*T*) matrices of our CNN model.(AP: Air Pollutant, SO_2 and PM_{10}; MAP:Air Polutant with missing data).

To predict 50 % missing PM_{10} concentration in Yenibosna:

$$A=\begin{bmatrix} 0.0426 & 0.0545 & 0.0521 \\ 0.0644 & 1.2885 & 0.0644 \\ 0.0521 & 0.0545 & 0.0426 \end{bmatrix} \quad B=\begin{bmatrix} -0.0615 & -0.0618 & -0.0613 \\ -0.0616 & -0.0614 & -0.0616 \\ -0.0613 & -0.0618 & -0.0615 \end{bmatrix} \quad I=\begin{bmatrix}-0.0614\end{bmatrix}$$

(8)

To predict 20 % missing PM_{10} concentration in Yenibosna:

$$A=\begin{bmatrix}-0.0054 & 0.0075 & -0.0280\\ 0.0048 & 1.005 & 0.0048\\ -0.0280 & 0.0075 & -0.0054\end{bmatrix}\quad B=\begin{bmatrix}0.0065 & 0.0068 & 0.0069\\ 0.0068 & 0.0069 & 0.0068\\ 0.0069 & 0.0068 & 0.0065\end{bmatrix}\quad I=[0.0069]$$

(9)

To predict 50 % missing SO_2 concentration in Yenibosna:

$$A=\begin{bmatrix}0.0537 & 0.0732 & 0.0636\\ 0.0592 & 1.4524 & 0.0592\\ 0.0636 & 0.0732 & 0.0537\end{bmatrix}\quad B=\begin{bmatrix}-0.0731 & -0.0734 & -0.0733\\ -0.0734 & -0.0734 & -0.0734\\ -0.0733 & -0.0734 & -0.0731\end{bmatrix}\quad I=[-0.0734]$$

(10)

To predict 20 % missing SO_2 concentration in Yenibosna:

$$A=\begin{bmatrix}0.0619 & 0.0697 & 0.0674\\ 0.0570 & 1.4848 & 0.0570\\ 0.0674 & 0.0697 & 0.0619\end{bmatrix}\quad B=\begin{bmatrix}-0.0752 & -0.0755 & -0.0754\\ -0.0754 & -0.0754 & -0.0754\\ -0.0754 & -0.0755 & -0.0752\end{bmatrix}\quad I=[-0.0754]$$

(11)

To predict 50 % missing PM_{10} concentration in Ümraniye:

$$A=\begin{bmatrix}-0.0024 & 0.0400 & 0.0308\\ 0.0541 & 1.0350 & 0.0541\\ 0.0308 & 0.0400 & -0.0024\end{bmatrix}\quad B=\begin{bmatrix}-0.0238 & -0.0237 & -0.0240\\ -0.0238 & -0.0239 & -0.0238\\ -0.0240 & -0.0237 & -0.0238\end{bmatrix}\quad I=[-0.0239]$$

(12)

To predict 20 % missing PM_{10} concentration in Ümraniye:

$$A=\begin{bmatrix}-0.0054 & 0.0097 & -0.0260\\ 0.0038 & 1.005 & 0.0038\\ -0.0260 & 0.0097 & -0.0054\end{bmatrix}\quad B=\begin{bmatrix}0.0090 & 0.0089 & 0.0089\\ 0.0088 & 0.0089 & 0.0088\\ 0.0089 & 0.0088 & 0.0090\end{bmatrix}\quad I=[0.0089]$$

(13)

To predict 50 % missing SO_2 concentration in Ümraniye:

$$A=\begin{bmatrix}0.0142 & -0.0182 & 0.0277\\ 0.0157 & 1.1553 & 0.0157\\ 0.0277 & -0.0182 & 0.0142\end{bmatrix}\quad B=\begin{bmatrix}-0.0271 & -0.0273 & -0.0271\\ -0.0272 & -0.0273 & -0.0272\\ -0.0271 & -0.0273 & -0.0271\end{bmatrix}\quad I=[-0.0273]$$

(14)

To predict 20 % missing SO_2 concentration in Ümraniye:

$$A=\begin{bmatrix} 0.0402 & 0.0131 & 0.0289 \\ 0.0276 & 1.2505 & 0.0276 \\ 0.0289 & 0.0131 & 0.0402 \end{bmatrix} \quad B=\begin{bmatrix} -0.0429 & -0.0433 & -0.0433 \\ -0.0433 & -0.0433 & -0.0433 \\ -0.0433 & -0.0433 & -0.0429 \end{bmatrix} \quad I=\left[-0.0433\right]$$
(15)

Here, neighborhood (*r*) is chosen as 1. To guarantee stability of CNN, templates are symmetric. We have replaced the template values obtained in Equation (8-15) to Equations (2-3). Then we have compared CNN predicted and actual {PM_{10} and SO_2} concentrations as in Figure 6 and 7 during 2002 and 2003.

Model results have also been checked by calculation five different statistical indices, given in Equation 5-7, which are based on the deviations between predicted values and original observations. The final results of statistical model evaluation for SO_2 and PM_{10} in Yenibosna and Ümraniye during 2002 and 2003 years have been presented in Table 3. For both pollutants, the results have been presented separately for each Air Quality Measurement Stations and each percentage of missing data. For PM_{10} in Yenibosna, index of agreement (*d*) of CNN is 0.69 and 0.92 for missing data percentage of 50 and 20, respectively. We have measured similar results for PM_{10} in Ümraniye, *d* is 0.74 and 0.91 for missing data percentage of 50 and 20, respectively. For SO_2 in Yenibosna and Ümraniye, *d* and *r* are the same value, 0.85 and 0.73, respectively, for missing data percentage of 20. For PM_{10} in Yenibosna and Ümraniye, *Bias* value is positive and for SO_2, it is mostly negative. This result has demonstrated that the prediction concentration of PM_{10} is less than observed PM_{10} concentration. However, the prediction concentration of SO_2 is high than observed SO_2 concentration. Table 2 and Figure 6,7 has demonstrated that CNN model for PM_{10} are producing considerably better predictions than SO_2. Furthermore, CNN model for missing data percentage of 20 are producing better predictions than missing data percentage of 50.

Table 2: Model performance indices for the CNN model. The results differ by the missing data percentage, Yenibosna and Ümraniye air quality stations and PM_{10} and SO_2 pollutions.

AQMS	AP	MDP (%)	Statistical performance indices						
			Max.	Min.	Avrg.	σ	r	d	Bias
Yenibosna	PM_1	50	218	13	47	36,1	0,57	0,70	16,3
		20	211	15	59	23	0,87	0,92	4,2
	SO_2	50	170	0,3	26	26,1	0,67	0,81	2,76
		20	148	2,2	30	25,5	0,73	0,85	-0,91
Ümraniye	PM_{10}	50	279	10	49	34,3	0,54	0,74	6,87
		20	244	2,5	54	24,3	0,86	0,91	1,95
	SO_2	50	164	5,5	21	30,3	0,67	0,73	-2,43
		20	170	6	21	24,3	0,73	0,85	-2,54

AQMS: Air Quality Measurement Stations, AP: Air Pollutans, MDP: Missing data percentage

4. CONCLUSION

In this paper, main air pollutants of Istanbul, Particulate Matter (PM), Sulfur Dioxide (SO_2) are estimated using CNN approach. There are many studies for air pollutant modeling. One of the frequently used methods is Artificial Neural Network (ANN). In ANN, the training process time increases as the problem becomes complex. In 1988, Chua and Yang have introduced Cellular Neural Network (CNN) as a new non-linear, dynamic neural network structure. In CNN, the correlations between neighbor pixels are modeled by cloning templates with limited number of elements in solving complex problems.

In previous similar study, index of agreement value has changed between 0.20 and 0.80 for other model techniques, for example Multilayer Neural Network, Regression Analysis etc. (Junninen et al., 2004). In this paper, we have measurement *d* between 0.69 and 0.92 for all study and for all pollutant. The elements of climatic system are commonly nonlinear, irregular and highly complex. As a result, CNN-based approaches can be considered as a compromising approach in air pollutant prediction.

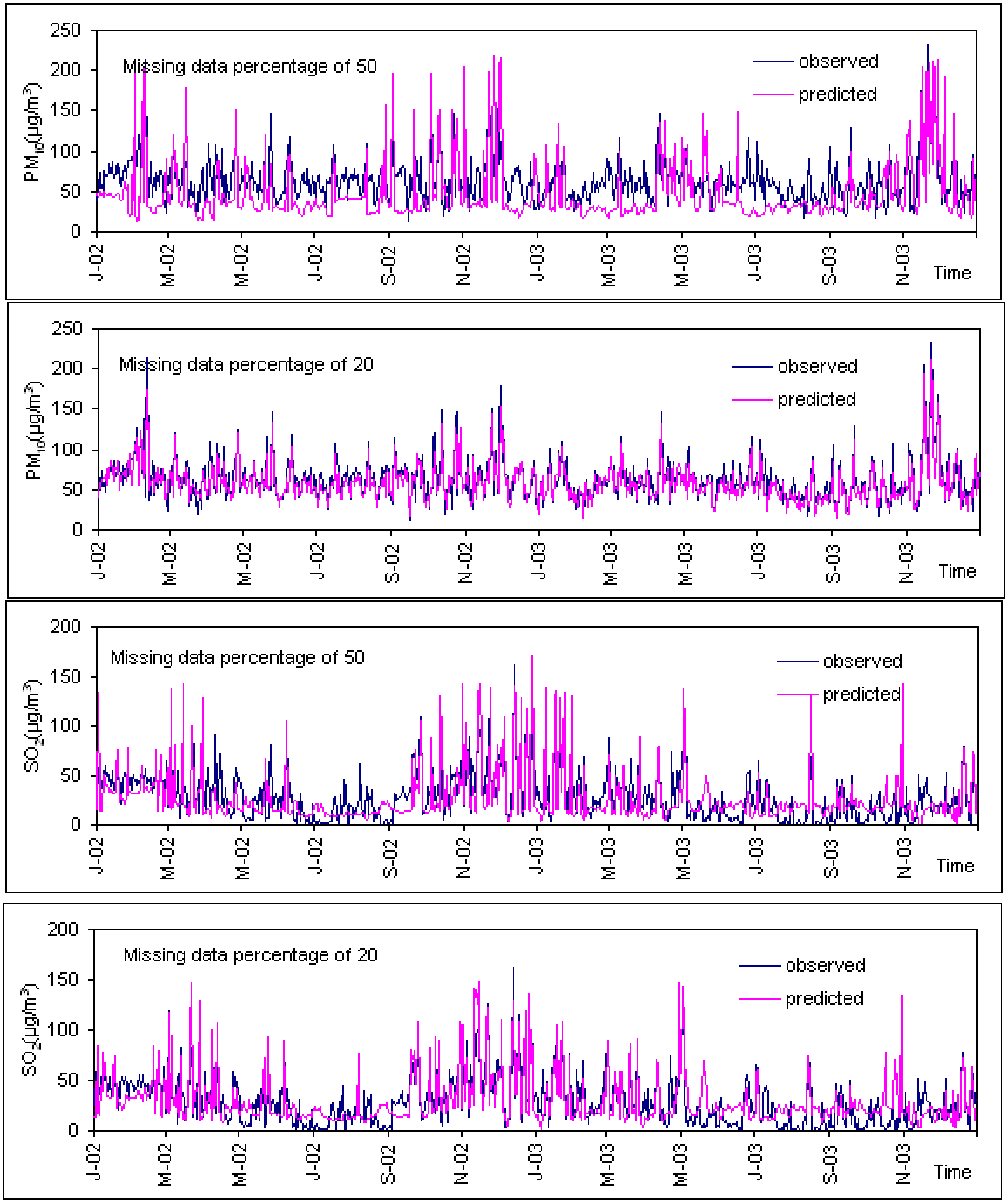

Figure 6: Two years of observed and CNN model predicted daily mean PM_{10} and SO_2 concentrations at the Yenibosna AQM Stations.

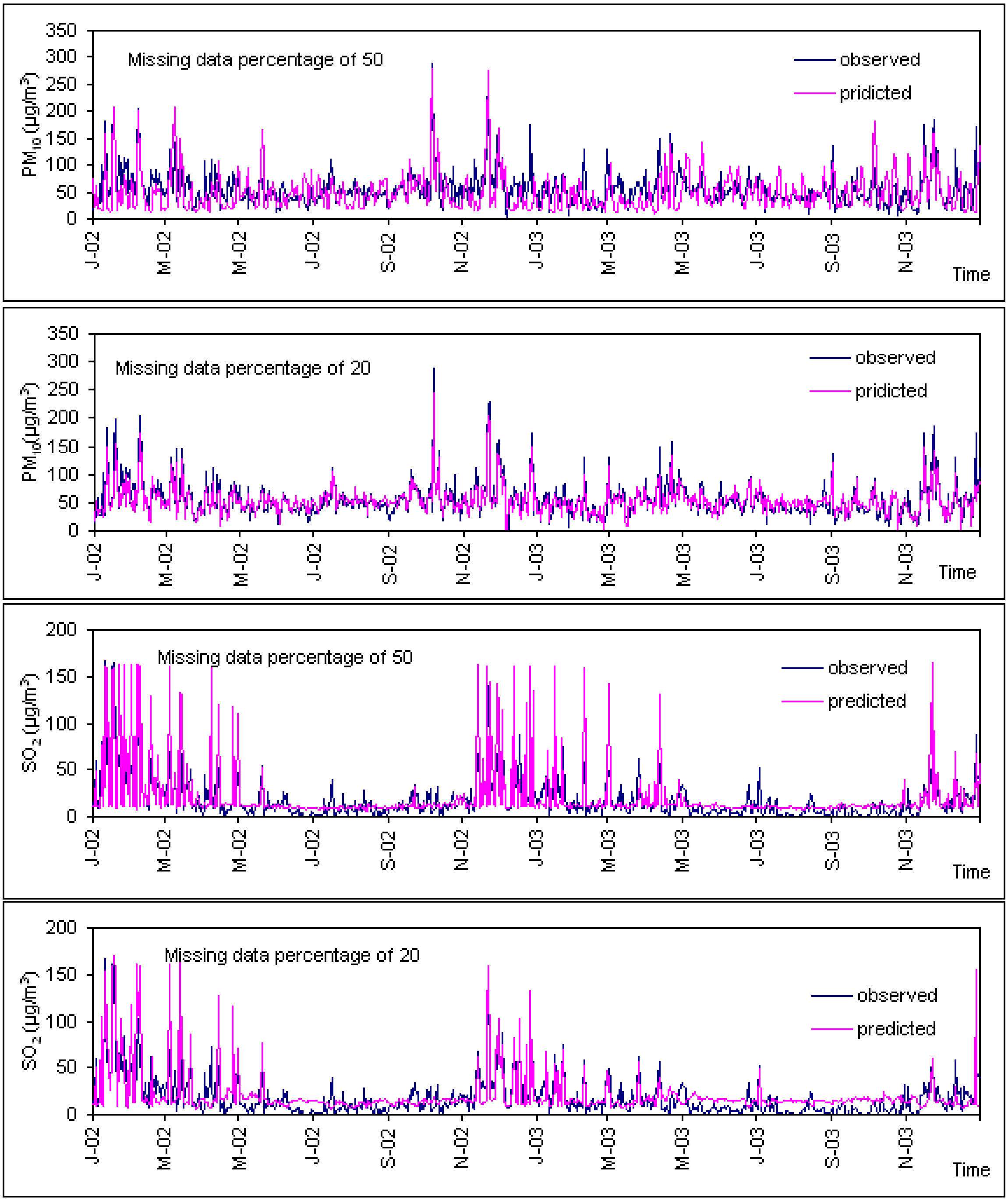

Figure 7: Two years of observed and CNN model predicted daily mean PM$_{10}$ and SO$_2$ concentrations at the Ümraniye AQM Stations.

5. ACKNOWLEDGEMENTS

We are grateful to Istanbul Municipality, Environmental Protection Directorate and Department of Meteorology in Istanbul for their help in obtaining real data. This work was supported by the Research Fund of the University of Istanbul. Project Number: T-486/25062004.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

AN ELECTRON MICROSCOPE STUDY OF THE AIRBORNE PARTICLES IN NORTHEAST MEDITERRANEAN

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ABSTRACT

The chemical and physical characteristics of airborne particulate matter in urban and in industrial environments are very complex and dynamic. The measurement and determination of the chemical and physical characteristics of particulate aerosols is essential in the application of environmental control by identifying sources and describing the origin and fate of the various products of atmospheric chemical interactions.

In Iskenderun Gulf Northeast Mediterranean there is a big industrial zone with several important metallurgical plants, pipeline terminals and is known that in the adjacent urban zone and coastal region.

In this study atmospheric particulate samples were obtained, using the impaction collector, from four very different sites in the Gulf: rural, coastal, industrial and urban.

In order to investigate chemical composition and associated morphological characteristics of airborne particles, an analytical transmission electron microscopy with energy-dispersive X-Ray (TEM-EDAX) was used. The combination of analytical methods (TEM-EDAX) allowed us to characterize these particles in more detail and identify its source.

Thus, the approach presented here can be used to determine the physical and chemical composition of particles and to refine source apportionment based on particles analysis.

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

SEASONAL VARIATIONS OF POLYCHLORINATED BIPHENYLS (PCBS) IN IZMIR, TURKEY

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ABSTRACT

Polychlorinated biphenyls (PCBs) are human made toxic chemicals which were first synthesized in 1920s. Because of their inverse effects on environment and human health the usage and production of PCBs were banned in 1970s in United States and all over the Europe. Due to their persistent structure, they are prone to long- range atmospheric transport they have been found even in remote areas.

In order to determine the atmospheric concentration levels in Izmir, total (gas+particle) PCBs (ΣPCB) and 41 PCB congeners, a long term sampling program were designed in the suburban atmosphere. In the sampling program fifty-two successive daytime (8.00 a.m.-8.00 p.m.) gas and particle phase air samples were collected between May 14, 2003 to and 4 April 2004 at the sampling station in Dokuz Eylül University, Tınaztepe Campus. Average sampling time was 12 h and average sampling volumes were 223±8. Meteorological data were obtained from a 10 m high tower located at the same site.

The concentrations of PCBs and their relation with temperature and wind direction will be reported in this study.

Keywords: Polychlorinated biphenyls (PCBs), suburban air concentrations, seasonal variation.

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

A STUDY OF SEMI-VOLATILE TOXIC ORGANIC AIR POLLUTANTS IN ALIAGA HEAVY INDUSTRIAL REGION

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ABSTRACT

Ambient air samples (n=14) were collected in Aliaga, in August 2004 to investigate the atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs). A modified high-volume sampler Model GPS-11 (Thermo-Andersen Inc.) was used to collect airborne PAH concentrations in both the particulate and gas phases. Particles were collected on 10.5 cm diameter quartz filters while the gas phase compounds were collected in a modified cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF) plugs. A second Hi-Vol air sampler deployed at the same site was used to determine total suspended particulate matter and its organic matter (OM) content, concurrently.

Air filters and sorbent cartridges were separately extracted with a Soxhlet extractor using a mixture of dichloromethane (DCM): petroleum ether (PE) (20:80) solution for 24 h. All samples were analyzed for PAHs using a Hawlett Packard GC-MS system consisting of a HP Model 5890 Series II gas chromotography (GC) and a HP Model 5971A mass selective detector (MSD).
Analyses results were evaluated for PAH levels in total, gas and particle forms. The main local sources of anthropogenic air pollution in the Aliaga region are petroleum refinery, a petro-chemical complex, iron-steel factories, scrap iron storage and classification sites, heavy traffic (train and trucks/cars), nearby agricultural areas and a number of ship dockyards, storage houses.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), gas/particle partitioning, total suspended particles (TSPs)

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

ODOROUS EMISSIONS IN THE ORGANIZED INDUSTRIAL ZONE OF ANKARA, TURKEY

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ABSTRACT

Ankara has an Organized Industrial Zone (OIZ), about 25 km away from the city centre, where different kinds and sizes of industries are located. Among these industries, there are iron foundries, paint factories, glass and stone wool productions, etc. which cause odour problems and need to control their emissions not to annoy the residents, although the residents are not in the immediate vicinity.

A number of industries at that OIZ have been visited several times and odorous gas samples were collected. These gas samples were analysed with olfactometer at METU Odour Laboratory and threshold concentrations were determined for these industries. Some of the measurement results of these industries were discussed in this paper.

Key Words: Odour Emission, Olfactometric Measurements, Odour Thresholds

1. INTRODUCTION

In order to control odorous emissions, potential odour sources should be determined first and then these sources should be evaluated quantitatively. For this purpose, various kinds of industrial facilities and production processes at the Organized Industrial Zone (OIZ) which is located 25 km away from the city centre were visited numerously to have an overview of the emission levels from different industries. At OIZ, different kinds of small and medium sized industries were found that cause odour problems and need to control their emissions not to annoy the people living around.

In this study "olfactometric method" was used for odour measurements. With the olfactometric measurements odorant concentrations were determined for various emission sources. Gas samples from industrial facilities located at the OIZ including foundry and forging operations, paint manufacturing, mineral wool production (glass and stone wool productions), battery factory, packaging industry, spice factory, food industry, washing machine factory, sponge factory, rubber coating plant, pipe and machine industry, dried fruit/nuts factory and cable element industry were taken by using the vacuum sampling device. Most of these industries have typical odours and they were chosen on the basis of odour complaints from the public.

2. MATERIALS AND METHODS

Considering the fluctuations in emissions and the changing work loads at the industry under investigation, at least three samples have to be taken per industry/ operation at different times. These odour sources are foundry and forging operations, paint manufacturing, and mineral wool production (glass and stone wool productions). Each of these industries/operations was visited several times and odorous gas samples were collected. In order to obtain reliable results with olfactometric measurements, 3 odorous gas samples were collected from each industry/ operation on each measurement day and each sample were measured for 3 times with olfactometer at METU Odour Laboratory. Analyses of the samples were carried out within the next 24 hours and they were in accordance with CEN 13725 and VDI 3881. Statistical procedure for measurements and evaluations is in accordance with CEN 1999.

In order to obtain reliable results, the standard deviations of the measurement results were examined. If the standard deviation for a measurement was greater than 1.5, that measurement result was discarded.

2.1. Sampling Procedure

Air samples were collected from aeration channels and exhaust stacks of selected industries/operations. Throughout the study static sampling method was used. Odorous gas samples were collected in "nalophan" bags using the vacuum sampling device. The schematic diagram of the sampling device is shown in Figure 1.

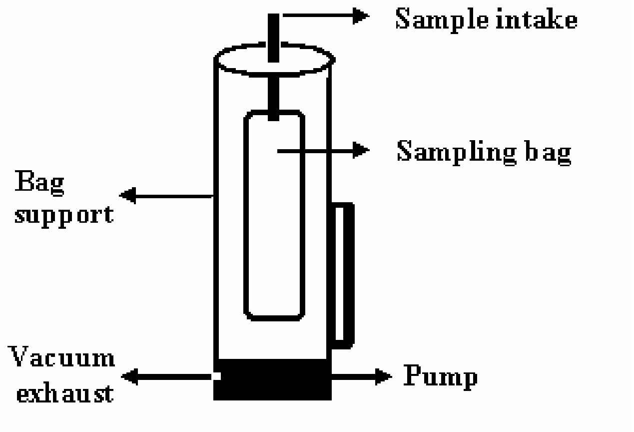

Figure 1. Schematic diagram of the sampling device

When samples were taken from stacks, an extension tube made of teflon, which was connected to the vacuum sampling device, was inserted into the stack and the gas sample was filled into the nalophan bags.

2.2. Olfactometer TO7

In order to determine the odour concentration of the gas samples, TO7 yes/no olfactometer as shown in Figure 2, was used throughout the experiments.

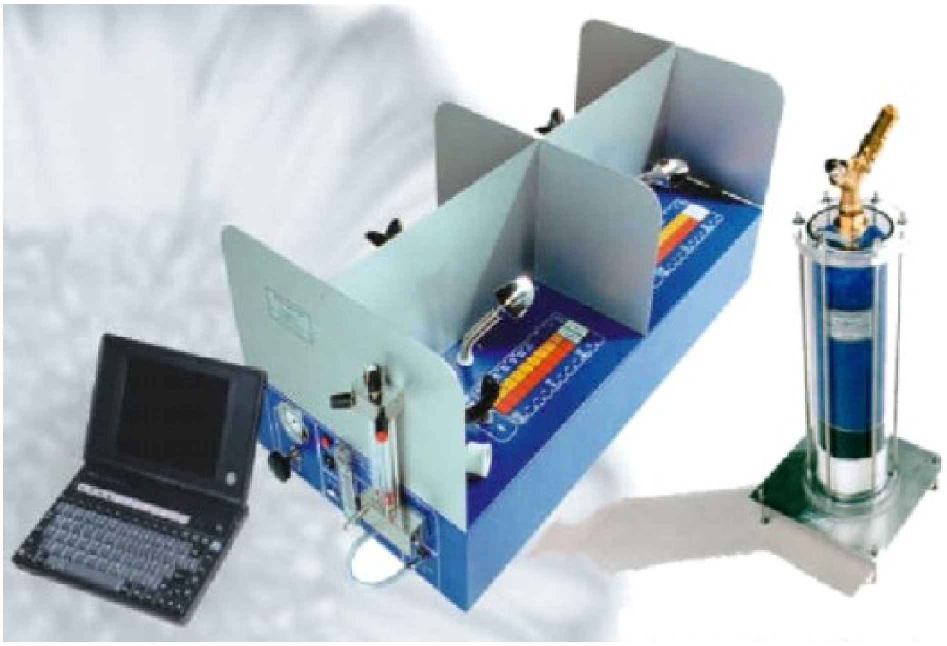

Figure 2. Picture of an olfactometer Model TO7 (ECOMA, 2001)

Olfactometer TO7 is a compact measurement system for odour measurement in the laboratory or in mobile operation. The Olfactometer TO7 is concurring with the German Guidelines VDI 3881 and 3882 and with the new European Standard, CEN 13725. The Olfactometer TO7 is in principle a dilution system in which a sample of odorous air is diluted with clean air. The principle of odour determination by olfactometry is given in Figure 3.

The diluted sample is offered to panel members who judge the sample for odour. The concentration of sample air is increased stepwise according to the method of limits. The step width is in factor of 2. The panel members usually start measurement with neutral air in which no odour is perceptible. The concentration of the sample is increased until the panellists can perceive it. The answers are collected according to yes/no-questioning (ECOMA, 2001). The measurement is run with four panellists at the same time.

The air sample is sucked from the sample-bag via the predilution unit and via the flowmeters. The flow-rate of odorous air is controlled in steps by the needle valves which are adjusted by the leader of the panel. The following dilution ratios are used: 1:2.5 to 1:640 without pre-dilution, 1:250 to 1:64,000 with a pre-dilution ratio of 1:100. The predilution ratio can be adjusted to 1:25 and to 1:100.

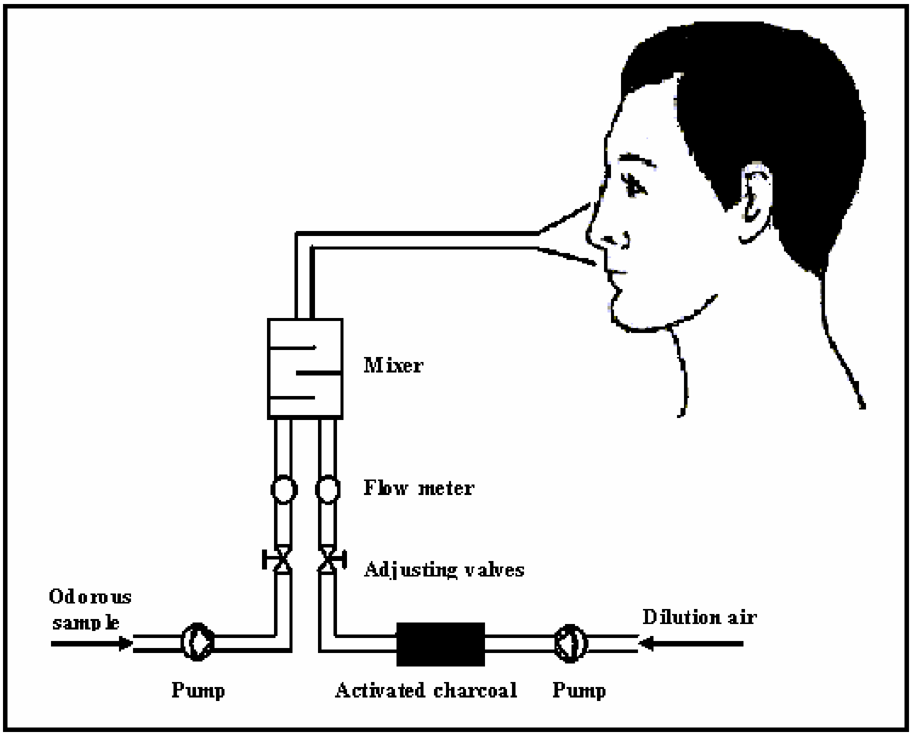

Figure 3. Principle of odour determination by olfactometry (Baumbach, 1996)

The odour concentrations of the gas samples were calculated by the special software according to the response of the panel members. The software is provided by the company selling the olfactometer. The resultant odour concentration is expressed by Z_{50} which is calculated by taking the geometric mean of the "panellists' odour thresholds" and Z_{50} is displayed in terms of OU/m^3 which indicates the amount of odorant material dispersed in 1 m^3 of neutral air. The standard deviations of measurements are also calculated by the software.

Sixteen panellists, who were selected among undergraduate and graduate level environmental engineering students, took part in odour measurements of this study. Nose sensitivities of all students were tested with n-butanol and those who pass the test were selected as panellists. The panellist screening test which is in fact called "calibration", was carried out at regular intervals in order to sustain panellist sensitivity.

3. RESULTS AND DISCUSSION

Emission measurements were conducted at several operations/industries at the OIZ of Ankara. A part of the emission measurement results which designate high odorous emissions are discussed in detail within this paper.

The operations/industries examined in detail are foundry and forging operations, paint manufacturing, and mineral wool production (glass and stone wool productions).

3.1. Foundry and Forging Operations

Odour emission measurements were performed at three different foundry and forging operations at different times. The characteristic smell for these gas samples were similar; metallic, coal-tar, bitter odour. Different odour concentrations were observed at different times. According to these observations, the odour concentrations for these operations ranged from 28 OU/m^3 to 2000 OU/m^3 and the corresponding odour levels were found to be 14.5 dB and 33.0 dB, respectively. The results of measurements are given in Table 1.

Table 1. Results of odour measurements at foundry and forging operations

Emission source	Foundry and Forging Operations
Sampling Unit	Aeration Channel
Range of Odour Concentration (Z_{50})	28 – 2000 OU / m^3
Odour Level	14.5 – 33.0 dB
Characteristic Smell	metallic, coal-tar, bitter odour

During odour sampling, parameters such as temperature, humidity and velocity of the gas in the stack were also measured. The cross-sectional area of the gas exit system was determined and used in determination of odour emission rate with other parameters.

The results of the olfactometric measurements are calculated by taking the geometric mean of the “panellists’ odour thresholds”. In this regard, it is more logical to take the geometric means of the measurement results to give an overall odour concentration.

In Table 2, geometric means of odour concentrations and related odour levels are given for each foundry operations with the above mentioned parameters. Odour emission rate was found by multiplication of odour concentration (OU/m^3) with gas flow rate in the aeration channel (m^3/s).

Table 2. Emission measurement results of foundry and forging operations

	Foundry 1	**Foundry 2**	**Foundry 3**
Odour Concentration (OU/m^3)	184	1843	30
Odour Level (dB)	22.7	32.6	14.7
Temperature (^{o}C)	45	65	30
Humidity (%)	16.0	8.4	26.5
Velocity (m/s)	1.06	1.75	1.10
Outlet Cross-Sectional Area (m^2)	0.60×0.60	0.80×0.80	0.60×0.60
Gas Flow Rate (m^3/s)	0.38	1.12	0.40
Odour Emission Rate (OU/s)	70.2	2064	11.9

According to these results, Foundry 2 seems to be a significant odour source. Not only the odour concentration, but also the gas flow rate for Foundry 2 was very high. Therefore, odour emission rate for this foundry was found to be high.

During sampling visits, information related with operational capacities of the foundries was also obtained. Foundries 2 and 3 were small scaled foundries and the work loads for these foundries were lower as compared to Foundry 1. However, the odour emission rate for Foundry 2 was found much higher than Foundry 1 and 3.

In foundries, molten metals are cast into objects of desired shapes. Castings of iron, steel, light metals (such as aluminium), and heavy metals (such as copper and zinc) are made. Odorous substances are emitted during melting of the raw materials soiled with oil, paints and plastics. In fact, in small foundries these kind of low quality materials are being used in order to decrease the costs. Therefore, the odour emission from these foundries basically depends on the selection of the raw materials used for processing.

On the other hand a relation between odour concentrations, temperature and humidity was observed. In regards to three foundries considered, as the temperature of the odorous gas increases the concentration has been observed to increase. This is again because of the dirt on the materials used. When these materials are burnt, the dirt on the materials evaporates and odours are released to the environment.

Therefore, the quality of the raw material should be improved by selecting clean metal scraps to reduce the release of pollutants and odours to the environment.

3.2. Paint Manufacturing

Odour emission measurements were performed at two different paint factories. In one of these paint factories both paint and varnish were produced and solvent-based process was used. In the other paint factory, water-based paint was produced.

Odorous gas samples were collected from paint and varnish aeration channels of the first factory by using the vacuum sampling device. The characteristic smell for the gas samples collected from the first plant was typical of paint and varnish manufacturing odour which includes solvents (esters, aromatics, ketons etc.). Odour was extremely strong inside and also outside the plant. The odour concentrations for paint manufacturing were found to vary between 1400 OU/m^3 and 13000 OU/m^3, and the corresponding odour levels were found to be 31.5 dB and 41.3 dB, respectively. The results of measurements are given in Table 3.

The odour concentrations for varnish manufacturing were found to vary between 1300 OU/m^3 and 1900 OU/m^3 and the corresponding odour levels were found to be 31.3 dB and 32.8 dB, respectively. The results of measurements are given in Table 4.

Table 3. Results of odour measurements at solvent-based paint manufacturing

Emission source	Paint Factory 1
Sampling Unit	Paint Aeration Channel
Range of Odour Concentration (Z_{50})	1400 – 11 000 OU / m^3
Odour Level	31.5 – 41.3 dB
Characteristic Smell	typical paint odour

Table 4. Results of odour measurements at solvent-based varnish manufacturing

Emission source	Paint Factory 1
Sampling Unit	Varnish Aeration Channel
Range of Odour Concentration (Z_{50})	1300 – 1900 OU / m^3
Odour Level	31.3 – 32.8 dB
Characteristic Smell	typical varnish odour

In the other paint factory where water-based process is used, odorous gas samples were collected from paint aeration channel by using the vacuum sampling device. These samples were analysed with olfactometer at METU Odour Laboratory.

The characteristic smells for the gas samples were typical of paint manufacturing odour, but was not as strong as the first factory. Additionally, outside the factory odour was not sensed very strongly. The odour concentrations for the second factory were found to be between 910 OU/m^3 and 1700 OU/m^3 and the corresponding odour levels were found to be 29.6 dB and 32.3 dB, respectively. The results of measurements are given in Table 5.

Table 5. Results of odour measurements at water-based paint manufacturing

Emission source	Paint Factory 2
Sampling Unit	Paint Aeration Channel
Range of Odour Concentration (Z_{50})	910 – 1700 OU / m^3
Odour Level	29.6 – 32.3 dB
Characteristic Smell	typical paint odour

In Table 6, the geometric means of odour concentrations and related odour levels are given for each paint manufacturing plant. The related information on gas temperature, humidity and velocity could not be obtained for this case.

For the first factory, the geometric means of odour concentrations were 4560 and 1581 OU/m^3 for paint and varnish manufacturing, respectively. The geometric mean of odour concentrations for the second paint manufacturing was 1112 OU/m^3.

Table 6. Emission measurement results for paint manufacturing

	F-1 Paint	F-1 Varnish	F-2 Paint
Odour Concentration (OU/m^3)	4560	1581	1112
Odour Level (dB)	36.6	32.0	30.5

As can be seen from Table 6, there is a big difference in odour emissions between the first and the second paint manufacturing factories. According to the results of measurements, the odour concentrations for water-based paint manufacturing were found to be lower than that of solvent-based paint manufacturing. In the solvent-based paint production, the solvents used have a higher vapour pressure than water, therefore they evaporate more. These measurement results again designate the importance of the process selection for cleaner production.

In fact, all results show that paint manufacturing is a big odour contributor and related odour control measures should be taken, especially, by the solvent-based paint manufacturers.

3.3. Mineral Wool Production

Mineral wool can be divided into two main categories: *glass wool* and *stone* (or *slag) wool*. The products are used in essentially the same applications and differ mainly in the raw materials and melting methods used.

Odour emission measurements were performed at a mineral wool producing factory on different days. Odorous gas samples were collected from glass and stone wool exhaust stacks by using the vacuum sampling device. The characteristic smell for these gas samples were extremely strong, irritant and had a bitter odour. The exhaust stacks were high (about 25 m and 10 m) that odour was not sensed right outside the plant. The odour concentrations for glass wool manufacturing were varying between 2000 OU/m3 and 6700 OU/m3, and the corresponding odour levels were found to be 33.0 dB and 38.3 dB, respectively. The results of measurements are given in Table 7.

Table 7. Results of measurements at glass wool manufacturing

Emission source	Glass Wool
Sampling Unit	Exhaust Stack
Range of Odour Concentration (Z_{50})	2000 – 6700 OU / m^3
Odour Level	33.0 – 38.3 dB
Characteristic Smell	irritant and bitter odour

The odour concentrations for stone wool manufacturing were varying between 18000 OU/m^3 and 27000 OU/m^3, and the corresponding odour levels were found to be 42.5 dB and 44.3 dB, respectively. The results of measurements are given in Table 8.

Table 8. Results of measurements at stone wool manufacturing

Emission source	Stone Wool
Sampling Unit	Aeration channel
Range of Odour Concentration (Z_{50})	18000 – 27000 OU / m^3
Odour Level	42.5 – 44.3 dB
Characteristic Smell	irritant and bitter odour

During odour sampling, parameters such as temperature, humidity and velocity were also measured in the aeration channel with an anemometer. The cross-sectional area of the gas exit system was determined and used in determination of odour emission rate with other parameters.

In Table 9, the geometric means of odour concentrations and related odour levels are given for glass wool and stone wool manufacturing. Odour emission rate is found by multiplication of odour concentration (OU/m^3), with the volumetric flow rate of the odorous gas (m^3/s).

Table 9. Emission measurement results for mineral wool manufacturing

	Glass Wool	**Stone Wool**
Odour Concentration (OU/m^3)	4049	22045
Odour Level (dB)	36.1	43.4
Temperature (^{o}C)	30	100
Humidity (%)	30.2	12
Velocity (m/s)	4	2.5
Outlet Cross-Sectional Area (m^2)	1.13	1.13
Gas Flow Rate (m^3/s)	4.52	2.83
Odour Emission Rate (OU/s)	18301	62277

The geometric means of odour concentrations for glass wool and stone wool manufacturing were 4049 and 22045 OU/m^3, and the odour emission rates were 18301 and 62277 OU/s, respectively. The temperature for stone wool manufacturing was very high that increased the strength of the odorant effect of the sample.

According to the results, it is obvious that glass wool and stone wool manufacturing are highly odorous operations. Moreover, these manufacturing processes take place within the same factory in different buildings. These are both large scaled operations. Because of the property of the raw materials used, they are both odorous operations.

The odour emission rates for both of these processes were found to be very high. Considering the intensity and the hedonic quality, it can be said that these odours were very disturbing. However, outside this mineral wool factory, odour sensation was very low because a right approach has been used by the factory and high stacks were built. For glass wool manufacturing stack height was 25 m and for stone wool manufacturing the stack height was 10 m. In fact, these high stacks increase the dispersion of odorous gas and reduce the odour impact at ground level. In case of lower stacks, these types of odours may affect the community's well being. In addition to high stacks, appropriate odour control technologies should be used in these industries to reduce odorous emissions.

Additionally, these types of industries should not be constructed in the vicinity of the residential areas or a setback distance must be defined by using appropriate odour dispersion models.

4. CONCLUSION

In this study, a number of industrial facilities at the OIZ of Ankara were visited to measure the odour emission levels from different industries. The process conditions, the indoor and the outdoor environment of the plants were examined and the samples were taken from emission sources. Odorous gas samples were analysed with Olfactometer TO7.

The results of the emission measurements have shown that there are numerous industries at the OIZ of Ankara which discharges odorous gases into the environment. Depending on the odour concentration, the impact of these gases can be quite annoying.

Among the industries studied, the odorous emissions of;
- glass wool and stone wool manufacturing,
- paint and varnish manufacturing (especially solvent-based),
- foundry and forging operations,

processes were found to be quite high. If odour emissions are not controlled they can be very annoying depending on the temperature and weather conditions.

5. ACKNOWLEDGEMENTS

This study is a part of the project funded by LIFE Programme under the Project Code: LIFE00/TCY/TR/009. LIFE, the financial instrument for the Environment, is one of the programmes of the EU on environmental policy. The financial support from the LIFE programme is greatly appreciated.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

REGIONAL AIR POLLUTION AND ABATEMENT MEASURES IN LEGISLATION

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ABSTRACT

With rapid industrialization, especially in the second half of the 20th century, industrial installations agglomerated in certain regions with logistic advantages (transport facilities, close to resources and market, etc.). Big industries attracted smaller ones and created supplier sectors, labor immigration and population intensity in these areas.

This unforeseen and uncontrolled movement facilitated by lack of planning, evolved industrial areas surrounded by residential areas or residential areas mixed with industrial zones, yielding intensive air pollution. The Constitution provides the rights to live in a healthy Environment for each individual, and the laws and regulations comprise of cautions to be taken for the protection of human health, ecosystems and physical environment. This study covers the elaboration of the provisions of the Regulation on Industry Sourced Air Pollution Control (RISAPC)

Key Words: Air Pollution, Industrial Pollution, Regional Air Pollution, Emission Limit Values

1. INTRODUCTION REGIONAL AIR POLLUTION

With economical incentives, industrial plants are installed in places with:

- Close to energy sources and raw material
- Providing good transport means
- Close to market
- Labor-easy,
- Terrain with little inclination and with infrastructural facilities.

Then these Regions become attraction zones in three types:

1. The ones surrounded by big populations
2. The ones mixed with residential areas
3. The ones with certain distance to residential areas.

Figure 1. A Typical "Emission Field"

Due to installation of highly polluting plants in the same region, REGIONAL AIR POLLUTION occurs with emission of several pollutants (dust, SO2, NOx, VOC, PAH, HM, etc.) in high rates and concentrations to the common receiving medium. Level of pollution is also effected by factors such as dilution capacity of the region, topography, meteorological conditions and operation patterns of the plants.

The key here is the air quality standards expressed in Air Quality Control Regulation (AQCR) Article 6. These standards should not be exceeded even in one parameter.

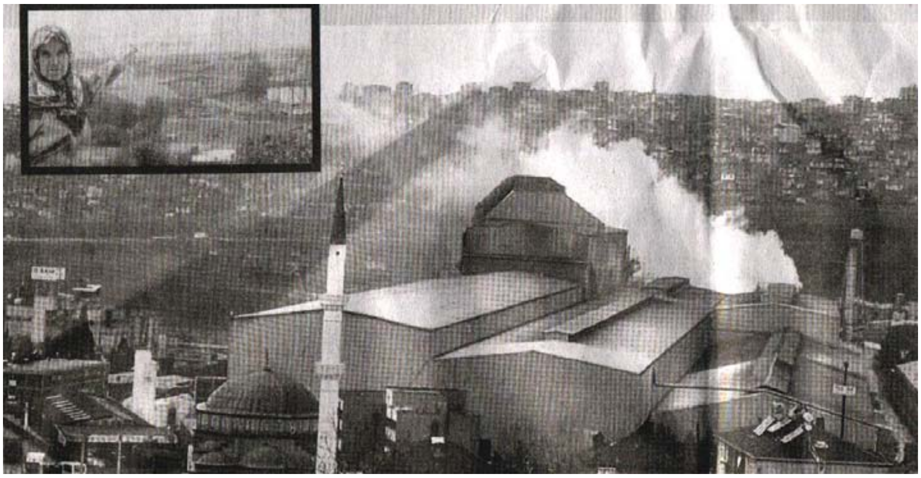

Figure 2. Industrial zone intersects with residential area

What are the competences of the authorities for combating against air pollution in sucha region? Before this, the issue is what requirements the Regulation introduces for the operation of the industrial plants.

The Regulation (RISAPC) requires that the operator of the plant:

- Reduce the pollutant emissions from the plant to the extent that's technologically and economically suitable.
- Meet the limit values
- Not cause any pollution hazard in the region the plant is established.
- Follow the instructions in the action plans prepared by the Competent Authority when air quality standards in the region are exceeded.

Relevant Regulation Provision:

Principles to be followed on the establishment and operation of Plants subject to permit

"Article 7: On the establishment and operation of Plants subject to permit, it is required that :

a) Reduction of the hazardous effects of the plant to the public and the environment, suitable to the technological level, and avoid any danger,
b) To comply with the conditions laid down in this Regulation,
c) Not to exceed the emission limit values laid down in this Regulation
d) Air quality limit values laid down in AQCR not to exceed in the plant effective zone
e) Measurement ….
f) Air quality assessment in the plant effective zone….
g) Stack gas emissions of the plants to be established and for the plants without stacks hourly mass discharges to be estimated
h) For the new plants to be established, in case the mass flow rates laid down in Article 40 Table 40.1 are exceeded, operator shall estimate the plant's contribution to air pollution in the plant effective zone by using a dispersion model for the determination of the degree of polluting of the plant; shall measure air quality according to the procedures laid down in this Regulation, if there is a suspect that the level of air pollution has reached significant dimensions in the area the plant will be established.
i) Wastes produced in the plant….
j) In the region where the plant stays, in case the air pollutants exceed the air quality limits laid down in AQCR owner and/or operator of the plant shall conform with the action plan prepared by the Competent Authority"

For the assessment of the pollution caused by an individual plant, The Regulation foresees the request for an emission report comprising of measurement of emissions and/or air quality and/or calculation of air pollution contribution by that plant.

In “Critical Regions”, where air pollution is very high, Competent Authority may also ask from the plants a report including emissions from the plants and their air Pollution Contribution Values that shows time and space variation of the pollutants. Plant Area has been identified in Article 40, where, Competent Authority shall coordinate the measurements to be carried out in order to determine the level of pollution. This assessment may be repeated yearly. (Article 27-a,b,c,d)

Identfication of Critical Regions and Enforcement Means:

In the intensively industrialized regions, in order to combat air pollution caused by one or several types of pollutant emissions, Regulation has provided vast authority to Provincial Governors.
One is the competence for identification of a Critical Region. In order to have a more effective and rapid response mechanism to pollution cases, Governors are authorized, but the Ministry may also take the initiative when required.

Cap Model-Total Emission Limiting:

“Article 33-
The Governor may require measures to limit total emissions released at any instant from all of the plants that operate in intensively industrialized critical regions. Governor identifies the critical regions. The Governor, related with the total emission levels, may take decisions to limit temporarily or permanently emissions of a new plant (either subject to permit or not) that will be established in such a region, or the Governor may not authorize establishment of such a plant at all. When required, the Ministry may use this competence.”

Protection of Definite Regions

Article 34:

“a) A Region, where hazardous effects on human beings and environment of air pollution rising from industrial plants, transport or heating cannot be eradicated by normal means, may be declared as a Protection Region by the Competent Authority.

Competent Authority is authorized, in Protection Regions, to:

1. prohibit the operation of mobile or stationary plants,
2. prohibit the establishment of stationary plants,
3. Allow operations of mobile or stationary plants only in certain intervals or allow operation requiring advanced operation techniques,

4. Prohibit or limit the consumption of fuel in the plants

b) In Regions where critical meteorological conditions occur or air pollution shows a rapid increase, Competent Authority, in response to hazards that may occur on human and their environment, is authorized to:

1. Allow operations of mobile or stationary plants only in certain intervals
2. Prohibit or only limit in the plants the consumption of fuels that may lead to significant pollution in air.

c) In cases where air pollution shows a rapid increase, warning levels laid down in AQCR shall be applied.

In cases when air quality limit values are exceeded and air pollution reaches levels determined in AQCR, measures to be taken according to the properties of the region, are published by the Governorship as a communiqué. Governorship shall get opinion of the Ministry in determining this Communiqué

Meteorological data shall be taken into account when measures for each level are regulated. In fog, inversion, meteorological stability conditions and isothermal conditions measures of the following higher level or additional measures may be applied. When relative humidity exceeds 90%, values 10% lower than the levels laid down in AQCR are considered in determination of warning levels."

"Limitation of Fuel and Raw Materials

Competent Authority, in cases or regions where air pollution reaches significant dimensions, in order to reduce air pollution, may require consumption of suitable fuel or raw material in plants where fuel or raw materials can be varied.
Article 39 of the RISAPC provides the competent Authority with the power to set emission limit values as for concentration and mass flow 1/3 of the existing ones in a regional scope for the pollutants such as dust, organic vapor and gases and carcinogens."

Future Scope: EU Harmonization:

EU practice in abatement of regional air pollution has certain principles:

- Relevant monitoring of the air quality in identified zones,
- Preparing action plans relevant to the level of air pollution considering source apportionment studies,
- Implementation of action plans on sources of the pollution.
- Responsibility distribution in case of exceedance in limit values.

Most significant change in Turkish Regional Pollution Prevention Strategy is the change of certain definitions and concrete measures against pollution. Air quality standards are evolving into air quality limit values not to be exceeded. These principles are being introduced into Turkish Environmental Management system by means of transposition and implementation of European Community Air Quality Directives (Air Quality Framework Directive and four Daughter Directives)

2. CONCLUSIONS

Combating Air Pollution in intensively industrialized areas requires additional measures. Implementation of these measures requires Regulatory reinforcement. Regulation on Industry Sourced Air Pollution Control (RISAPC) proves to provide the enforcement officials with the tools for flexible pollution management. Where emission limit values are not enough to achieve environmental quality standards, using these tools, which function as insurance of meeting the quality standards; the competent authority has been given the power to set stringent limit values without impairing the level playing field in the market.

Then it comes to the query whether these tools are utilized in a satisfactory manner in order for the control of intensive pollution. When the above-mentioned hotspots are considered it is seen that the tools provided are not being used to reduce the degree of pollution. This requires certain capacity in the competence authorities to enforce the Regulation and its requirements. What Turkey needs to do first to cope with this lack is to give environment sufficient priority among other policy incentives, integrate environmental policies with the economical and other policies, and provide the competent authorities with the capacity to run these tools

European Union approach puts emphasis on achieving the environmental quality standards and setting the limits accordingly is being introduced to Turkish legislation. But it will take certain time to implement and see the results.

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Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

REGULATION ON CONTROL OF INDUSTRY-SOURCE AIR POLLUTION, AND ACTIVITIES FOR PREVENTION OF AIR POLLUTION

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ABSTRACT

The first legal arrangement in Turkey aimed at controlling the pollutants emitted as a result of all activities and maintaining the air quality, prepared and issued based on the Law no. 2872 on Environment is the **Regulation on Protection of Air Quality** which entered into force on November 2, 1986.

Both increase in demand for arrangements for maintenance of air quality on the basis of pollutant sources (industry, heating, motor vehicles), and the studies implemented for harmonization of the EU Acquis in the process of accession to the EU necessitated revision of that regulation which was prepared quite comprehensively.

In this context, **Regulation on Control of Industry-Source Air Pollution** was published on October 7, 2004 to control the emissions into atmosphere as a result of activities of industrial and power generation plants in the form of heat, fume, dust, gas and vapor, to protect the humanbeings and surrounding against pollution in receiving environment, to remove adverse effects on public and neighboring relations due to air pollution, and to prevent occurrence of such effects.

Efforts in progress in the EU Member States to implement a permission procedure taking into account the emission from the plant into air, water and earth, waste formation, raw material use, energy efficiency, noise, prevention of accidents, risk management, etc. For the purpose of minimizing the pollution from various sources and preventing it at its source.

There is no legislation / permission scheme in our country similar to EU approach yet, handling the activities of industrial and power generation plants with all receiving environments. Considering, however, the period of accession to the EU, the **Regulation on Control of Industry-Source Air Pollution** is a step among the studies implemented to prevent / minimize the air pollution caused by major industrial and power generation plants, and not to allow operation of such plants without obtaining permission from competent authorities.

Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. 26-30 September 2005, Istanbul – Turkey

INTRODUCTION INTO THE TWINNING PROJECT „AIR QUALITY"OF THE EUROPEAN COMMISSION

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ABSTRACT

The Twinning Project "Air Quality" started in October 2004 and has to fulfill four main tasks:

- Transposition of the Air Quality Framework Directive 96/62/EC and the Large Combustion Plants Directive 2001/80/EC into Turkish (Draft) Regulation
- Draft Agreed Framework Regulation on Air Quality which defines the Roles and the Responsibilities of the involved ministries (considering both directives)
- Strengthening of the qualification of the administration (Know-How-Transfer) – Strengthening of the Quality management and preparation of the accreditation of the two laboratories – Refik Saydam Hygienic Center (RSHC) and Gölbasi
- Agreed strategic Action Plans on further implementation steps of the two directives

During the first year legal gap analysis, a structure analysis concerning the administration and assessments were carried out with the aim to develop a draft for a Turkish Air Quality Framework Regulation. This Regulation is supposed to fulfill the requirements of the European Air Quality Framework and Large Combustion Directives. In addition, first trainings based on the assessment have taken place to strengthen the Quality Management in the two above mentioned laboratories.

Key words: Air Quality, Air Quality legislation, Quality Management