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LOCAL AIR POLLUTION IN FAST DEVELOPING COUNTRIES

(Technical Report)

Report based on Proceedings of the International Workshop held in Cheng De, near Beijing (China), 20–21 July 1994. Organized by the Center for Environmental Sciences, Peking University, Beijing, in collaboration with the Netherlands Energy Research Foundation (ECN) and the Council for Environmental Relations, China/Netherlands

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Local air pollution in fast developing countries (Technical Report)

Abstract – Local air pollution is one of the most pressing environmental problems in developing countries.The patterns of local air pollution are similar in many countries. In the initial stages of economic development the demand for energy, coupled to economic expansion, rises sharply. This increased consumption of power for heating, electricity, industrial processes etc. must lead to an increase of emissions. Dust, SO_2 and secondary products like sulphuric acid are responsible for severe impairments of human health and large scale damage to nature and buildings. Many developing countries have reached this stage of local air pollution or will be exposed to this type of environmental hazards in the near future. Economically developed countries, like the US, Japan and many countries in Western Europe have passed this stage one to three decades ago.In the next phase of economic development transportation, especially by means of lorries and cars becomes a determining factor in local air pollution and cause high concentrations of ozone, peroxyacetyl nitrate (PAN) and other oxidants are present as secondary products of traffic emissions. A number of developing countries are now entering the stage when this "Los Angeles" type of smog starts to become an important environmental problem. Developing countries should benefit from transfer of knowledge obtained in research programs and development of abatement policies in countries, which have been exposed to these problems in the past. But exchange of ideas between developing countries, regarding assessment of air pollution and implementation of emission controls is also very useful to derive optimal abatement strategies.

CONTENTS

INTRODUCTION

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The problem

Local air pollution is one of the most pressing environmental problems in developing countries. The perception in many developing countries is that large-scale and global problems are obviously important and that they should receive attention, but that the highest priority should be given to the solution of the local environmental problems. This point of view of the developing countries is easy to understand. The need for fast economic development as a basis for better living conditions in general, is so pressing in many countries that environmental issues are perhaps not taken lightly but do not always get sufficient attention.

On the other hand, the awareness is increasing that an unbridled economic development can result in such extensive damages to human health, to ecosystems and materials, that this environmental impact will impair and at the end even slow down economic development. This situation is encountered in the former East-European socialist countries.

Many developing countries are introducing abatement measures to keep local air pollution problems within certain limits. But in most cases the priorities are clear: Economic development comes first and environmental measures follow later.

The patterns of local air pollution are similar in many countries. In the initial stages of economic development the demand for energy, coupled to economic expansion, rises sharply. This increased consumption of power for heating, electricity, industrial processes etc. must lead to an increase of emissions. Especially if coal is the primary fuel and if no or little measures for emission control are applied, these increased emissions can cause local air pollution problems with smog episodes of the "London" kind. In the period around 1950 severe smog episodes plagued London and the main cause were sulfur compounds, due to large emissions of SO_2. Dust, SO_2 and secondary products like sulphuric acid were responsible for severe impairments of human health and large scale damage to nature and buildings. Many developing countries have reached this stage of local air pollution or will be exposed to this type of environmental hazards in the near future.

Economically developed countries, like the US, Japan and many countries in Western Europe have passed this stage one to three decades ago.

In the next phase of economic development transportation, especially by means of lorries and cars becomes a determining factor in local air pollution. Emission of traffic, mainly Volatile Organic Compounds, nitrogen oxides and CO, play a dominant role in this phase and cause a different kind of smog episodes, the "Los Angeles" type. During smog episodes of this kind high concentrations of ozone, peroxyacetyl nitrate (PAN) and other oxidants are present as secondary products of traffic emissions. Many economically developed countries are confronted with air pollution in the form of photochemical oxidants nowadays. Severe problems are encountered in the US and many countries in Europe. A number of developing countries are now entering the stage when this "Los Angeles" type of smog starts to become an important environmental problem. One could even argue that the transition phase between "London" and "Los Angeles" smog marks different stages of economic development or even the passage from category developing to developed country, expressed in terms of economical status.

Developed countries are still suffering from the impacts of photochemical smog and though abatement measures, ranging from catalytic conversion of exhaust gases in cars to low-NO_x burners, have been taken or are planned, it is still unclear how successful the abatement measures will be in the long run.

Some developed countries, like The Netherlands, have local air pollution problems caused by the large ammonia emissions connected to intensive agricultural activities. Other countries in Western Europe are finding out that they are encountering the same problem. These recent developments in Europe can provide a warning for some developing countries to avoid certain local air pollution problems.

The rationale of this workshop

Developing countries are facing comparable problems in terms of local air pollution. Developed countries have either encountered the same problems in the past or are still in the process, as in the case of photochemical smog, to develop efficient abatement measures. So an exchange of knowledge and expertise should be beneficial for all concerned

parties.
Much of the research on "London" type smog has been carried out quite a while ago in the US and Europe, so much of the information, gained in these studies, is no longer easily accessible for scientists and others, concerned with this type of problem in developing countries. So expertise and experience gained in the past elsewhere should be made accessible for developing countries which are now facing analogous problems. And that is one of the functions of this workshop.
It is evident that developing countries should benefit from transfer of knowledge obtained in research programs and development of abatement policies in countries, which have been exposed to these problems in the past. But exchange of ideas between developing countries, regarding assessment of air pollution and implementation of emission controls is very useful too to derive optimal abatement strategies. Different methods for assessment and emission control are employed in different countries.

Many international organisations are promoting international collaboration in areas of large scale and global pollution. IGBP (International Geosphere–Biosphere Programme) is a good example for the increased international cooperation. But only few international organisations are active in the area of local air pollution. The RAINS program (Regional Acidification Information and Simulation), is one of the exceptions and is engaged in the assessment of acid deposition in South–Asia. IUPAC has always promoted activities, which can contribute to exchange of ideas and collaboration between scientists of the developing countries with their colleagues of the developed part of the world. In this cadre Commission VI.4, Atmospheric Chemistry, has tried to make a contribution in promoting this Workshop on Local Air Pollution in Fast Developing Countries.

LOCAL OXIDANT PROBLEMS AND STRATEGIES FOR THEIR ABATEMENT

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Abstract– The non–linear chemistry, responsible for ozone formation poses problems in developing an optimized abatement strategy. Estimates of emissions are often quite uncertain, e.g. in estimates of biogenic emissions and car emissions. Effective abatement should be based on a careful evaluation of local conditions regarding oxidant formation. Some control strategies are effective in one place, but not in another. A good example offers control by means of limiting of hydrocarbons. This strategy is not effective in regions where large emissions of biogenic hydrocarbons are encountered.

I. Introduction

While ozone **depletion** in the stratosphere has become a major environmental concern, the **build–up** of ozone within the troposphere, particularly in industrialized urban areas, continues to be a problem. The formation of ozone and other oxidants (hydrogen peroxide, organic hydroperoxides, peroxyacetyl nitrate, nitric acid, etc.) is a common phenomenon in densely populated urban centers around the world. There is evidence that the ozone concentration in the troposphere of the USA, Europe, and Japan (**e.g.**, see Kley **et al.**, 1994; Akimoto **et al.**, 1994) is increasing at about 1% per year. Its concentration can be expected to increase in many rapidly developing countries as the demand increases for power production, industrial operations, transportation, and other processes that involve the combustion of fossil fuels. Although rather stringent control measures have been adopted in the USA, unexpected ozone exceedances continue to occur, and there is considerable debate as to why the controls have not been more effective (National Research Council, 1991).

The general features of ozone generation within the troposphere have been identified for many years (**e.g.** Calvert & McQuigg, 1975). However, the non–linear chemistry which is responsible for this phenomenon is sufficiently complex that its representation in models is usually highly simplified, and both meteorological data and precursor concentration information necessary to compare an observed episode with theory are rarely available to allow a definitive test of our understanding.

II. The mechanism of oxidant generation in the polluted troposphere

Ozone is a naturally occurring constituent of the troposphere. Natural tropospheric ozone arises from both stratospheric insertions of ozone and generation in sunlight from natural emissions of NO_x from biological sources on land, lightening, forest fires, etc., and hydrocarbons from trees, vegetation, and other natural sources. However, the relatively large ozone concentrations which are often observed in urban areas of the world today, are obviously generated in large part by anthropogenic input of its precursors. Many studies have demonstrated that key ingredients to the development of ozone and other oxidants within the polluted troposphere are: 1) the oxides of nitrogen (NO, NO_2); and 2) the reactive, non-methane hydrocarbons (NMHC) and their oxidation products (CO, aldehydes, ketones, alcohols, etc.). Ozone generation occurs through the involvement of several key transient species which react rapidly with hydrocarbon to trigger a series of chain reactions. One key transient is the hydroxy (OH) radical, generated through the photodissociation of ozone itself in (1) and the subsequent reaction of the highly electronically excited $O(^1D)$ atom in (2). When O_3 is lost in reaction (1), it can be reformed in (3) followed by (9). In view of these competitive reactions for $O(^1D)$-atoms, for a given $[O_3]$ and solar flux, it is clear that the rate of generation of OH-radicals increases as the concentration of water in the troposphere increases (relative humidity rises). The success of the OH-radical in building ozone lies in its generation of hydroperoxy (HO_2) radical and many organic peroxy radicals (RO_2) through reactions with the great variety of hydrocarbons and their oxidation products; these transformations are generalized in reactions (5–7):

(1) $O_3 + h\nu\ (\lambda<330\ nm) \rightarrow O(^1D) + O_2$
(2) $O(^1D) + H_2O \rightarrow 2OH$
(3) $O(^1D) + N_2, O_2 \rightarrow O(^3P) + N_2, O_2$
(4) $OH + RH\ (+ O_2) \rightarrow H_2O + RO_2$
(5) $RO_2 + NO \rightarrow RO + NO_2$
(6) $RO + O_2 \rightarrow HO_2$ + Aldehyde or Ketone
(7) $HO_2 + NO \rightarrow OH + NO_2$
(8) $NO_2 + h\nu\ (\gamma<430\ nm) \rightarrow O(^3P) + NO$
(9) $O(^3P) + O_2\ (+ N_2, O_2) \rightarrow O_3\ (+ N_2, O_2)$

In this reaction sequence, RH reaction with OH, generates RO_2 and HO_2 radicals which oxidize NO to NO_2, and through NO_2 sunlight photolysis in (8) followed by (9), newly regenerated NO_2 develops **new** ozone. Note that in reaction (7) a **new** OH radical is formed to replace the one which reacted in (4), and the repeat of the entire sequence can occur again and again until the HO, HO_2 and RO_2 radicals are removed by chain terminating processes; reactions (10–12) are the most common of these:

(10) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
(11) $HO_2 + RO_2 \rightarrow RO_2H + O_2$
(12) $OH + NO_2 \rightarrow HONO_2$

In an atmosphere which is highly polluted in NO_x ($[NO_x] = [NO] + [NO_2]$), the number of molecules of ozone formed per NO_x removed is much less than that obtained in less polluted atmospheres (Liu **et al.**, 1987; Lin **et al.**, 1988). When one considers the reactions of the many hundreds of different individual hydrocarbons present in an urban atmosphere, the few generalized reactions above mushroom into many thousands of compound-specific reactions all of which contribute to ozone development, each individual hydrocarbon with it own characteristic efficiency. It is clear that modeling such systems with a precision which can duplicate reality, is a difficult task. Yet this is what is demanded in the development of advanced oxidant control strategies.

Smog chamber experiments have provided much useful information on ozone generation in relatively simple RH-NO_x systems (**e.g.**, see Carter **et al.**, 1979). However, information from such systems, especially those containing complex mixtures of hydrocarbons, is of limited usefulness for several reasons: 1) extrapolation must be made of the smog chamber results to derive those expected for the much lower atmospheric concentrations of reactants; and 2) it is necessary to correct the chamber results to remove effects of wall-sources of free radicals, peculiar to the smog chamber, yet unimportant in the troposphere.

It has been possible to check key aspects of the ozone generation through detailed measurements within the troposphere itself. Simultaneous measurements of most of the trace gases have been made in several field studies, including the transient OH, HO_2 and RO_2 free radicals which drive the oxidant generation. Since the lifetimes of the radicals are short (seconds to minutes), their rates of formation and their rapid chemical reactions alone determine their concentrations; meteorology and transport are unimportant for these systems. It appears from such studies that the theory outlined here is sound, and matches between measured and theoretical radical concentrations are often within the uncertainties in the measurements (**e.g.**, see Cantrell 1993). However, the results show as well that some uncertainties in the details of reactions in the polluted atmosphere remain unexplained. Modeling the development of ozone, a much longer lived atmospheric component than the transient free radicals offers much greater challenges, since emissions, deposition, and meteorology, as well as the complex chemistry, must be incorporated into the modeling scheme (**e.g.**, see Seinfeld, 1988).

III. The development of control strategies for tropospheric oxidant

Choice of control strategies always involves some compromise between the complete protection of the health of every person (zero risk), injury to crops, ornamental plants, animals, and materials, and the economic costs of the possible control measures. Such choices are inevitably political judgments that should be built upon sound scientific inputs that define the extent and severity of the pollution problem as well as alternative control strategies. These are considered briefly here.

a) **Is there a problem?** Usually the answer to this question is evident. Urban smog, including high ozone levels, has many characteristics which give strong indications of a problem. There are recognized health problems associated with high oxidant levels (**e.g.**, see Bates, 1994). Certain sensitive plants and crops may show serious damage or diminished yields as oxidant levels (O_3, peroxyacetyl nitrate, etc.) climb. As early as 1958 bioassays of bluegrass and pinto bean in the Los Angeles area were used to judge the extent of the oxidant problem; **e.g.**, see the review of Heck & Brandt (1977). High oxidant levels are usually accompanied by the presence of haze resulting from light scatter from aerosols which are formed in part by condensation of the less volatile, SO_2 and hydrocarbon oxidation products formed in ozone-rich, polluted air masses.

Estimates of the severity of an existing problem and development of control strategies require a knowledge of the concentrations of O_3 and its precursors as well as the major sources of the precursors. This information is best gained through direct measurements of the concentrations of several key pollutants and trace gases: nitrogen dioxide (NO_2), nitric oxide (NO), ozone (O_3), water vapor (H_2O), the hydrocarbons and their oxidation products [carbon monoxide (CO), formaldehyde (CH_2O), etc.]. Simultaneous measurements should be made of the meteorological variables (temperature, pressure, mixing height, wind speed and direction) as well as the solar flux ($\lambda < 430$ nm) which is important in the photodissociation of NO_2, CH_2O, H_2O_2, CH_3O_2H, O_3 and other light-absorbing compounds in the troposphere. One other parameter should be measured: $[NO_y]$, the sum of the concentrations of all of the reactive nitrogen compounds $\{([NO] + [NO_2] + [HONO_2] + [PAN] + 2[N_2O_5] + [RONO_2] \ldots\}$ (Fehsenfeld **et al.**, 1987; Trainer **et al.**, 1993). $[NO_y]$ is useful in identifying the age of a sampled air mass, its ozone generating ability, and a useful indicator of the most effective precursor to control to reduce ozone (Milford **et al.**, 1994); see section IId.

b) **What are the major sources of oxidant precursors in the area?** An emission inventory of all the major sources should be prepared in order to pinpoint the major sources of the measured pollutants, both stationary and mobile, and to help determine the extent of control that will be necessary for each. Especially important to the development of ozone control strategies is the determination of the nature and the extent of all sources of emissions [NO, NO_2 (NO_x), and the reactive hydrocarbons including both anthropogenic and biogenic hydrocarbons, isoprene, α- and ß-pinenes, etc. and their oxidation products (aldehydes, ketones, CO, etc.)]. Counts of traffic flow, power consumption, and other emission activities as a function of time, day of the week, season, and physical location (gridded) will be required in the proper use of these data. Measurements in addition to those at surface monitoring sites are necessary to establish the vertical distribution of ozone and its precursors.

c) **Are the emissions expected from the inventory consistent with those observed?**
There should be a rough mass balance between the emissions of the longer-lived pollutants (less reactive hydrocarbons, NO_y, SO_2, etc.) and those found by analysis (taking into account the proper dilution, etc.). The observed $[NMHC]/[NO_x]$ ratios (for early in the day) should be in rough accord with those estimated from the emissions inventory. If there are striking discrepancies, the source of the problem should be found and corrected.

Experience from scientists and engineers in many countries shows that emissions estimates from mobile sources (cars, trucks, etc.) which are often based upon dynamometer tests using a selected driving cycle, can underestimate the real emissions of these vehicles when they are operated as they usually are, on the streets and highways. It has become increasingly apparent that most of the mobile source emissions are caused by small percentage of the vehicles. In many of the major cities in the USA, about 50% of the CO and NMHC emissions come from 10% of the vehicles (Stedman **et al.**, 1991). Remote sensing of the CO/CO_2 or hydrocarbon/CO_2 ratios can be measured using infrared beams which scan the exhaust plumes of passing vehicles. It appears that the largest immediate impact which can be made on the reduction of ozone precursors often may be in identifying, removing or repairing the broken vehicles which are the "high emitters". Integrated sampling procedures can also provide checks on the mobile fleet inventories, and they can also be good indicators of inventory problems. **E.g.**, the air accumulated in tunnels can be used to check the quality of the mobile fleet emission inventory (**e.g.**, see Pierson & Gertler, 1992).

d) **What is the best strategy for controlling ozone in the area?** Since both NO_x and the NMHC are important reactants in the generation of urban and rural ozone, it appears logical that the reduction of either or both will result in a lowering in the ozone production. Although this is normally true, in the case of very high NO levels in an urban atmosphere, the ozone generation can be suppressed locally with further increase in [NO]. A program to control ozone build-up in large urban areas of the rapidly developing countries will necessarily include the development of regulations to control emissions from both mobile and stationary sources. Clearly there are disadvantages and large economic costs involved in switching from a transportation scheme dominated by pedestrian and bicycle traffic to one involving large mobile fleets with internal combustion engines. As a logical start to any such programs, there should be encouragement to use relatively pollution-free transportation sources; clearly the use of RH- and NO_x-catalyst-equipped vehicles is favored over the uncontrolled use of small motor scooters with operating cycles which often have very high emissions. Use should be made of relative clean fuels; emissions controls may be required for power plants, chemical manufacturing, and home fuel in order to achieve the desired suppression of precursor and oxidant levels.

Some qualitative judgments can be made from pollution inventories and ambient air analyses which have been performed, and some initial decisions can be made as to the precursors for which control will be most effective in lowering the ozone. In the USA, control strategies were originally based largely upon diagrams which related qualitatively non-methane hydrocarbon and NO_x early morning measurements to peak ozone development during the day (**e.g.**, see Finlayson-Pitts & Pitts, 1993). There are problems determining a unique ratio of [reactive hydrocarbons]/[NO_x] applicable to an actual air basin, but the qualitative concept of the sensitivity of ozone generation to this ratio is useful (see Milford **et al.**, 1989). Control strategies in the United States and in many other countries originally focused on the reduction of the hydrocarbons, largely because this appeared to be the most cost effective method of ozone control. However in some areas where trees and other natural vegetation are very abundant and average temperatures are high (**e.g.**, in the southeastern United States), a large fraction of the ozone generation is derived through the reaction of OH radical with isoprene and other hydrocarbons emitted from trees and other natural growth. In these cases control of the anthropogenic hydrocarbon input can be an ineffective and wasteful control strategy (Chameides **et al.**, 1988; Cardelino & Chameides, 1990), and NO_x control should be much more effective.

Important guides to decisions on the necessary controls can be had from studies such as that by Sillman **et al.**, 1990. Some qualitatively useful information on alternative control strategies is also presented by Milford **et al.**, 1994 and Liu **et al.**, 1994 and other references in these studies. E.g, for the representative polluted conditions which Liu **et al.** (1994) considered, their results show that near urban and some suburban areas a given fractional reduction of NMHC is a more effective strategy for controlling ozone build-up than the same fractional reduction of NO_x. However, beyond urban areas, NO_x reduction is about four-times more effective than NMHC reduction. These appear to be very common scenarios for US cities, but in some areas, dominated by biogenic hydrocarbon emissions (presumably, Atlanta and some other cities in the southeastern US), NO_x controls may be more effective. Liu **et al.** point out that for the typical case of relatively low [NMHC]/[NO_x] ratios, the limiting precursor of photochemical ozone production gradually shifts from NMHC in urban areas to NO_x in the rural areas (see also McKeen **et al.**, 1991). When both NO_x and NMHC emissions are reduced, the resulting ozone decrease is approximately equal to the sum of the individual values. Therefore, they conclude, that the most effective control strategy is to reduce both emissions. They caution, however, that the average reduction of ozone over a large domain is only about 12% when both NO_x and NMHC are reduced by 50%. Note that there is a far less than linear response. In control strategy development, this inefficiency in precursor control in lowering the extent of ozone build-up must be remembered.

Recent modeling studies (Milford **et al.**, 1994) suggest that [NO_y] can be a useful indicator of the best choice of precursor to control. For episodes in which the meteorological conditions were conducive to high ozone concentrations (conditions of strong inversion and air stagnation), ozone is predicted to be most effectively reduced by NMHC controls at locations where NO_y concentrations exceeded a threshold between 10 and 25 ppbv, whereas NO_x controls were more effective where NO_y concentrations were below this threshold.

If appropriate scientific personnel and the necessary funding are available in a given rapidly developing country, a less ambiguous answer to the question posed in this section, specifically tailored for the measured local precursor concentrations and meteorology, can be had combining the emissions data, meteorological data, and the ambient trace gases measurements in a suitable chemical-transport model of the particular area under study. Although this is an expensive and scientifically demanding task, the answers obtained will have the scientific credibility that we seek in solving complicated problems, provided that the experimental input data to the model are reliable. In the development of a strong modeling program for air quality management, it is very important that a scientifically sound and well-documented 3-dimensional model (Seinfeld, 1988) be adopted to account in a realistic manner for the chemistry and meteorology that applies to the area.

e) **How is acceptable air quality maintained?** The continued use of either the same monitoring network employed in the original ambient air sampling studies [outlined in section IIIa], or an improved network designed to obtain more representative air samples throughout the area, will continue to provide the needed information to monitor the degree of control which remains operative. The establishment of inspection and maintenance programs are a key to detecting and correcting deteriorated mobile sources. This may include static tests on dynamometers, and/or remote sensing measurements of the mobile fleet in operation.

The problems which are encountered as scientists attempt to achieve some prescribed "acceptable air quality" are many. This has been particularly true in the history of our attempts to reach acceptable ozone levels in the USA. Calvert **et al.** (1993) have reviewed this progress recently, and their discussions of alternatives for further improvement may prove useful to those in the rapidly developing countries who are assigned responsibility for developing urban and regional ozone control strategies.

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NATURAL HYDROCARBON COMPOUNDS EMITTED FROM VEGETATION IN CHINA

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Abstract - The emission of terpenes and isoprene from 15 types of trees, bamboo, grass and paddy rice have been measured by means of the enclosure sampling method and GC-FID analysis. The measurement results show a diurnal and seasonal variation of the emission with peaks at noon and in summer months, which are closely related to temperature and irradiation. Average emission rates for Pine, Cypress, Poplar and Scholar, the primary trees in Beijing and China, are measured to be 2.7, 0.009, 4.7 and 1.3 $\mu g.g^{-1}h^{-1}$ respectively. Annular amount of HCs emitted from the 4 type of trees are estimated to be $9.1x10^3$ and $8.3x10^6$ for Beijing city and China respectively.

Introduction

It is known that many volatile organic compounds found in ambient air, including isoprene and a series of terpenes, are mainly emitted from vegetation. These natural hydrocarbon compounds (NHCs) play an important role in the formation of photochemical oxidants such O_3 and PAN, are a significant part of the global carbon cycle, and contribute significantly by way of organic acids to acidic deposition in rural and urban areas according to recent findings. On regional or global scales these biogenic non methane organic compounds emissions may dominate over anthropogenic emissions (Zimmerman et al., 1978, 1988; Lamb et al., 1987).

China started research of NHCs emission from vegetation in different cities and areas in 1990. The emission rates of 10 different kinds of tree were measured and the annual emission amounts over the Beijing area and China were estimated as well.

Experimental

Sample method

Three different sampling methods for the measurement of NHCs emission rates in the world have been confirmed recently to be reasonably consistent (Zimmerman 1979, 1981; Lamb et al, 1985 and 1986). In this study, one of these methods - an enclosure technique developed by Zimmerman - was used by means of a polyethylene bag with a diameter of 1 m and a length of 1.5 m, placed around a living branch of known biomass. The NHCs air samples accumulated in the bag are pumped into a canister after a fixed interval and taken back to the laboratory for analysis. During the period of sampling, temperature and irradiation were also measured (Fig. 1).

Analysis procedure

The samples were determined using a Varian 3400 GC-FID with a capillary column and temperature programming (from 0°C for 5 min to 200°C at 3°C/min) after being pre- concentrated at -50°C in a trap of the GC. The compounds in biogenic emissions are identified by matching of retention times in the GC-FID analysis, and confirmed by retention time and mass spectrum matching in the GC/MS analysis, which was performed by USEPA.

Quantification methods were based on GC-FID peak area with n-pentane as standard sample (10.5 ppm, ± 2%).

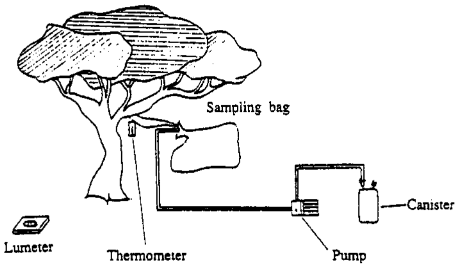


Fig. 1. Biogenic sampling system (Reference: Zimmerman 1979)

Calibrations of the instruments were carried out frequently with n-pentane and a series of liquid standard terpene samples, including: ß-pinene, carene, α-terpinene, limonene, and ocimene. The calibration curves for pentane and terpenes show adequate precision (Fig. 2.). Good linearity for chromatographic calibration was obtained by means of the least squares method, which shows the performance of this apparatus and the reliability of measurements results.

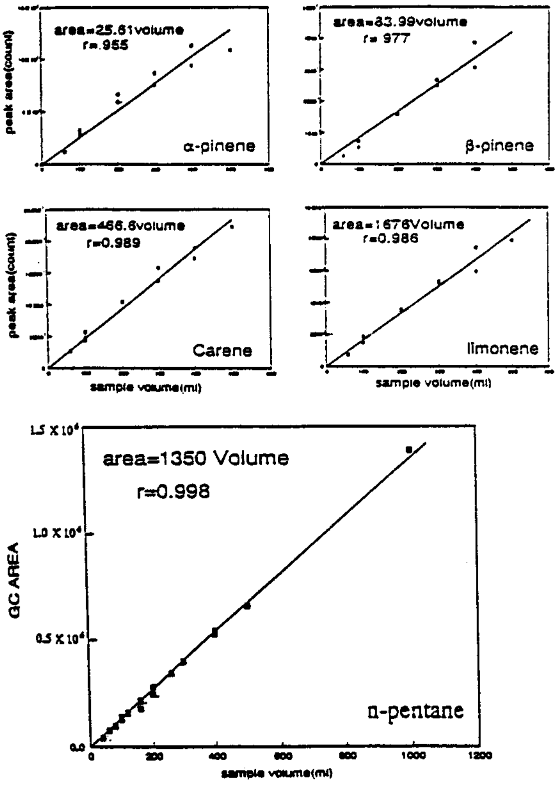
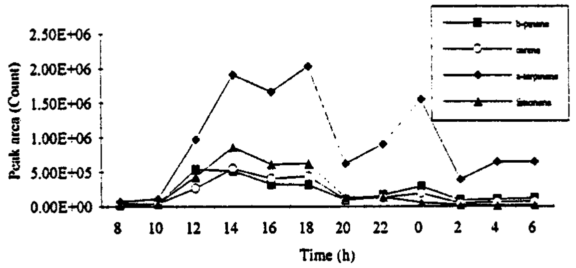


Fig. 2. The calibration curves for GC peak area vs. sample volume



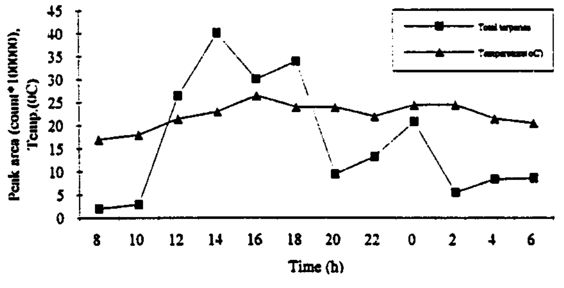


Fig. 3a. Diurnal variation in the concentration of terpenes and Temperature (14/5, 1991)

Fig. 3b. Diurnal variation in the concentration of total terpenes and temperatures (14/5, 1991)

Results and discussion

1. The qualitative determination

13 types of tree, which have been planted commonly in Beijing and other areas of China, were chosen for this study; additionally, the emissions from paddy fields, meadows, bamboo and apricot trees were investigated.

The emission pattern of NMHCs from vegetation in China is generally consistent with those reported in literture (C. Anastasi et al., 1990). Isoprene is mainly emitted from coniferous trees, and terpenes mainly from deciduous trees. The emissions from paddies and meadows are in accordance with other reports. Bamboo and apricot trees were investigated and showed no detectable emissions. It is interesting that the blossoms of the scholar tree only emit terpenes rather than isoprene, of which ß-pinene and limonene were the main compounds and accounted for 32.2% and 38.3% respectively of the total emissions.

2. The measurements of emission rates

The emission rates of 10 different trees were measured in this program and calculated by the following equation:

$$Emissionrate(\mu\cdot g^{-1}h^{-1}) = \frac{40.9\ (C_i\ M\ V)}{W\ t}$$

Where, 40.9 is the conversion factor from ppm to $\mu g/m^3$, C_i: concentration (ppbv) increment of i species emitted by plant in sampling bag, M: molecular weight of i species (M=68 for isoprene), V: gas volume in sampling bag(m^3) W: biomass of leaf (wet weight) t: sampling time (h). The average emission rates and the total biogenic emissions are listed in Table 1.

Table 1. Mean NHCs emission rates from trees in China ($\mu g.g^{-1}h^{-1}$)

Type of tree	No.	temperature range (°C)	Major compunds ($\mu g \bullet g^{-1}h^{-1}$)	Average rate ($\mu g \bullet g^{-1}h^{-1}$)	Total emission rate ($\mu g \bullet g^{-1}h^{-1}$)
Snow pine	9	18-27	Sabinene	0.036	
			Carene	0.024	
			α-terpinene	0.11	
			Limonene	0.026	
			Ocimene	0.02	0.22
Black pine	5	19-27	isoprene	0.22	
			α-pinene	0.02	
			β-pinene	0.04	
			Sabinene	0.43	
			Carene	1.2	
			α-terpinene	6.0	
			Limonene	2.4	
			Ocimene	0.6	10.8
Oil pine	7	15.0-20.8	Sabinene	0.15	
			Carene	0.31	
			α-terpinene	1.75	
			Ocinene	0.5	2.7
Cypress	20	0-27.1	Carene	0.0001	
			α-terpinene	0.0006	
			Ocimene	0.0018	0.009±0.019
Metasequoia	5	19-28	Carene	0.24	
glyptostroboides		α-terpinene	2.65		
			Limonene	0.16	
			Ocimene	0.16	4.1
Poplar	8	16.8-21.3	Isoprene	4.7	4.7
Scholar	17	15.7-27	Isoprene	1.24	1.3±0.34
French Parasol	10	23-28	Isoprene	23	23

3. Diurnal variation

The determinations of diurnal variation of the emissions of isoprene from poplar and terpenes from oil pine were carried out in Beijing on 8-9 May 1991 and 15-16 May 1992 respectively. Fig. 2 and 3 show the diurnal variation of each HC compound. Obvious differences have been found not only between the NMHC species emitted by the two trees but between the diurnal variation patterns as well. Oil pine emits terpenes day and night, and two emission peaks can be found during noon and midnight, with a much larger peak at noon than that at midnight. Poplar emits isoprene only during the day time. The emission peak value of isoprene appeared at noon when the atmospheric temperature and the irradiation were the highest over the day.

4. Seasonal variation

The monthly and seasonal variation of NHCs emission rates from both about 10 year old cypress and scholar trees were determined one day per month during a whole year period (June 1992 -April 1993). Environmental factors such as temperature, humidity and irradiation were monitored outside the sampling bag. The detected monoterpenes from cypress were α- and ß-pinene, carene, limonene, α-terpinene and ocimene. Table 2 shows the results. It can be seen that throughout the study period of one year, no significant difference was found in the terpene composition pattern, however, the emission rates of each monoterpene, varied greatly from month to month and from season to season. The values during fall and winter months were relatively low with little variation, in contrast to the results obtained in spring and summer. Peak values appeared in June, which were almost 100 times as high as the value in winter time.

Table 2. The seasonal variation of terpene emission from cypress ($\mu g \bullet g^{-1} h^{-1}$)

Date	6/30/1992	9/22/1992	10/07/1992	11/20/1992	12/15/1992	3/13/1993	4/23/1993
No.	3	3	5	2	1	3	2
Temp.	23-27	19-21	12-15	0-1.8	4	6-11	17-18
Light flux (lux)	115-315	82	92	30	23	24-149	65-70
α-pinene	3.0	0.04	0.04	0.02	0.005	0.12	0.28
β-pinene	2.4	0.11	0.04	0.015	0.01	0.22	0.86
carene	10.9	0.62	0.008	0.02	0.005	0.29	1.46
limonene	8.4	0.34	0.1	0.02	0.01	0.18	1.30
α-terpinene	6.7	0.82	0.19	0.015	0.015	0.11	1.19
ocinene	21.1	0	0	0	0.035	0.25	2.06
total	52.5	1.93	0.39	0.08	0.085	1.19	7.17

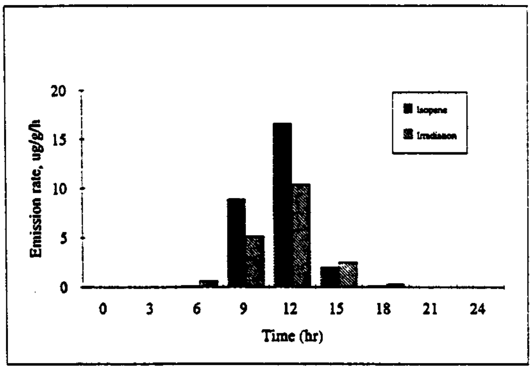


Fig. 4. Diurnal variation of Isopene from Popular

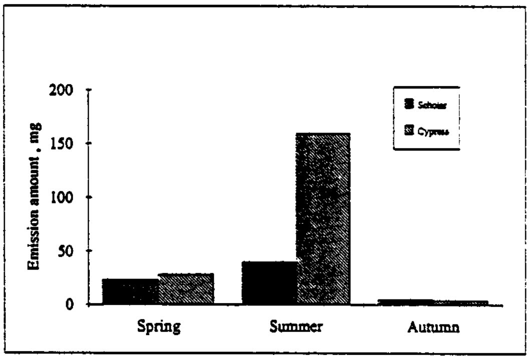


Fig. 5. The seasonal variation of NHC from trees

The emission rates of isoprene from scholar trees also showed obvious seasonal variation (see Table 3 and Fig. 4). The highest emission was during summer time; lower in spring and fall. No emission occurred during winter due to loss of leaves.

Table 3. The emission rate of isoprene from scholar tree in different seasons ($\mu g \bullet g^{-1} h^{-1}$)

Date	Sampling time	No.	Temp.(°C)	Ira.(Lux)	Emission Rate
05/07/92	08:20-09:35	5	18.4-21.3	84-206	1.24 ± 0.30
05/14/92	14:22-15:37	5	25.6-26.0	119-162	0.87 ± 0.34
07/02/92	08:30-10:00	6	25.3-27.0	126-292	2.30 ± 0.50
09/28/92	08:40-10:45	5	15.7-19.4	61-110	0.79 ± 0.20

5. The initial estimation of total emissions amount of natural HCs

The total biomass (dry) of the leaves of a tree can be calculated by following empirical equations summarised by Kittredge and Cable early in 1940's and 1950's:

$$\log w_l = 1.67 \log D - 1.85 \qquad (1)$$
$$\log w_l = 1.89 \log D - 1.58 \qquad (2)$$

w_l: leaves weight of a tree (kg); D: the diameter of trunk (cm)

We tried to estimate the biomass of a tree not only for deciduous but also for coniferous by following equations:

$$W_t(\mathrm{kg/m^3}) = W_u(\mathrm{kg/m^3})\ V(\mathrm{m^3})\ f \qquad (3)$$

Where, W_t: weight of total tree's leaves (wet leaf weight), W_u: weight of unit volume (1 m^3) of tree crown, V: total volume of tree crown (m^3), f: the conversion coefficient from wet biomass to dry, 0.2 for deciduous, 0.5 for coniferous.

If the area of a forest is known, the total volume of the forest crown can be estimated by the product of area times average height of the tree. The results calculated by using the above three equations agreed for the same trees, which demonstrates the possibility estimating the total emission amount of NMHCs with equation (3).

Beijing is located in forty degrees north latitude, the north-west edge of Huabei plain in China, the annual average temperature is about 11.5°C, the illumination is 2600–2800 h./a. Oil Pine, Cypress, Popular and Scholar tree are the main type of trees, their annual emission amounts are estimated to be about $5.1\mathrm{x}10^3$,51,$1.5\mathrm{x}10^3$ and $3.0\mathrm{x}10^3$ T/a respectively, so the total emission amount by the four kinds of tree is perhaps $9.7\mathrm{x}10^3$ T/a. The area of forest in Beijing accounts for 0.12% of the area in China, therefore a first order estimate of the total emission amount of NHCs are about $8.3\mathrm{x}10^6$ T/a for China.

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MEASUREMENT OF EXPOSURE TO LOCAL AIR POLLUTION

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The problem

Exposure to air pollution has to be defined as a function of possible hazards or damage.

Damage, due to acid deposition and eutrophication is a function of the load (the integrated deposition flux) of pollutants. Calculation of loads includes the contribution by wet and dry deposition processes. Estimates of wet deposition near local sources cannot easily be derived from measurements made at larger distances from these sources. Very local wash-out of components like hydrochloric acid and hydrofluoric acid, e.g. in the case of coal-fired plants, can change the pattern of wet deposition considerably. Dry deposition fluxes of pollutants near sources can be influenced by the accumulation of compounds on the surface of vegetation or materials. Evidence exists that the surface resistance for sulfur dioxide increases at higher ambient concentrations. Factors such as surface wetness and co-deposition of compounds can influence deposition fluxes to such an extend that simple first-order estimates can produce errors of 100 % and more.

The present state of knowledge does not permit on estimate dry deposition fluxes on buildings, as they represent extremely "in-homogeneous terrain". The enhanced turbulence near buildings will cause high deposition fluxes, but it is difficult to make trustworthy estimates of the loads of pollutants under these conditions.

Enhanced wet deposition under plumes of coal-fired power plants

The contribution of plume wash-out to the wet deposition of pollutants in the vicinity of a 1000 MW coal-fired power plant in The Netherlands has been investigated. 50 open collectors were placed in an arc, encompassing (an arc of) about 55° north-east of the power plant at a distance of 3.5 to 7 kilometres, see fig.1 (ten Brink et al., 1988). The collectors consisted of a polyethylene funnel and bottle, placed in a polyethylene holder. The collectors were put in place just before the onset of a precipitation event and the samples were collected as soon as possible after the end of the event, but were not exposed longer than 12 hours.

A significant wash-out of chloride, fluoride, H^+ and boron compounds out of the plume was observed for all experiments. No significant sulfite depositions were observed under the plume.

In the model calculations use was made of MPADD (Multi-Pollutant Acid Deposition and Depletion model); a framework for plume wash-out calculations in which specific scavenging processes can be incorporated. It has been adapted and modules have been added describing the scavenging of the most important pollutants found in our experiments (SO_2, HCl, HF and boron compounds in gaseous form and elements found in the particulate phase like Al and Ba). The general properties of the model are:

- Gaussian plume dispersion, including plume rise over the first few kilometres from the source;
- Plume depletion by dry deposition according to the source depletion concept;
- Plume depletion by wet deposition derived from wet deposition fluxes at a number of crosswind locations, for increasing downwind distances. These fluxes are derived from pollutant concentrations in raindrops of different sizes and the contribution of these drops to the rain rate. Concentrations in individual raindrops falling through the plume are calculated by determining pollutant absorption/desorption processes and chemical reactions inside the drops;
- Background concentrations in the gas-phase and in precipitation can be specified for individual pollutants.

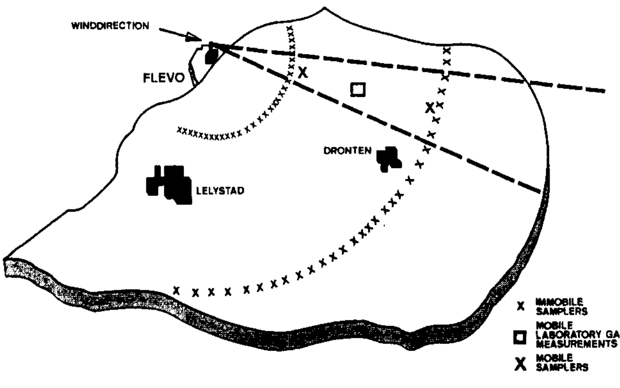

Fig. 1. Plume washout experiment

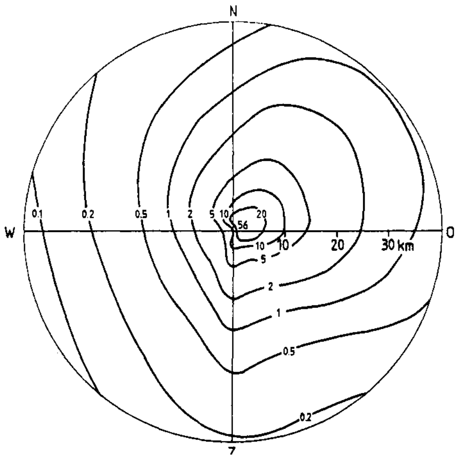

Fig. 2. Enhanced deposition in moles per m^{-2} per year of fluoride

Whereas the extra wet deposition of heavy metals, emitted in the form of fly-ash, is not of importance as compared to the background deposition, drastically increased wet deposition of chloride, fluoride (fig. 2) and especially boron compounds was observed. Little extra deposition of sulfur compounds was found, due to the fact that increased acidity in precipitation, associated with wash-out of hydrogen chloride and, to a lesser extent, hydrogen fluoride, limits the uptake of sulfur dioxide. These contributions depend on the chemical composition of the coal used, which in this case contained relatively little fluoride and chloride.

At short distances plume wash-out may double local acid deposition under conditions prevalent in The Netherlands. This is mainly the result of wash-out of HCl, whereas the contribution of SO_2 is negligible. Significant plume contributions to the depositions of HF and boron compounds may also be expected. Application of desulfurization units ("scrubbers") will reduce the emission and deposition of acids.

Complications in estimates of dry deposition fluxes near sources

The uncertainties in the estimates of the load by dry deposition are quite high (40 to 100%) under all conditions. These uncertainties are partly caused by insufficient knowledge on the parameterisation of dry deposition processes in general, but also complications near sources can be quite important. If the best possible instrumentation is applied during extended periods, general parameterization of surface resistances, needed to procure better descriptions of depositions in Europe, is in principle possible. Recently results were presented of flux measurements in The Netherlands, which allow the determination of governing parameters for parameterization of surface resistances of NH_3 and SO_2. This parameterisation can be expressed in the form of resistances and the deposition flux can be expressed as function of these resistances:

$$F(\mathrm{dep}) = C(\mathrm{amb}) \times \left(1/(R_a + R_b + R_c) \right)$$

F is the deposition flux, C the concentration and R_a, R_b and R_c represent resistances of turbulent transport in the atmosphere, transport through the diffusion layer near the surface and deposition on the surface.

During episodes with high relative humidity (see fig. 3) water layers on vegetation are present, which are a very good sink for both SO_2 and NH_3 at low concentration. If the water layer is not present, the surface resistance is much higher. If either an acidifying or basic compound is available in very high concentrations, the change in the pH of the water layer will inhibit further uptake of this compounds. These findings explain the different surface resistances observed in flux measurements of SO_2 and NH_3 at different locations in Europe. Measurements of SO_2 fluxes in Southern Europe indicate surface resistance for vegetation, which results in deposition velocities in the order of 0.5 to 0.8 cm s^{-1}. Measurements in Germany seem to indicate higher values, in the order of a deposition velocity of about 1 cm s^{-1}, while very high values up to 1.3 cm s^{-1} are found in The Netherlands. The conclusion is that the existence of

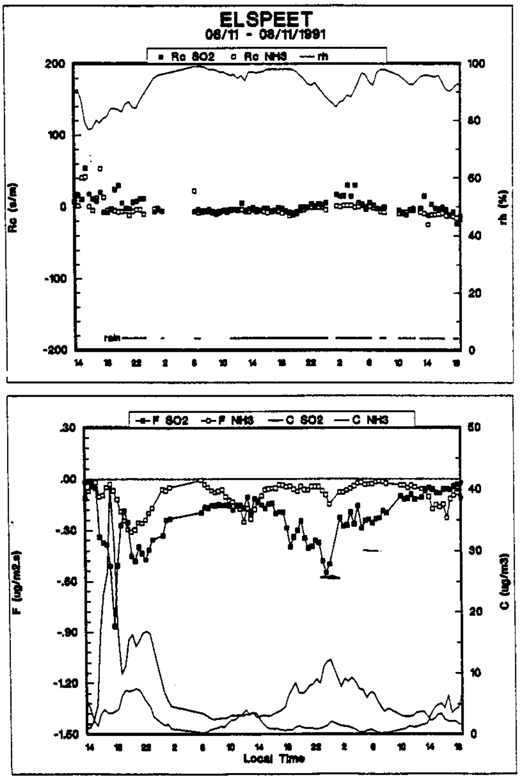

Fig. 3. SO_2 and NH_3 deposition

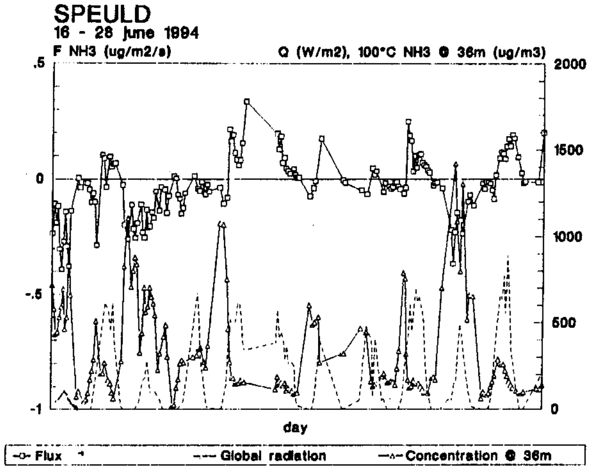

Fig. 4. Reemission of ammonia

surface water layers, more abundant in The Netherlands compared to Southern Europe, are responsible for the phenomenon that the same SO_2 concentration in the air leads to differences of a factor three in loads, depending on the location.

The same results indicate that dry deposition fluxes at high ambient concentrations near sources are reduced, probably by changes of the surface due to chemical interactions. In the case depicted in fig. 3, high SO_2 loads have probably generated so much acidity in the surface water layer that further uptake of SO_2 is clearly hindered. The surface resistance Rc rises considerably at higher SO_2 concentrations and leads to serious overestimations of the deposition load if the assumption is made that the surface resistance is more or less independent of the ambient concentration, as usually is done in this type of calculation.

Another important source of error can be re-emission of deposited pollutants, as represented in fig. 4. Forests, exposed to high loads of ammonia, re-emit ammonia during conditions of relatively low ambient concentration and low humidity. In fact emission of ammonia was found during 30% of the measurement period, which was more than one year. This results indicate that an error of 50% can be easily made if this phenomenon of re-emission is not taken into account for the relevant substances.

Enhanced dry deposition on buildings and monuments

Dry and wet deposition on a church tower at Schagen, The Netherlands, was estimated by means of sampling with exposure panels, located at a height of 20 m on the West and East side of the tower during a pilot study of seven months. These panels contain several test stones and the run-off water was collected for each stone separately, see figure 5. The run-off samples were analyzed for: Cl^-, NO_3^-, NH_3^+, SO_4^{*} and major cations.

After the exposure period of seven months, the depth of weathering of the stone samples was studied by grinding off layers of 1 mm at different depths and analysing the chemical composition as a function of depth. Gradients of sulfate, nitrate, and chloride were found in the investigated stone, consisting of calcium carbonate, indicating weathering of the stone due to reaction with deposited pollutants.

The concentrations of gaseous HCl, HNO_3, NH_3, SO_2 and Cl^-, NO_3^{--}, NH_4^+- and SO_4^{2-}-containing aerosols in air were measured during this field experiment. Precipitation was sampled by means of bulk and wet-only samplers. The sum of total flux measured in the run-off water plus accumulation in the stone minus the wet deposition flux observed in the precipitation samplers provides an estimate of the dry deposition flux on the stones of the panel.

The conclusion of the experiment was:

(1) Passive sampling by means of exposure panels and analysis of the run-off water is a simple method to estimate the total deposition on buildings or monuments;

(2) Dry deposition contributes more than 80% of the total pollution load on this investigated church tower;

(3) As a result of the increased turbulence around the church tower, dry deposition is increased by at least a factor of 10 compared to lower vegetation and dependant on the characteristics of the material. The results of figure 6 are based on deposition velocities of gases and aerosols of 20 and 2 cm s^{-1} respectively.

(4) On this type of stone (consisting mainly of calcium carbonate) dry deposition fluxes of acidic compounds as SO_2 and HNO_3 is enhanced more that the load of basic compounds, such as ammonia. So local circumstances have a strong influence on enhanced deposition on buildings. Simple extrapolations cannot be made under these conditions.

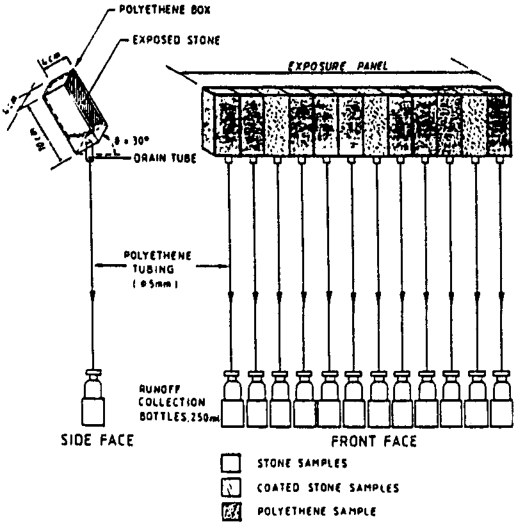

Fig. 5. Exposure panel

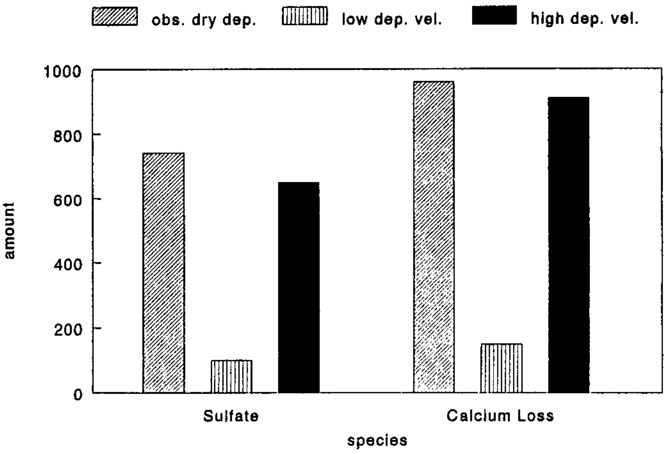

Fig. 6. Dry deposition on stone in mmol m^{-2} in 7 months.

Conclusions

The assessment of wet and dry depositions of pollutants near sources is complicated by a number of important factors.

Enhanced wet deposition under plumes of sources can be assessed if sufficient knowledge of these plumes is available.
The estimates of dry deposition fluxes near sources and especially on buildings is still very problematic and extensive research in this area will be needed to reduce this uncertainty to a margin of e.g. 50 %.

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THE USE OF DIFFUSIVE SAMPLERS TO ASSESS LOCAL AIR POLLUTION PROBLEMS

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Abstract- Diffusive samplers, devices which sample air controlled by diffusion processes and not by means of pumps, can offer attractive possibilities for monitoring ambient air. Comparison of passive samplers with commonly applied monitors indicates that passive samplers can provide cheap methods for ambient monitoring. But insufficient work has been performed to optimise the methodology and to validate the results for most compounds.

Diffusive monitors have been used for workplace air monitoring for many years, and in many cases have been found to be valid and cost-effective alternatives to conventional pumped or active samplers. Potentially, similar or adapted devices could be used for assessing local air pollution problems and in a very few cases (mainly for nitrogen dioxide) are already being used. Because of their low cost, they would be particularly useful in developing countries. However, there are some theoretical and practical problems to be overcome before such samplers can be used with confidence. In particular; can samplers be used to measure concentration levels some three orders of magnitude lower than in the workplace; are blanks and sensitivity adequate? Is the sampling rate affected by concentration? What is the effect of ambient air movement? Are there sufficient validation data? Can diffusive samplers measure particulates? This paper examines what is already known from the published literature, reaches some tentative conclusions and indicates some fruitful areas for future research.

A diffusive sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler (Berlin et al, 1986). Currently, such devices are used in a number of designs (charcoal badges, charcoal tubes and sorbent tubes) for monitoring volatile organic compounds (VOCs). Reagent-impregnated media can also be used to monitor compounds such as aldehydes, isocyanates and mercury. However, there have been few applications to date for measuring inorganic gases (there are a few direct-reading gas indicator tubes) mainly because in the occupational environment these gases are acute hazards, and diffusive samplers are best suited to long-term measurement.

Potentially there is a requirement to monitor similar compounds in ambient air, although at much lower concentrations. Within Europe, there are statutory requirements to monitor sulfur dioxide, nitrogen oxides, ozone, black smoke, suspended particulates and lead and there is likely to be a requirementsoon to monitor benzene (amongst other compounds). In principle, diffusive samplers can be used to monitor the first three statutory compounds and also benzene, although currently these are usually monitored in fixed stations with continuously monitoring instruments utilising 'active' or pumped sampling; an expensive option for developing countries.

The technical objections to the use of diffusive samplers for environmental measurement noted in the opening paragraph are discussed fully in a review undertaken by the IUPAC Commission on Atmospheric Chemistry (Brown, 1993). This review concludes that more research is needed into these theoretical aspects and more well-planned and well-executed field trials are needed as part of a validation protocol. To achieve the sensitivity necessary for ambient measurement, diffusive samplers need to be exposed for extended periods - from days to weeks - but this is a convenience if long-term time-weighted average measurements are required. Moreover, large numbers of samplers can be exposed simultaneously, offering spatial mapping to complement continuous single-site measurements. For the moment, therefore, diffusive samplers should be seen as a complementary approach to fixed instruments.

This is not to say that there are no existing comparisons of field measurements taken simultaneously with diffusive and active samplers. One of the earliest comparisons was between Palmes diffusion tubes and a chemiluminescent analyser, monitoring NO_2 levels in kitchens (Atkins, et al 1978). The data are reproduced in Table 1. More recently, Boleij et al have reported a similar study involving 40 comparisons in the range 15 - 229 mg/m^3 (approx. 7 to 100 ppb) where the ratio of diffusive to chemiluminescent result was on average 1.03. However, the range of individual ratios (1.96 to 0.30) indicated some variability in the measurement method(s). Many similar studies have been reported more recently, for example Atkins & Quirino (1990).

Table 1. Comparison of NO_2 levels in kitchens (gas cooker)

House	Duration (days)	NO_2 (pbb)	
		Diffusion tubes	Chemiluminescent analyser
1	5	146	142
2	6	6	7
3	5	93	85

Data on other analytes, however, are scarce. A few references relating to sulfur dioxide, ammonia, organic gases, formaldehyde and ozone are cited in Brown (1993) and a more recent comparison of diffusive (Dräger ORSA-5) and continuous (GC) methods for measuring monthly average concentrations of benzene in urban streets has been reported by Striefler (1993). In the main, the limited data support the validity of the diffusive methods, but also highlight potential problems of calibration, interferences (especially blank levels) and secondary reactions.

In practice, because of the convenience and relative cheapness of diffusive samplers, these devices are increasingly being used even where they have not been properly validated. The main application area is in mapping concentration profiles of environmentally significant pollutants. This is usually at local or regional level, for example the survey of the Victoria area of London (Atkins, 1990a) or the survey of Paris (Atkins & Quirino, 1990). However, it can also be done at street level (measuring spatial profiles across city streets) or at national level, for example over the whole of Great Britain (Atkins, 1990b). All these examples are for NO_2, except for the street survey, which was for benzene (Striefler, unpublished).

In conclusion, the evaluations of the environmental usage of diffusive samplers reported so far are very encouraging, but the diffusive sampling method needs to be put on a firmer technical footing. A research programme is therefore to be implemented at the Health and Safety Laboratory to investigate the technical objections highlighted above, utilising calibrated test atmospheres and varying the exposure parameters (concentration, temperature, etc.) to simulate environmental conditions. A thermally-desorbable tube-type sampler will be evaluated for VOC measurement and a reagent-impregnated badge-type sampler will be evaluated for aldehydes. Field testing of these samplers will also be conducted in parallel with conventional pumped samplers. In addition, area surveys will be conducted in Sheffield in conjunction with the Sheffield Environmental Health Department.

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USING A PRINCIPAL COMPONENT ANALYSIS TECHNIQUE TO EVALUATE RATIOS IN THE NAPAP AREA EMISSIONS

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Abstract - Accurate pollutant emission inventories are needed in regional air quality models for reliable predictions. The NAPAP emission inventories have been prepared for modeling acid deposition and regionally elevated ozone in eastern North America but have rarely been evaluated on a regional scale. In the present paper, to evaluate area emission ratios in the NAPAP inventories, a principal component analysis technique was tested against simulated data and then applied to measurement results at a site in rural North America. The test suggests that the technique is appropriate to derive emission ratios given suitable field data. The area emissions have the following ratios: $NO_y/CO = 0.11 \pm 0.04$, $HCHO/CO = 0.0056 \pm 0.0022$, $HCHO/NO_y = 0.05 \pm 0.007$, and $SO_2/CO = 0.005 \pm 0.003$. In comparison, the first three ratios in the NAPAP area emission inventories are in excellent agreement, but the SO_2/CO ratio is three times higher than the field results.

Statement of the problem

In eastern North America, two prominent regional air quality problems are acid deposition and elevated oxidant levels. To abate these problems and to regulate emissions, two Eulerian numeric models (RADM and ADOM) (1,2) have been designed to simulate the underlying processes. Both models use the NAPAP 1985 emission inventories (3), which consist of three categories of anthropogenic emissions: point sources, mobile area sources, and non-mobile area sources. The accuracy of the inventories affects the performance of the models. For example, it is assumed implicitly that the 1985 emissions are applicable to the present time, although there is evidence that emissions of certain species may be changing. Yet, because of the enormous efforts in compiling the absolute inventories, their validation on a regional scale is difficult at best. Most validation work was carried out on road side in cities (4) or in tunnels (5,6) measuring combustive emissions from mobile sources. Extrapolation of these results to a regional scale has to be made with a number of assumptions.

Given the difficulties in validating the absolute inventories, evaluation of the ratio of species offers a good alternative. Principal component analysis (PCA) is well suited for such a task. It was briefly reported (7,8) that area emission ratios may be obtained using PCA and rural field measurement results. In the present paper, a PCA technique was first tested against a simulated data set, and then applied to regionally representative field data to deduce area emission ratios. The area emission ratios were then used to assess the accuracy of those given in the NAPAP area emissions.

Testing PCA with a simulated data set

PCA was tested before it was applied to appropriate field data. First, a simulated data set $[X]_{13x500}$ was created with three guidelines: (1) The data must mimic those from the field measurements. Thirteen chemical species were chosen, identical to a field study in rural southern Ontario, Canada (8–10), including: O_3, HCHO, H_2O_2, organic peroxides, CO, NO_2, NO, HNO_3, PAN, NO_y, SO_2, $SO_4^=$ and NH_4^+. (2) The processes affecting the data variances must be related to physical processes in the atmosphere. The simulated concentrations were determined by three processes: transport, a diurnal cycle, and area emissions. The transport indices were derived as a linear function of equivalent potential temperature (θ_e) from the field study, which is used as a tracer for different air masses. The diurnal cycle indices were a sinusoidal function and related to observed J_{NO2} in the field data. The emission indices mimicked area traffic emissions for the region of study, with high morning and late afternoon emissions. All random and independent noises were added to all three indices to simulate instrument variances in field studies.

The entries of $[X]_{13x500}$, namely, the concentrations of the species, were calculated using scoring coefficients q_{ik} (Table 1) following:

$$x_{ij} = q_{i4} + \Sigma\, q_{ik}\, p_{kj} + \epsilon_{ij}, \quad k = 1,2,3. \tag{E1}$$

where p_{kj} was the index of the three processes, q_{i4} the "background level" in a rural environment, and ϵ_{ij} normally distributed noise with a zero mean and a variance that was a predetermined fraction (0.1) of the variance in $\Sigma\, q_{ik}p_{kj}$.

The scoring coefficients q_{ik} have distinctive ratios among different species i for each process k; for the transport process the ratios O_3/CO and $O_3/(NO_y-NO_x)$, were chosen to be 0.4 and 12, respectively, to represent photochemically aged air masses over eastern North America (8,10); for the diurnal cycles the ratios among the species were the same as those found during the field study (8); for the emission component the ratios to CO were the area emission ratios in the NAPAP inventories. The simulated concentrations agreed well with the field results and were a reasonable representation of real field data. Below it is shown that the ratios, q_{jk}/q_{ik} for all i, j, and k, can be resolved properly with PCA techniques.

$[X]_{13x500}$ was then subject to a PCA technique known as Absolute Principal Component Analysis (APCA) (11) in which a dummy sample, with zero value for each species, was added to $[X]_{13x500}$ to derive the mean scores for the principal components. Then the standard PCA procedures were followed, including standardization, eigenvalue and eigenvector extraction, and varimax rotation. As expected, three components were found significant which explained 96% of the total variance in $[X]_{13x501}$. This compares to 90% of the total variance accounted for by the $\Sigma\, q_{ik}p_{kj}$ part in (E1). Thus, the three components had also partially included variance due to ϵ_{ij}. The component scores were calculated, followed by the derivation of the absolute principal component scores ρ_{kj} using the mean scores[11]. Lastly, the partitionings of species i in the components were obtained using multiple regression as

$$x_{ij} = \alpha_{i0} + \Sigma\, \alpha_{ik}\rho_{kj} + \epsilon'_{ij} \tag{E2}$$

From equation (E2), for species i the product $\alpha_{ik}\rho_{kj}$ was averaged over j for the kth component. The averages represented the mean partitions of the species in each component. They were, however, different from the averages of product $q_{ik}p_{kj}$ over j. Thus, the partitions of species among the components based on the APCA technique were biased, caused by the rotation scheme. In other words, the bias problem may be generic to all PCA apportionment techniques, including the APCA. Here, both the default rotation (i.e., no rotation) and the varimax rotation failed to reproduce the original p_{kj}. With *a priori* knowledge of original processes, one could devise a specific rotation to derive a data structure that resembles the original. But in applications to field data, the original data structure is not known, and therefore the biases cannot be determined no matter what rotation is used.

Yet the correct ratios of species in each component can be derived using the APCA technique. Figure 1 shows significant linear relations between p_{kj} and ρ_{kj}. The magnitudes of ρ_{kj} relative to p_{kj} manifested the mentioned biases: ρ_{kj} was a factor of 0.60, 1.24, and 2.48 of the corresponding p_{kj} for the transport, diurnal cycle, and emission components, respectively, as shown by the regression slopes. However, the linearity between p_{kj} and ρ_{kj} leads to

$$q_{ik} = \alpha_{ik}\beta_k \tag{E3}$$

where β_k is the coefficient of the linearity between p_{kj} and ρ_{kj} (cf. Fig. 1 caption) and only depends on k, and therefore can be factored out by ratioing the partitioning of different species in each component as

$$q_{ik}/q_{(i+1)k} = \alpha_{ik}\beta_k/\alpha_{(i+1)k}\beta_k = \alpha_{ik}/\alpha_{(i+1)k} \tag{E4}$$

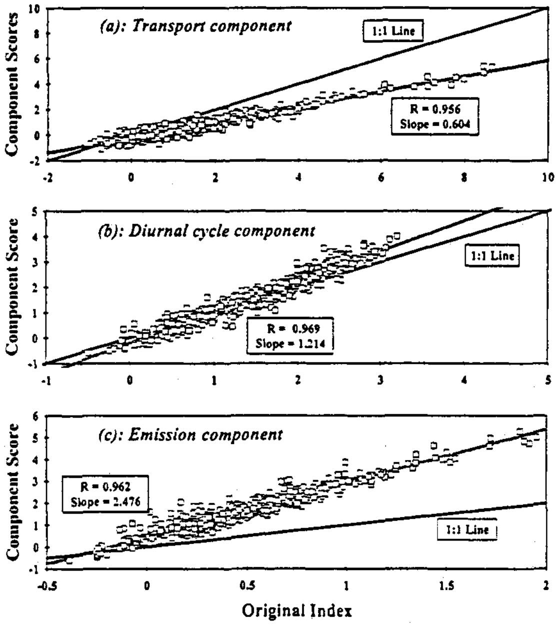

Fig. 1 The absolute principal component scores ρ_{kj} versus the original time indices p_{kj}: (a) transport, (b) diurnal cycle, and (c) emissions. The linear relations $\rho_{kj} = \beta_{k0} + \beta_k p_{kj} + \epsilon'_{kj}$ were used to show that species ratios in each component remain unchanged after PCA.

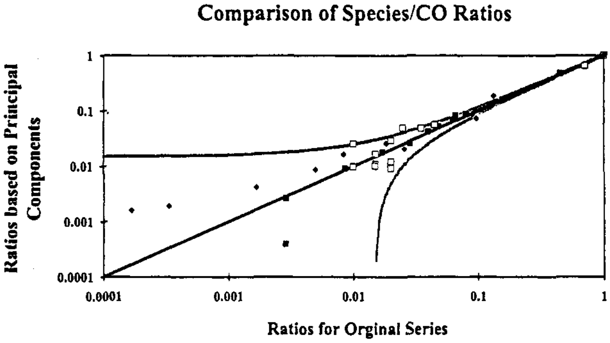

Fig. 2. Comparison of the species to CO ratios for the APCA components resolved from simulated data the versus those based on original scoring matrix in Table 1. Three different symbols indicate the ratios for the three components. The two light shaded lines indicate the 96% confidence intervals for the APCA ratios.

namely, the ratios should remain the same as derived from Table 1 after the APCA of the original data. Equation (E4) shows that the relative partitioning in a given component was independent of the bias factor β_k. The relationship is further demonstrated using the comparison of ratios of the 12 species to CO for each component from (E2) with the corresponding ratios from (E1). The comparison (Figure 2) shows that the ratios were indeed within a narrow uncertainty band of the one-to-one line, thus confirming (E4).

Table 1. Scoring coefficient matrix $[Q]_{13x4}$ for the 13 chemical species to construct the simulated data set from the time series indices of the three processes.

	Transport	Emission	Diurnal	Constant
O_3	15.7	-5.4	14.1	0.0
SO_2	1.7	1.1	0.2	0.2
$SO_4^=$	2.2	0.01	0.7	0.2
NH_4^+	2.8	0.02	0.5	0.4
NO_2	1.0	5.82	0.4	0.0
NO	0.1	1.55	0.4	0.0
HNO_3	1.4	0.5	0.4	0.0
PAN	0.3	0.1	0.2	0.0
NO_y	2.3	8.0	0.9	0.0
HCHO	0.6	0.3	0.3	0.5
H_2O_2	0.1	0.002	0.3	0.0
Organic Peroxide	0.1	0.003	0.3	0.0
CO	35	60	20	100

Area emission ratios based on field data and comparison with NAPAP

The field data were the results from the Eulerian Model Evaluation Field Study during July - September, 1988 at Egbert, a rural site in southern Ontario, Canada (8,9). Data selection criteria, analysis, and results for an APCA application are elsewhere[12]. Here, the APCA technique was applied to the final data matrix of 240 samples for the 13 species. Three components were retained, accounting for 78% of the total variance, and were varimax-rotated. Using chemical species ratios and the temporal variations, the components represented a transported and aged component, a diurnal cycle, and a local area emission component as demonstrated below. The partitionings of species in the emission component were then used to calculate the emission ratios for the comparison with those in the NAPAP inventories.

The emission component was shown (8,12) to be from area emission sources based on: (1) The composition of NO_y and variation of this composition with time of day: NO_y was dominated by NO_x (95%); the daily variation of NO_y exhibited a sharp morning peak comprising mostly of NO, with $NO/NO_y > 0.2$ at 0700 local time; and O_3 was titrated by the freshly emitted NO. (2) The wind-direction dependencies: the scores ρ_{3j} showed essentially the same values for all wind direction except in the 330-360 sector, suggesting an area source in this region. (3) The diurnal pattern of ρ_{3j} showed a strong elevation between 0700 - 0800 hours, and a broader elevation from 1600 - 1900 hours, again indicating emissions from area mobile sources.

Table 2. Ratios of species in the area emission component from field study and comparison with other reported area source emission ratios.

	Field Results	Buhr et al.[7]	NAPAP[3]
NO_y/CO	0.11±0.04	0.12	0.133
HCHO/CO	0.0056±0.0022	-	0.005
$HCHO/NO_y$	0.05±0.007	-	0.04
SO_2/CO	0.005±0.003	0.006	0.18

Therefore, the ratios in the component should be representative of area emissions, and are compared with the area emission ratios in the NAPAP inventories. In Table 2, the following emission ratios are shown from the field study and PCA analysis: $NO_y/CO = 0.11 \pm 0.04$, $SO_2/CO = 0.005 \pm 0.003$, and $HCHO/CO = 0.0056 \pm 0.0022$. The ratios NO_y/CO and SO_2/CO for area sources in eastern rural USA derived from a field study[7] are in good agreement with these results. Table 2 gives the ratios for area emissions in the NAPAP inventories, and clearly shows that the NO_y/CO and HCHO/CO ratios are reasonably accurate, but the SO_2/CO ratio is three times higher than reality. The discrepancy in the SO_2/CO ratio may be in part attributed to the declining sulfur emissions not taken into account in the NAPAP emission inventories.

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ACID DEPOSITION AND MATERIAL DAMAGE IN EASTERN ASIA

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Abstract - The impact of local wet and dry deposition of acid compounds was investigated by means of exposure of different materials, copper, bronze, marble etc. under indoor and outdoor conditions. Different corrosion products are formed, depending on the local pollution climate. Especially the ratio between SO_2 and NO_x is important. Rates of damaged have been assessed and are proven to be significant.

Introduction

In recent years, different pollutants are transported over long distances and affect ecosystems and materials in many countries (ref.1-3). The quantitative damages of material, caused by acidic air pollutants in eastern Asia, was studied. Bronze, ancient copper, electrolytically refined copper, steel and marble have been exposed to wet and dry acidic depositions at 9 sites: Tokyo, Ishikawa, Kyoto, Nara, Osaka (2 sites) in Japan, Chongqing, Shanghai in China, and Taegu in Korea from June 1, 1993 to May 31, 1995. In this paper, some results of the atmospheric corrosion tests for the first year are considered.

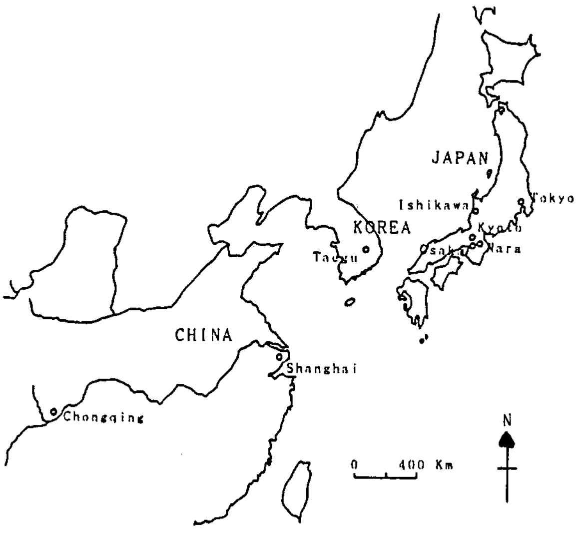

Fig. 1. The location of the 9 experimental sites.

Experimental

Experimental sites

The location of the 9 sites is shown in Figure 1. The sites cover a northern part in eastern Asia.

Test Pieces

The materials, sizes and surfaces of test pieces are shown in Table 1. The ancient copper was a reproduction of Budder hole's copper roof (about 350 years ago) in Tohdaiji temple. The metallic test pieces were ultrasonically cleaned with acetone for a few minutes and dried by a drier. The marble pieces were ultrasonically cleaned with distilled water for 10 minutes and dried in a desiccator for 24 hours. The test pieces were accurately weighed (<0.1 mg) and stored in a desiccator.

Table 1. Test pieces.

materials	size	surface
bronze JIS-H-5111 BC6(Cu85%,Sn5%,Pb5%,Zn5%)	2.0x30x40mm	#400 treatment
ancient copper (Cu99.285%,Pb0.58%,As0.02%, Zn0.002%,Fe0.001%)	0.8x30x40mm	#400 treatment
copper JIS-H-3100 C1201P(Cu>99.9%)	0.4x30x40mm	#400 treatment
steel JIS-G-3141 SPPC	1.2x30x40mm	#400 treatment
marble	5.0x20x20mm	

Exposure method and period

The test pieces were exposed to dry and wet depositions in unsheltered experiments (outdoors), and exposed to dry deposition in rain-sheltered experiments (indoors). Exposed periods were either 4 months (3 times) or 1 year (from June 1, 1993 to June 1, 1994).

Analytical procedure

After every 4 months, exposed test pieces were collected, and water-soluble corrosion products on the test pieces were extracted with 25 mL distilled water in an ultrasonic bath for 10 minutes. The ions were analyzed by ion chromatography (IC). The bronze and coppers pieces were immersed in a 10% ammonium-thioglycolic-acid solution at 80 °C for about 10 minutes, washed with distilled water, dehydrated with acetone and dried by a drier. The steel pieces were immersed in a boiling 10% diammonium hydrogencitrate solution repeatedly and scraped with a blush to remove remaining rust, washed with distilled water, dehydrated with acetone and dried by a drier. The marble pieces were dried in a desiccator for 24 hours. Weight losses were recorded with an accuracy better than 0.1 mg.

X-ray diffraction

A test piece (30 x 40 mm) was directly fixed on the sample holder of a Rigaku (Tokyo, Japan) RINT 1500 X-ray diffractmeter (Target: Cu, X-ray power: 40 kv x 150 mA), and corrosion products were identified by a nondestructive method.

Table 2. Annual average meteorological conditions, dry and wet depositions

sites	period	meteorological conditions				dry depositions						wet depositions				
		Temp ^{0}C	RH %	TOW hr	WV m/sec	SO_2 ppb	NO_2 ppb	Ox ppb	SPM ug/m^3	s-salt mg/dm^2	rain-f mm	pH	ES25^{0}C uS/cm	Cl^- ug/mL	NO_3^- ug/mL	SO_4^{--} ug/mL
Tokyo	93. 6. 2-93.10. 5	22.8	77.8		2.3	8.0	27.3	15.0	37.0			5.8	22.8	1.27	1.21	1.89
Kyoto	93. 6. 1-94. 6. 1	14.7	73.6	4132	1.3	4.3	16.3	17.6	32.8	1.0	1745	4.7	13.2	0.49	1.12	1.44
Nara	93. 6. 1-94. 6. 1	17.3	72.4		1.8	4.1	19.9	16.6	36.3	5.5	1375	4.3	26.2	0.61	1.02	5.10
Osaka[1]	93. 6. 1-94. 6. 1	16.6	68.1	4907	2.1	7.2	34.2	17.2	41.3	5.9	1487	4.2	41.0	0.92	1.40	4.88
Osaka[2]	93. 6. 1-94. 2. 2	16.4	72.6		2.5	6.0	26.5	20.6	53.0	12.0	1310	4.4	38.1	1.31	1.53	4.53
Chongqing	88.10.16-89.10.16	17.9[3]	81.4[3]			105[3]			250[3]	2.7[3]	1053[3]	4.2[3]		1.24[3]	3.18[3]	15.4[3]
Shanghai	93. 6. 1-94. 6. 1					17.5[4]			260[4]	2.8		6.5	121	2.13	2.97	32.1
Taegu	93. 8. 5-94. 8.22									2.8	689	4.9	51.0	0.80	1.94	12.9

[1] Environmental Pollution Control Center Osaka Prefecture, [2] University of Osaka Prefecture, [3] Chongqing (ref.4), [4] Shanghai city in 1991.

Meteorological conditions, dry and wet depositions

Temperature, relative humidity, the time of wetness and wind velocity were recorded. The time of wetness (TOW) is defined as the time with RH > 80 % and Temp > 0 °C.

SO_2, NO_2, O_3 and SPM in ambient air and the chemical composition of precipitation have been monitored. Long-term (one month) diffusion samplers for measuring SO_2 and NO_2 are used in China and Korea from June 1, 1994 because it was difficult to get dry deposition data there. Sea-salt particulate was collected by using a cotton gauze collector. After every 4 months, cotton gauze samples (effective area: 200 cm^2) were collected and NaCl (sea salt) was extracted with 50 mL distilled water in an ultrasonic bath for 10 minutes. Na^+ and Cl^- ions were measured by IC.

Results and discussions

Meteorological conditions, dry and wet depositions

The annual average meteorological conditions, dry and wet deposition loads are shown in Table 2. All sites were situated in the temperate climatic zone. The RH varied between about 68.1 % in Osaka to 81.4 % in Chongqing, the concentrations of SO_2 range between 4.3 ppb in Kyoto and 105 ppb in Chongqing, NO_2 between 16.3 ppb in Kyoto and 34.2 ppb in Osaka and SPM between 32.8 $\mu g/m^3$ in Kyoto and 260 $\mu g/m^3$ (TSP) in Shanghai. In China, the concentrations of SO_2 and SPM were about 10 times higher than those in Japan. In Kyoto, both SO_2 and NO_2 concentration levels were low.

Regarding wet deposition, rainfall varied between 689 mm in Taegu and 1745 mm in Kyoto, the pH-values varied between 4.2 in Chongqing and 6.5 in Shanghai, conductance between 13.2 $\mu S/cm$ in Kyoto and 121 $\mu S/cm$ in Shanghai, nitrate concentration between 1.02 $\mu g/mL$ in Nara and 3.18 $\mu g/mL$ in Chongqing and SO_4 concentration between 1.44 $\mu g/mL$ in Kyoto and 32.1 $\mu g/mL$ in Shanghai.

Corrosion products

The results of X-ray diffraction are shown in Figure 2-5. $CuSO_43Cu(OH)_2$ (brochantite) was formed on the copper pieces after only 4 months exposure in China (see Figure 2). In Japan (except Kyoto), $CuNO_33Cu(OH)_2$ (gerhardtite) was formed (see Figure 3). In Taegu, both products were identified. In Kyoto, both products could not be detected after 4 months exposure.

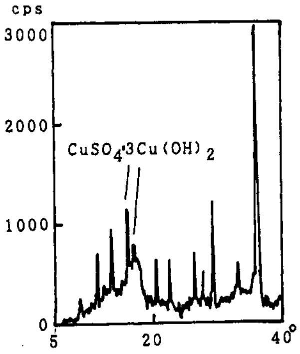

Fig. 2. $CuSO_43Cu(OH)_2$ (brochantite) on copper outdoors in Chongquing.

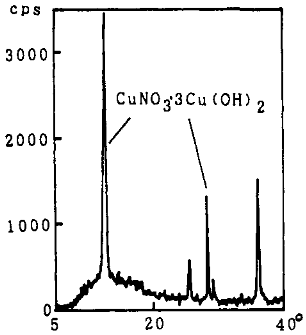

Fig. 3. $CuNO_33Cu(OH)_2$ (gerhardtite) on copper indoors in Osaka (1).

The results above described indicate that brochantite could be formed on copper at elevated SO_2 concentrations, and gerhardtite if NO_2 is available. In fact, brochantite could be detected on copper pieces, exposed in Japan about 30 years ago, because SO_2 concentration levels were very high in Japan in those days.

On the bronze pieces exposed outdoors, $PbCO_3Pb(OH)_2$ (basic lead carbonate) was identified in Kyoto only after 4 months' exposure (see Figure 4). At the other sites, brochantite and/or gerhardtite were detected. In rural atmospheres, carbonates would be formed on bronze.

On the steel pieces, alpha type FeOOH (goethite), gamma type FeOOH (lepidocrocite) and alpha type Fe_2O_3 (hematite) were formed in Japan, and furthermore Fe_3O_4 (magnetite) was identified in China after 4 months' exposure.

On the surface of marble exposed indoors, $CaSO_42H_2O$ (gypsum) was formed at all sites (see Figure 5), but no gypsum could be detected on the outdoor specimena because gypsum is more soluble than $CaCO_3$ (calcite).

Corrosion rates

In the outdoor samples, the increase of weight cannot be used to estimate corrosion rates, as the corrosion products of copper are very soluble in rain. Weight gains of steel are incorrect because the steel rust easily peels off from the test pieces in highly polluted areas. The corrosion rates were estimated on the basis of mass loss. The coefficients of variation of the mass loss for 3 copper pieces (4 times) were 1.2 - 8.6 % (outdoor) and 0.9 - 3.4 % (indoor).

The corrosion rates for the 1 year's exposure experiment are shown in Table 3. The corrosion rates (outdoor) were steel > marble > bronze > = ancient copper > copper. The indoor tests showed a similar tendency. Impure copper like ancient copper and bronze is more sensitive to the atmospheric corrosion tests than electrolytically refined copper.

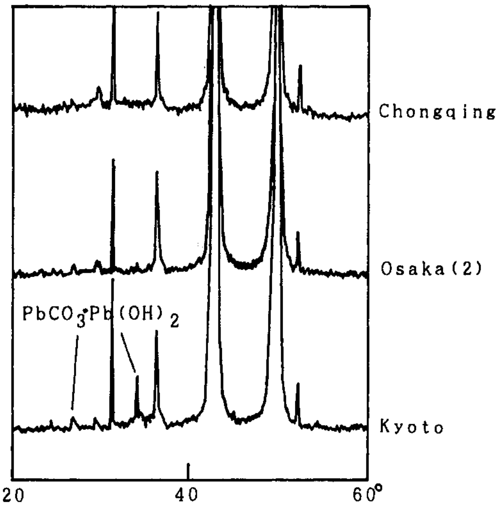

Fig. 4. *$PbCO_3Pb(OH)_2$ (basic lead carbonate) on bronze outdoors in Kyoto.*

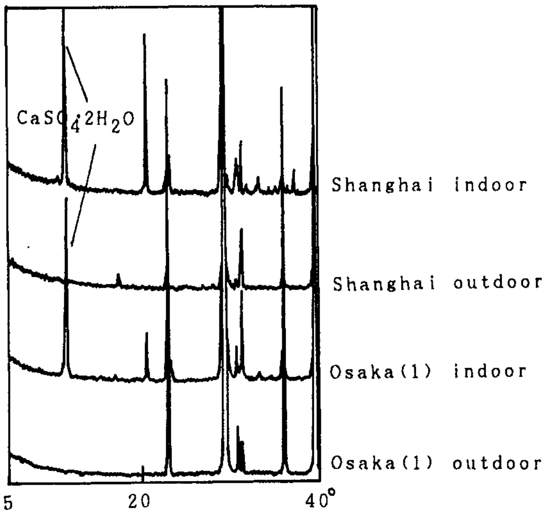

Fig. 5. *$CaSO_42H_2O$ (gypsum) on marble outdoors and indoors.*

In highly polluted areas like Tokyo, Osaka and China, the corrosion rates of bronze and copper in the outdoor tests were only 2-3 times larger than those in indoor tests, but in a slightly polluted area like Kyoto, the rates outdoor were 3-7 times larger than those indoor. It is obvious that acid rain in highly polluted areas made the highly polluted surfaces of the test pieces slightly cleaner.

Table 3. Corrosion rates for the 1 year's exposure experiment.

sites	period	bronze		ancient copper		copper		steel		marble	
		out[1] μm/y[3]	in[2] μm/y[3]	out[1] μm/y[3]	in[2] μm/y[3]	out[1] μm/y[3]	in[2] μm/y[3]	out[1] μm/y[3]	in[2] μm/y[3]	out[1] μm/y[3]	in[2] μm/y[3]
Tokyo	93. 6. 2-94. 2.14	2.68	0.88	2.09	0.60	1.93	0.67	60.3	23.4	26.9	14.4
Ishikawa	93. 6. 1-94. 6. 1	1.78	1.17	1.72	0.50	1.56	0.59	28.6	12.6	21.2	4.2
Kyoto	93. 6. 1-94. 6. 1	0.75	0.27	1.29	0.19	0.99	0.19	22.1	8.6	11.1	0.5
Nara	93. 6. 1-94. 6. 1	1.32	0.58	1.05	0.47	1.00	0.33	23.6	11.5	10.4	1.0
Osaka[4]	93. 6. 1-94. 6. 1	1.14	0.68	0.94	0.45	0.84	0.33	24.6	18.2	9.9	5.1
Osaka[5]	93. 6. 1-94. 6. 1	1.24	0.80	1.12	0.76	1.01	0.62	24.4	22.8	11.6	6.1
Chongqing	93. 6. 4-94. 6. 4	6.11	2.73	6.14	2.28	4.72	2.12	131.9	33.7	40.7	8.9
Shanghai	93. 6. 1-94. 6. 1	2.19	1.50	2.74	0.93	2.21	0.83	77.9	52.6	20.3	8.0
Taegu	93. 8. 5-94 8.22	1.50		1.72		1.45		41.1		15.5	

[1]outdoor,[2]indoor,[3]μm/year,[4]Environmental Pollution Control Center Osaka Prefecture,[5]University of Osaka Prefecture

In China , the corrosion rates of steel were extremely large compared with those in Japan. A large amount of SO_4^{--} (6.7 mg/dm^2 in the 4 months' exposure experiment indoors in Chongqing) was detected in water extracts from corrosion products on the steel pieces.

The results of X-ray diffraction have shown that SO_2 significantly contributes to the degradation of marble indoors. It has also been shown that wet deposition and natural dissolution by rain are important.

Conclusions

The analysis of the results from the atmospheric corrosion tests leads us to believe that brochantite and gerhardtite are formed at resp. elevated SO_2 and NO_2 concentrations. In rural atmospheres, carbonates would be formed on bronze. Gypsum was formed on the surface of marble in indoor tests in all sites, but no gypsum could be detected in outdoor tests. The results have shown that SO_2 significantly contributes to the degradation of marble indoors. It has also been shown that wet deposition and natural dissolution by rain are important.

The corrosion rates were estimated on the basis of the mass losses. The coefficients of variation of the mass losses for 3 copper pieces (4 times) were 1.2 - 8.6 % in outdoor and 0.9 - 3.4 % in indoor. The corrosion rates both in outdoor and indoor were steel > marble > bronze > = ancient copper > copper. Copper load with impurities would be more sensitive to the atmospheric corrosion tests than electrolytically refined copper. It is obvious that acid rain in highly polluted areas made the highly polluted surfaces of the test pieces slightly cleaner. In China, the corrosion rates of steel were extremely large compared with those in Japan. A large amount of SO_4^{--} ion was detected in water extracts from corrosion products on the steel pieces in China.

This work was partly supported by the Sumitomo Foundation (Grant No.93-104-203) and Suga Weathering Technology Foundation.

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ABATEMENT OF AIR POLLUTION IN THE FORMER GERMAN DEMOCRATIG REPUBLIC (GDR)

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Abstract- The large changes in power production, industrial production, agriculture and traffic, which took place in the former german Democratic Republic after unification with the Federal Republic of Germany (Western Germany), have caused a tremendous shift in emissions of pollutants. Most emissions, notably of SO_2, CO, VOC (Volatile Organic Carbon) and dust have been reduced considerably, but NO_x emissions are increased, due to traffic. Formerly smog periods of the "London kind", characterised by high concentrations of sulfur compounds and dust, were frequently observed in the area of the former GDR. This kind of smog is now being replaced with "Los Angeles kind", caused by high concentrations of oxidants.

Starting situation

The economical strategy of the former GDR (16.6 million inhabitants) was characterized by the following facts (1):
- extensive use (ca. 310 Mt/a) of sulfur-rich lignite (0.6-3.5% S) for energy production and home heating;
- use of old technologies;
- subordination of ecological requirements to economical interests.

Hence it follows that the former GDR has the third highest energy consumption in the world (ca. 233 GJ per inhabitant), a worldwide leading position of SO_2-emission (ca. 316 kg per inhabitant), considerable air pollution concentrations in industrial regions and high emission rates of other polluting substances.

In 1989 the following emission rates were reported (2):
5.25 Mt SO_2/a, 2.2 Mt dust/a, 0.7 Mt NO_x/a, 3.75 Mt CO/a, 1.05 Mt Volatile Organic Compounds/a, 353 Mt CO_2/a, 0.3 Mt NH_3, amines/a, 0.046 Mt S-comp./a, 6.5 Mt Cl_2,Cl-comp./a, 0.002 Mt/a of F-containing compounds.

A comparison of the main emissions with the FRG (61.0 million inhabitants) in the same year shows only a smaller specific NO_x-emission rate of the GDR: SO_2: 316/17, dust: 133/5, NO_x: 42/48, CO: 226/144, VOC: 63/42, CO_2: 2,127/ 1,179 kg/a per inhabitant (3).

The reason for the lower NO_x-emission rate is the lower temperature in the combustion processes of low caloric lignite and in two-stroke engines of motor cars and motorcycles, which were produced in the former GDR. In 1989 2.1 resp. 1.3 million motor cars and motorcycles with two-stroke engines were available. Additional factors are the smaller number of motor cars (total: 3.9 million = 235 cars/1000 inhabitants), the lower levels of commercial transport by trucks (only 24000 trucks), of gasoline usage in industries and agriculture and speed limits on the roads.

By way of contrast, in the Federal Republic of Germany (FRG) there were a total number of 29.8 million motor cars (489 cars/1000 inhabitants), 1.19 million motor cycles (four-stroke engines with and without catalyst, diesel engines) and 3.5 million trucks. Accordingly the contribution of traffic to the total emissions of pollutants differed in the GRD and FRG (percentages GDR/FRG respectively) are: NO_x: 37.1/62,1%, CO: 25.9/75.0%, VOC: 55.2/52.9%, CO_2: 6.7/20.0%. The use of lead-free gasoline in the FRG led to an emission of BTX (sum of benzene, toluene, xylene). In contrast, in the former GDR, an emission of 1.0 kt Pb/a resulted from the use of leaded gasoline.

Consequently extreme air pollution situations in the former GDR are characterized by the so-called "London-Smog" in the period when heating is required with large SO_2- and dust- concentrations. In the FRG, the high concentrations of nitrogen oxides and hydrocarbons produced by traffic lead during the summer period to the development of photochemical smog ("Los Angeles Smog"), which is characterized by large O_3-concentrations.

Trends of emission in the former GDR after the German unification

After the German unification in October 1990 significant changes took place in the former GDR including an increase in traffic, a structural change in industry, a removal of uneconomic and ecologically unsound production firms, a change in fuel of (natural gas, mineral oil) and modernizing of factories with new abatement technologies. This process is not yet finished.

Traffic

- The number of motor cars: has sharply increased: The number of cars per 1000 inhabitants is given in the table below:

	1989	1990	1991	1992	1993
number of cars per 1000 inhabitants	235	298	380	397	413

  Already in 1991 the number of cars had increased to 162%; in 1993 the value corresponds with the FRG;
- The mileage per vehicle increased, caused by increased transport on the road, (transport of goods, movement of people between east and west part of Germany), and the end of limitations of the supply of gasoline.
- A change in the of emissions by a number of processes scrapping of two-stroke cars/cycles (today only ca. 15% of the total number), use of second hand four-stroke cars without catalyst, decrease in the use of leaded gasoline.

By summer 1991 nearly the same emissions from traffic (NO_x, VOC) were observed in the former GDR as in the FRG (similar CO/O_3- ratios!). The emission of lead rapidly decreased, but the emission of BTX increased.

Industry

- A considerable reduction of production took place by the breakdown of the eastern market such as former Soviet Union.
- Old, non-profitable and non-competitive plants were shut down.
- Energy-intensive plants in the chemical industry, metallurgy, potash mining, machine-building industry, glass and ceramics plants, textile industry were closed.
- New technology was introduced in all sectors of industry.

These developments led to a considerable decrease in energy consumption and in industrial emissions (10 to 60% of the values in 1989). Removal of a large amount of old burden (soil and water pollution) is started. The change in industrial and agricultural production has led to extensive social problems in the former GDR, in spite of employment programs of the government.

Power industry

- Energy consumption is reduced (large power stations ca. 30%) due to change in industrial consumption.
- Old power stations have been closed.
- The other power stations are modernised (improvement of dust filters, lower NO_x-emissions, improvement of the

efficiency: 32.4% to 34.4%, in: cleaning technologies for SO_2-removal) will be applied.
- Planning and construction of new power stations in the near future is on its way including stack gas cleaning and improved efficiency $\eta > 40\%$ by coupling of electricity generation and heat production;
- Lignite of better quality and new fuels (hard coal, natural gas, oil, wind, water) reduce emissions considerably.

The rapid reduction in energy consumption by industry has enabled a totally new concept for large power stations to be introduced. Basic electricity supply is fuelled bij lignite (production: max. 50 Mt/a), medium electricity load is provided by hard coal while for peak load hydroelectric storage is used. Additionally, a remarkable decrease in air polluting emissions took place (1989 = 100%): dust: 85%, SO_2: 35%, NO_x: 45%, CO_2: 30%. A larger reduction of SO_2- emission is possible, but not before 1996. Therefore acification of clouds is increased by the reduction of dust which neutralised acid in the past. Up to 1993, the changes in home heating were small in comparison to large power stations (mostly lignite burning). The total restructuring of the energy base of industry in the former GDR also led to social problems (unemployment).

Local air pollution problems of Leipzig-town

Leipzig-town has about half a million inhabitants, who live on an area of 146 km^2. The town is in the centre of the Middle German Lignite Territory (Leipzig-Halle-Merseburg-Bitterfeld-Borna) with an extension North to South of 80 km and West to East of 40 km (see Fig. 1).

In 1989 in this district 105.6 Mt lignite, 33% of the total volume of the former GDR was produced. This coal was the basis of carbon-chemistry (90%), production of briquets (35%) and electricity (14%) of the former GDR, as well as used in metallurgy, metal working and machine-building industry.

In 1989, the following emission rates in Leipzig-town were reported (5):
83.2 kt SO_2, 20.8 kt dust, 3.4 kt NO_x, 29.5 kt CO, 3.6 kt VOC, 6 t NH_3, amines, 1 t heavy metals. The emissions of SO_2 and dust were caused by home heating (ca. 40%), industry (ca. 40%) and long range transport (ca. 20%). The sources of long range transport were primarily the plants located near Bitterfeld (N), Merseburg/Leuna, Buna (W) and Borna/Böhlen, Espenhain (S). The local emissions of SO_2, NO_x, dust of Leipzig-town were about 6 - 7 times larger than the mean emission rates of the former GDR.

Accordingly in the smog episode of 1989 (November/December) SO_2-concentrations between 0.5 and 2.8 mg/m^3 in the ambient air were measured. Maximum SO_2-concentrations of 5 mg/m^3 in January 1985 were observed by the author. Ambient air values of the centre (5) and the east part (Permoser Straße) of Leipzig-town (see Table 1) are available for 1991. The mean values of both locations are in good agreement. The maximum values of SO_2 in February/March correspond with the earlier values taking in consideration the low mean temperatures of both months. Already in July-September large peak values of O_3 were measured, caused by the increase in the number and the mileage of cars.

The development of Leipzig-town and its surroundings after the German unification is characterized by the following developments:
- shutdown of the carbon-chemistry and other industries;
- reduction of briquet-production (new: briquets with additives for SO_2 removal by ca. 50%);
- reduction of lignite production (max. 25 Mt/a);
- from 1992: substitution of lignite-fired power stations by power stations using natural gas to be completed in 1996;
- substitution of lignite for home heating and gas production by natural gas (Leipzig-rural district: already 100.000 households, in the town in preparation).

These activities have led to a rapid reduction of emmissions of Leipzig-town and of long range transport. The main emission source is at this moment home heating (ca. 60% of immission) by the ineffective burning of lignite, and the traffic.

Measurements in Leipzig-town in 1994 (see Table 2) show a reduction of the ambient air concentrations of SO_2, dust, CO by about 50% in comparison with the values of 1991. The concentrations of NO_x, O_3 are similar. Measurements of O_3 in June/July 1994 (of temperatures in excess of 30 °C) give values between 150 and 220 μg/m^3.

Conclusions

After the German unification, a total change in industry, agriculture, power economy and traffic in the former GDR took place, which is today not yet finished. In a short time in comparison with the West European countries the air pollution situation has been transformed. The typical "London smog" will be substituted by the "Los Angeles smog". In the present time a transition stage exists, which is characterized by a simultaneous occurence of both kinds of smog, especially in winter and spring.

Unfortunately "old" mistakes of the "West" were repeated in the form of increased traffic (BTX, mileage and number of cars without catalyst, ...) and industry (sequential removing of dust and SO_2, creating problems regarding acid deposition).

Social problem (e.g. unemployment) connected with the changing process in the former GDR by employment programs (mostly in environmental protection!) of the German government were minimized.

Table 1. Pollution in Leipzig–town 1991 < $\mu g/m^3$ >
Centre (5), Permoser Straße [1]

month	SO_2	dust	CO	NO_2	NO	O_3	VOC
February 1.9° C	303 389/680[1]	144	1900	40 -/147[1]	33	25/100	
March 2.4° C	216 209/987[1]	135	1700	44 -/130[1]	37 -/150[1]	28/104	
April 3.8° C	145 101/368[1]	104	1400	47 -/ 63[1]	29 -/ 48[1]	46/132	
May 4.8° C	72 74/381[1]	68	1100	38	27	48/124	
June	36	56	700	33	11	55/120	
July	41	68	500	40	19	67/195	3300[1]
August	60	88	1000	41	18	60/203	
September	72	75	1100	44	25	49/230	
October	145	79	1600	42	32	27/110	
November	194	84	1600	34	39	17/ 65	
December	224	82	1600	31	39	9/ 49	
Mean 1991	**137**	**82**	**1300**	**39**	**29**	**39**	

Table 2. Pollution in Leipzig–town 1994 < $\mu g/m^3$ >
Mean values/max. values: Centre (6),
Permoser Straße [1]

month	SO_2	dust	CO	NO_2	O_3
Januar 3.6° C	39/142 44/ 169[1] 57/539	55/426	792/4100 980/2450[1] 1000/7900	30/93 35/127[1]	21/57 25/70[1] 17/48
Februar 0.4° C	93/482 77/>300[1]	92/338	1524/6271 1280/5134[1]	10/78 19/ 60[1]	15/48 18/77[1]
March 6.8° C	33/545 19/ 240[1]	58/274	925/4234 933/2684[1]	25/68 20/ 71[1]	27/79 39/86[1]
April 9.5° C	35/346	66/370	1000/4700 733/1170[1] 1050/5400	37/100	38/75 52/86[1] 41/145
May	28/363	48/358	850/3600	34/79	40/128

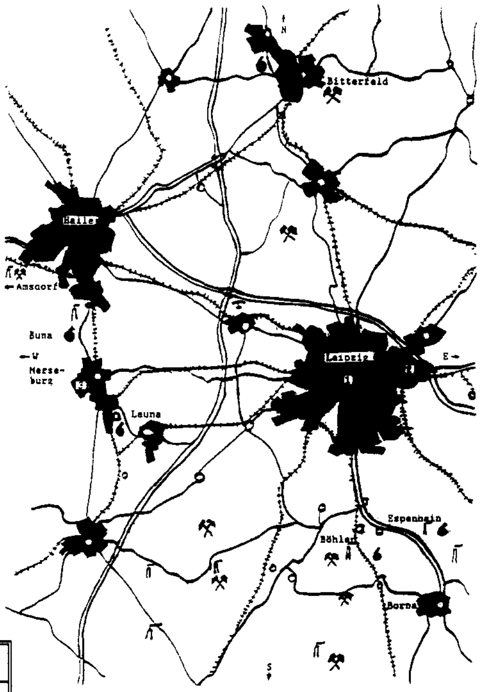

Fig. 1. Middle German Lignite Territory (Leipzig-Halle-Merseburg-Bitterfeld-Borna). Measuring Stations: 1-Centre, 2-Permoser Straße, 3-FH Merseburg - Lignite mine, - power station, -chemical plant.

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THE CHARACTERISTIC OF ACID PRECIPITATION OVER GUILIN MAOER MOUNTAIN DISTRICT

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Abstract - Samples of cloud water, rainwater and ambient aerosol were collected in Guilin downtown and Maoer Mountain district during the spring of 1988. The measurement results show that the precipitation is seriously acidified during spring season in this area, and that acidity of precipitation increases with lower altitudes. The average pH value of rainwater and cloud water over Maoer mountain and of Guilin rainwater were 4.85, 4.34 and 3.91 respectively. Sulfate, nitrate, ammonium, calcium and hydronium were the principal ionic species. Sulfate was the major contributor to acidity, while calcium was the important neutraliser in the rainwater samples in this area.

Key words: cloud water, rainwater, ionic composition, Below cloud scavenging.

Introduction

Since the late 1970s, research on acid precipitation has shown that there is serious acid rain pollution in the region of southern Yangtze River in China. Most previous field work has been based only on the sampling and analysing of rainwater, few reports are related to the measurement of cloud water, although it is known that clouds play an important role in the formation of acid rain. This paper presents the measurement results of rain water and cloud water collected in Guilin city and on Maoer mountain in Guongxi province during March 14–24, 1988, including the results of sequential sampling of events in the above districts.

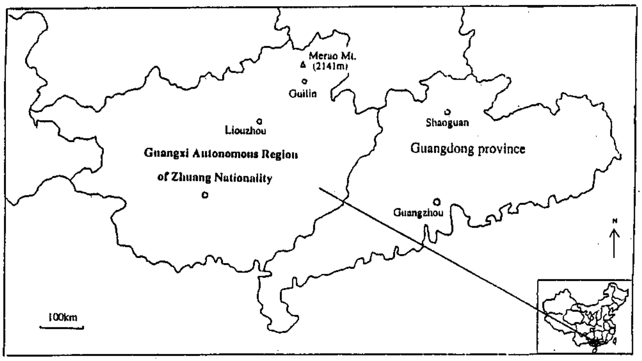


Fig. 1. The position of sampling sites

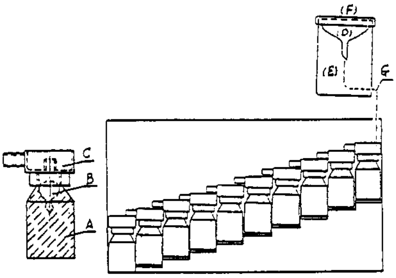


Fig. 2. Apparatus of semiautomatic sequential rainwater collector
(A) polyethylene bottle; (E) plastic tank;
(B) hollow glass ball; (F) cover;
(C) cap of manifold; (G) connecting tube.
(D) collecting funnel of rainwater;

Sampling site and measurement techniques

Maoer mountain with an elevation of 2141 m, a prominent mountain in the south of China, is located in the northeast of Guangxi province, the north end of the Hunan–Guangxi corridor and about 65 km to the north of Guilin city (Fig. 1), so it is one of the very few locations in both provinces to provide open exposure to impacting clouds. Moreover, it is located near Guilin city so that it is a convenient location to study the action of below-cloud scavenging, especially during air flow from the north. Guilin (elevation 165 m) is a famous city in China and is encircled by mountains and hills. Although there are no extremely heavy industries in this area, gaseous pollutant concentrations are quite high due to the high frequency of inversion layers above the city. The measurement results have shown that the precipitation in this area is seriously acidified during winter and spring season.

The methods of collection and measurement for cloud water, rain water and aerosol have already been described elsewhere (Yao. et al, 1993); the detailed information about the semi-automatic sequential collector (see Fig. 2) developed by Peking University to collect sequential rain samples in events based on a fixed rainwater volume, was also described in an earlier paper (Bai. et al, 1994).

Results and discussion

During the period of observation, the samples of rain and cloud of high elevation and rainwater of groundlevel were collected in order to understand the spatial distribution pattern of acidity and possible sources in this area.

Frequency and spatial distribution of acidity in precipitation

The results in relation to acidity of precipitation collected in different altitudes are shown in Table 1 and Fig. 3.

Table 1. The acidic range of precipitation

Site	Sampling date	Precipitation	No.	Range of pH	Average of pH	Acidified* Frequency.(%)
Maoer	1988	seq. rain	16	4.22–6.88	4.85	68
Mount.	3/14–24	rainwater	9			
		cloud	24	3.37–6.20	4.34	83
Guilin	1988	seq. rain	43	3.24–5.30	3.91	100
		rain	23			

*The percentage of samples with pH < 5.6 related to the total number of samples.

An obvious spatial distribution for the precipitation could be observed by comparing frequencies of increased acidily in samples collected on the mountain and on the ground level respectively. The conclusion is: the closer to the ground level, the lower the pH value and higher frequency of increased acidity in precipitation is observed. For example, the rain samples collected in Guilin city represent the impact of acid precipitation on ground level, the average pH was as low as 3.91 and the frequency of increased acidity was 100%. In other words, the average H^+ concentration in those samples was about 4 times as large as found in cloudwater and 10 times the value observed in rainwater on Maoer Mountain.

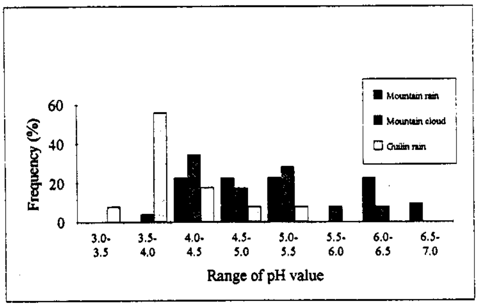


Fig. 3. The frequency distribution of pH in events on March 1988

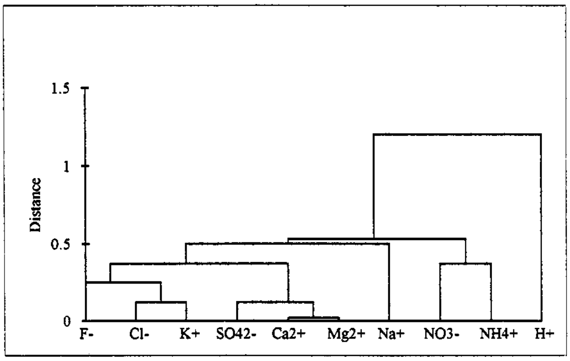


Fig. 4. The cluster analysis of Guilin rainwater

The ionic composition of precipitation

In Table 2 and 3 the ionic composition of precipitation and the ratios of some important species in concentration in the samples of aerosol, cloud and rainwater collected over the Guilin–Maoer mountain district are given.

Table 2. The ionic composition of precipitation and aerosol

Site	Altit.(m)	deposition	No.	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	H^+
Maoer.	2100	aerosol	3	10.5	3.4	9.5	88	146	50	11.8
Mount.	>2140	rainwater	25	10.7	33.2	54.7	52	62.8	77.8	14.1
	>2140	cloudwater	24	9.7	18.4	59	114	129	72.5	45.8
Guilin	165	rainwater	66	18.7	34.4	62	240	141	107	122

Table 3. The ratio between important species in the samples of aerosol and precipitation

ratio	aerosol Mountain	rainwater Mountain	cloudwater Mountain	rainwater in Guilin	rainwater upper air
SO_4^{2-}/NO_3^-	9.2	0.94	1.93	3.86	1.09
NH_4^+/Ca^{2+}	2.9	0.81	1.78	1.32	1.92

These preliminary results lead to the following conclusions:

1. The principal ions found in the precipitation were H^+, SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+}. Among them SO_4^{2-} was found to be the most important, which accounted for around 34%, 57 % and 68% of the total amount of anions in mountain rain, cloud and in rain at ground level respectively. The dominant cation found in cloudwater was NH_4^+, which accounted for 44% of the total concentration of cation. Ca^{2+} was the most important cation in rainwater, it accounted for about 36% and 38% of the total concentration of cations in samples from the mountain and at ground level.

2. SO_4^{2-} and NH_4^+ rather than NO_3^- and Ca^{2+} showed an obvious vertical distribution with higher values near surface level, which resulted in the same vertical variation for the ionic ratio of SO_4^{2-}/NO_3^-.

3. There was a close agreement between the ratio of main ionic species in Maoer mountain rainwater and that of rainwater, sampled at an altitude of about 5000m by means of an airplane; for example, NH_4^+/SO_4^{2-} was 1.54 and 1.22, SO_4^{2-}/NO_3^- was 1.09 and 0.94 for the precipitation sampled by plane and Maoer mountain respectively, which strongly indicated that the rainwater in Maoer mountain represented the situation of precipitation in the free troposphere.

The relation between ionic composition and acidity of precipitation.

To investigate the source of acidity and the contribution of different compounds, multiple regression analysis for cloud water and Guilin rainwater was carried out:

Cloud water (n=24);

$$[H^+] = 20.27 + 0.556\,[SO_4^{2-}] - 0.528\,[Ca^{2+}]$$

$$R = 0.9896,\ F\!: [SO_4^{2-}]\ 511.8,\ [Ca^{2+}]\ 51.63.$$

Guilin rainwater (n=23):

$$[H^+] = 118.7 + 0.722[NO_3^-] + 0.778[SO_4^{2-}] - 0.410[NH_4^+] - 1.018[Ca^{2+}]$$

$$R = 0.5913,\ F\!:[NO3],\ 4.21;\ [SO_4^{2-}],\ 19.32;\ [NH_4^+],\ 2.23;\ [Ca^{2+}]\!:11.35.$$

The statistical results show that the acidity of Guilin rainwater is primarily controlled by the major ions such as SO_4^{2-} and Ca^{2+}, NO_3^- and NH_4^+; SO_4^{2-} and NO_3^- contribute to acidity while Ca^{2+} and NH_4^+ neutralise H^+. To examine the reliability of this regression analysis, cluster analysis of Guilin sequential rainwater (n=43) was made (see Fig. 4). Good correlation was observed between H^+ and the sum of all major ions rather than H^+ and any single ion. This result suggested that the acidity resulted from the combined action of the main ions in precipitation.

The contribution of cloudwater to the acidity of precipitation at ground level.

During the period of observation, the wind direction near Guilin at ground level was primarily controlled by a northerly air flow. Cloudwater can be taken as the precursor of precipitation at ground level. In order to observe the

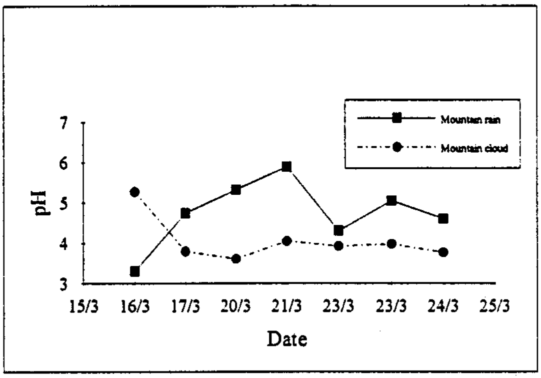


Fig. 5. The variation of pH for cloudwater and Guilin rainwater occurred at the same time

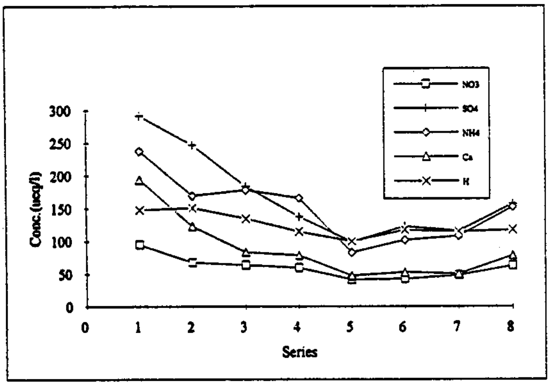
contribution of cloudwater to the acidity of precipitation, the pH values of cloudwater and rainwater were measured at the same time during all sampling days and the results are presented in Fig. 5. The variation in both precipitation and cloudwater agreed extremely well except for the first two days, but the pH value of precipitation at ground level was always approx. 1 unit lower than that in cloudwater. The results showed that cloudwater was an important source of acidity in precipitation, below-cloud scavenging constitutes a secondary source.

The effect of below-cloud scavenging on the acidity of precipitation at ground level.

Below-cloud scavenging usually is dependent on the level of local air pollution. By means of the semi-automatic rain collector, sequential samples of four events were collected on March 17 over Maoer mountain and March 23, 24–25 and March 26–27 in Guilin city respectively. Fig. 6 and Fig. 7 show the variations of main ionic concentration of events in both areas. A marked decrease in the concentration of SO_4^{2-}, Ca^{2+} and NH_4^+ at the first three stages of events sampled at ground level can be seen with the exception of H^+ and NO_3^-. For the event over Maoer mountain, however, no obvious variation was found in comparison with Guilin's. The below-cloud scavenging efficiency of species was calculated using the following equation and the measured results of sequential samples of rainwater. The results are given in Table 4.

$$Scavenging\ Ratio(j) = \frac{sum.(1\ to\ 7\ stages)(j) - \text{min.}(j)}{sum.(1\ to\ 7\ stages)(j)} * 100$$

where sum.(1 to 7)(j) represents the total concentration of species j in all stages during an event, the min.(j) is the lowest concentration of species j in platform (5–7 stages), which approximately represented the concentration of species j within the cloud layer near the ground.



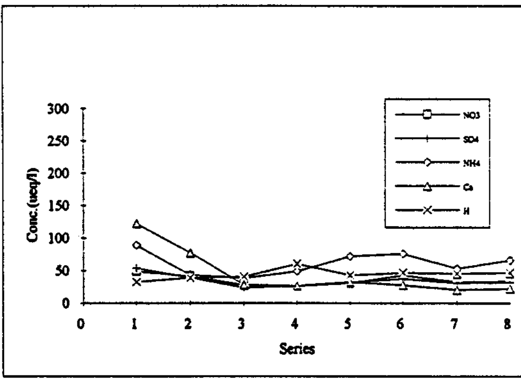


Fig. 6. Ionic conc. variation in sequential sample of Gulin rain (23/3, 1988)

Fig. 7. Ionic conc. variation in sequential sample of Maoer Mountain rain (17/3, 1988)

Table 4. The average scavenging ratio of events occurred in Guilin city (1988.3)

date	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	H^+
23/3	59.1	49.0	30.2	42.1	97.1	44.3	60.5	46.8	37.7	20.6
24–25/3	35.1	16.5	9.8	57.9	73.1	22.5	77.7	44.4	36.0	31.4
26–27/3	58.7	38.2	30.4	66.7	84.8	29.6	-	52.4	49.2	46.7

Although the scavenging ratio was different for each event, and was dependent on factors precipitation intensity and amount such as time interval between two events, precipitation intensity and amount, the similar pattern could be found in that SO_4^{2-} and Ca^{2+} had the largest scavenging efficiencies, NH_4^+, and Mg^{2+} are secondary and the ratios for NO_3^- and H^+ were much smaller than others. Approximately 70–90% of the total SO_4^{2-}, Ca^{2+} and NH_4^+ deposition occurred during the first three stages of the rainwater. This conclusion can be observed from Fig. 6 and strongly indicates that local pollutants are an important source for acid precipitation in Guilin area.

Summary and conclusion

1. The precipitation during spring over Guilin–Maoer mountain district is obviously acidic. The frequency of excess acidity increases with the lower attitude.
2. The main ions influencing the acidity of precipitation were SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+}. SO_4^{2-} and NO_3^- generate acidity and NH_4^+, Ca^{2+} were the important neutralizers.
3. The acidity in Guilin precipitation at ground level primarily originates from cloudwater and below-cloud scavenging. The scavenging efficiencies have been calculated and show that the contribution of SO_4^{2-} and Ca^{2+} to acidity precipitation is larger than the contributions of other ions.

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SURVEY OF AMBIENT POLLUTION IN CHENGDE CITY AND THE CONTROL MEASURES

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Abstract – The combination of unfavourable siting of industry and housing areas, of the use of low grade coal and of stagnant meteorological conditions is responsible for high pollutant concentrations in Cheng De. As this city is famous for its Mountain Resort, an array of temples and palaces of great historical value, assessment of air pollution and of the contribution of different sources and the development of abatement measures is necessary. Control schemes to prevent health problems and damage to buildings are proposed.

General condition of Chengde city

Chengde is located in the northeast of Hebei Province China at 115°55'--119°15' W and 40°11'--42°40'N. It is situated in the mountainous area of northern Hebei in the transitional zone between Yanshan Mountain geosyncline and Mongolian Plateau with declining altitudes from 1800 m northeast to 200 m southeast. It is divided into two natural regions, i.e. the north hilly region and Bashang Plateau. This landscape of mountains, undulating hills and criss-crossed valleys is obviously important in the assessment of air quality.

Chengde's climate is a transition one between a warm temperate zone and a cold temperate with a dry, and a damp continental mosoon season. The non-frost period varies from *82-180* days and rainfall between 400- 800 mm per year, 80% of which is concentrated in summer. The wind mainly blows from the northwest with an average annual velocity of 1.4 m/second. There are 25 days on average per year with wind velocities greater than 17 m/s. The calm weather occurs for 49% of the year. Large variations in temperature are observed between night and daytime.

Chengde Municipality has 3 districts and 8 counties under its administration with a territory of 39 548 km^2 and a population of 3 402 900 people. Shuangqiao District is the political, economic and cultural centre of the municipality with a built-up area of 17.6 km^2. Due to fast economic development and sharp increase of population in the city, the emission of ambient pollutants has increased continuously in the district. By the mid-eighties, the ambient environmental quality was showing obvious deterioration.

Present situation of ambient pollution

In 1986, Chengde Municipality had its record air pollution in history in its built-up area. The annual average daily TSP reached 0.795 mg/m^3 and SO_2 0.34 mg/m^3. In January, the worst month, Total Suspended Material, TSP and SO_2 reached 1.68 mg/m^3 and 1.07 mg/m^3 respectively. This serious air pollution caused detriment to the residents' health, damaging the urban ecological system and adversely affecting the economic and tourist trade development. Hence, prevention and treatment of air pollution were urgently needed.

The results of the two ambient monitoring programs and a survey of emission sources, carried out in 1986, showed that the serious air pollution in Chengde is mainly due to the following factors:

- The main fuel is coal of a poor quality with a high ash- and sulphur-content and a low thermal value.
- The inefficient use of coal and coke.
- Poor horizontal and vertical mixing of pollutants, due to frequent episodes of stagnant conditions.

Survey of Air Polluting Sources

The results of the above mentioned survey in the built-up area of Chengde Municipality show that in Chengde coal is used as the major energy source, supplying 76% of the total energy consumption in 1986. The annual total coal consumption was about 400,000 tons in the urban area. Heating accounts for 66% of the total coal consumption in the year with a daily average of 1,800 tons. Coal consumption of boilers is most important, followed by the domestic uses, industrial kilns and restaurants and offices. This evaluation shows that SO_2 emission rates vary a factor 2 depending whether heating is applied and TSP with 50%. Moreover, the distribution of air polluting sources in the city area is fairly uniform with many sources of ground level. Most of the chimneys have an altitude of 10 to 20 meters with a maximum of 30 and a minimum of 5 meters.

Characterization of air pollution in Cheng De

The distribution of air pollutants in a city under the conditions of Cheng De is dependent on the position and emission strength of sources, and frequency of meteorological inversion. Chengde is a typical basin surrounded by mountains. Local meteorology favours constraints in mixing of the boundary layer.

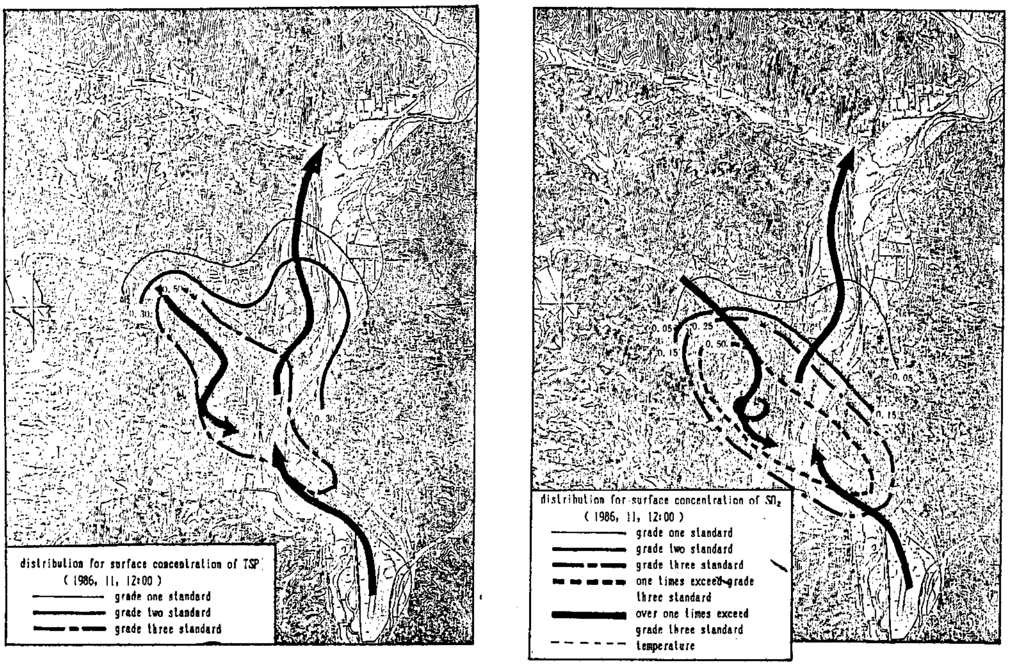

Fig. 1. Airflow and exceedence of limits for TSP and SO_2 at noon

1. The daily average SO_2 exceeds the level encountered in other tourist areas in China.
   The air pollution in Chengde is of the "London smog" type. The main pollutants are TSP and SO_2.

2. Strong seasonal variation of air pollution
   The air pollution in Chengde Municipality has a seasonal character. Heavy pollution is encountered in wintertime. On-site monitoring shows that in general TSP, NO_x and SO_2 during the season, when heating is employed, is increasing by 2.7, 2.4 and 12.4 times compared to periods which do not require heating. In winter,

the main wind direction is northwest along the gorges and valleys converging on the city centre and leading to stagnant conditions in morning and evening. The other typical meteorological condition is the high frequency of very stable atmospheric conditions. Inversions are observed during 46% of the year and of nearly 70% of the winter period. Horizontal transport of pollutants is responsible for 20% of the observed concentrations.

3. The two-maxima and two-minima character of daily air pollution variation.
   The daily pattern of air pollution in Chengde shows two maxima and two minima values. The minima are observed between 2 to 5 am and 2 to 5 pm, the first maxima between 7 to 9 am and the second between 7 to 9 pm. This is not only related to the height of the mixing layer, but also reflects the pattern of life of the citizens.

4. The local variation of air polllutants
   Due to the unique distribution of sources and the meteorological parameters the distribution of air pollutants is depending on location. As factories, offices and residential buildings are located along the narrow valley, a belt of heavy pollution is formed in the northwest-southeast direction where the pollutant concentration exceeds the national grade 2 standard by more than 100%. The worst polluted zone is the mixed commercial and residential area, where air pollutants exceed the national grade 3 standard by 400%. The environmental air quality in the northern part is fairly good, generally within the national grade 2 standard.

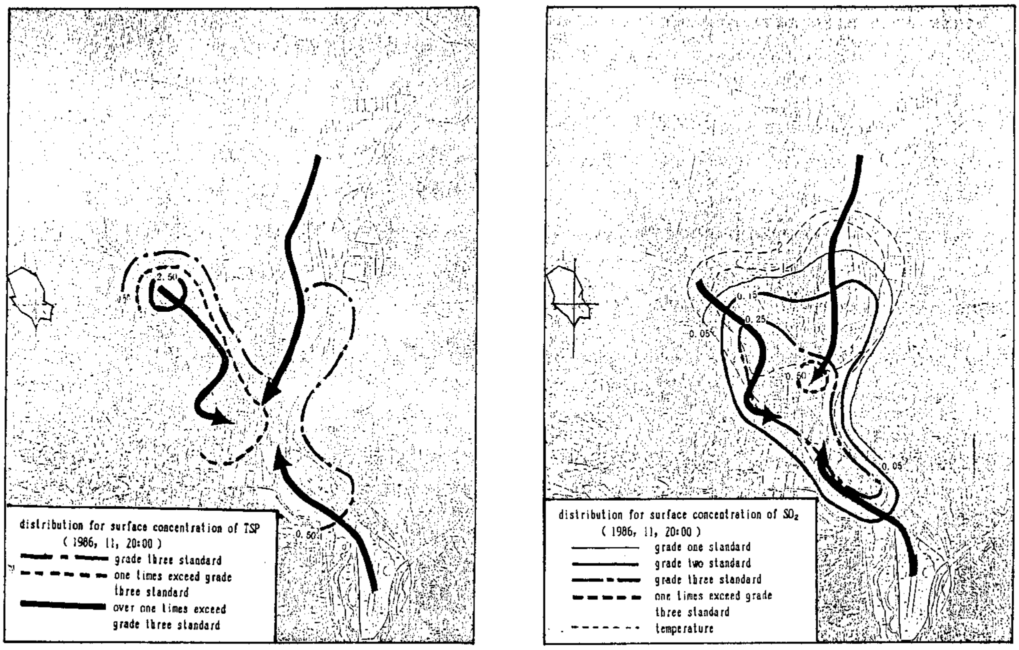

Fig. 2. Air flow and exceedence of TSP and SO_2 limits at 20.00

The control of emission of air pollutants

According to the objectives of the development strategy for tourism and the national ambient environment quality standard, the ambient environment quality of Chengde should be controlled to comply with the national grade 1 standard. But considering the city's development the present pollution level and financial possibilities, it is extremely difficult to reach this required standard within a short period of time. Therefore, abatement is organized in three stages with corresponding maximum levels of pollutant emission.

The first stage is that the Mountain Resort, an area which contains many historically temples and places will comply with the national grade 2 standard and the city to the grade 3 standard. This scheme will be realized in the near future to avoid the present serious exceedences of standards. The maximum SO_2 emission will be set to 3110 tons and TSP to 6415 tons during the cold season. According to the 1986 source survey the SO_2 emissions were estimated at 1042 tons and TSP at 10,767 tons during the cold season. Therefore, SO_2 and TSP will be cut by 70% and 40% respectively in the above mentioned scheme.

In the second stage the city area will comply with the national grade 2 standard and the Mountain Resort to grade 1. The maximum SO_2 emission allowed is 1772 tons and TSP 3746 tons during the winter period, which requires a decrease by 82.99% and 65% respectively compared to the present emissions, and by 43.2% and 41.6% compared to the level reached in first stage.

The third stage control is that both the city area and the Mountain Resort comply with the national grade 1 standard. The maximum SO_2 and TSP emissions will be 863 tons and 138 tons respectively, which necessitates a decrease by 91.72% and 87.13% in comparison with the current emission, and by 51.32% and 63.02% with the second stage.

The control measures for ambient environmental quality

1. In order to conserve the beautiful scenery and expand the fame of the historical city and develop tourism, the built-up area of the city is designated as the key control zone.

2. The heating of houses and industry represents 60% of the total sources contributing 80% of the total pollutant emission. Therefore, abatement measures for industrial and residential sources will have the highest priority.

3. SO_2 and TSP are the major pollutants. Reduction of these pollutants is emphasized.

4. Improvement of ambient environment quality during the cold season is deemed to be very important.

Ambient pollution prevention and treatment measures

After analyzing abatementschemes, employed in China and abroad to control air pollution and taking into account the local conditions of Chengde, the following control measures will be taken:

1. Boilers characterised by high emissions will be replaced to reduce the emission of TSP by 85–95%. The same measure will be carried out for industrial kilns.

2. Replacement of coal by cokes for use in residential areas, which reduces SO_2 emissions.

3. Application of sector heating systems will reduce the number of polluting sources and prepare for the introduction of central heating.

4. Contructon of the city's central heating plant. To reduce the domestic pollution and pollution from heating boilers in the enterprises and offices.

5. Construction of a coal gasification plant in order to reduce sulfur and TSP emissions. The resulting low sulfur cokes will be used as fuel in residential areas.

ENVIRONMENTAL IMPACT STUDY OF ENERGY STRUCTURE AND POLLUTANT SOURCE CONSTITUTION ON AIR QUALITY IN SHENZHEN

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Abstract - Based on the latest two-years' survey of sources of pollutants and the results of continuous monitoring of both energy consumption and air quality, a detailed quantitative study is made on the influence of different pollutant sources on the air quality. NO_x is the main air pollutant with an estimated contribution of about 70%. Vehicles are the main pollutant source contributing 46%, of which NO_x is 64% expressed as mass. The contribution of point sources to NO_x emissions is of a second order but point sources are responsible for most of the SO_2 emissions. Area sources have only a limited impact.

Key words: Pollutant source, energy structure, air quality.

The Shenzhen city is located in the south of Guangdong province, facing the estuary of the Pearl River to the west and Dapeng Bay to the east, and linked to New Territory of Hongkong in the southern part. There are five districts in the city, i.e., Luohu, Futian, Nanshan, Baoan and Longgang; the total area is 2020.5 km^2 of which 327.5 km^2 is designated a special zone. Since it was founded in 1980, the gross productivity of Shenzhen industry increased by the rate of 54% annually, and thus great changes in the social economic conditions have taken place and attracted world-wide attention [1,2]. There is a close relationship between economic development and the increase in energy consumption and the latter will, in turn, influence the local environment, especially regarding air quality. Based on statistical data from the last decade, a detailed discussion is given on the relationship between changes in energy production, increasing energy consumption, changes in emissions of pollutants and the corresponding air quality in order to provide a scientific basis for the control of air quality.

Energy production and other emissions of pollutants in Shenzhen

Energy production in Shenzhen has changed in order to follow economic development and, depending on the resources available, has mainly relied on electricity and petroleum over the past few years. Figure 1 shows the use of coal, non-coal primary sources including all kinds of oil, gas, etc. and electricity from Hongkong and the provincial net from 1985 to 1992. Although the total consumption of coal increased from 85 000 tons in 1985 to 372 500 tons in 1992, its contribution to the total amount of energy consumed declined. Table 1 shows the consumption of different types of fuel in different districts. Diesel oil is the most important, the amount of heavy oil used in industry is the largest in Nanshan, and the largest amount of coal is used in Longgang and Baoan which together account for 78%. The statistical results show that the ratio of coal to the total use of primary energy is 11% in 1992, which is very different from the national average where coal accounts for 78% of the total energy consumption [3].

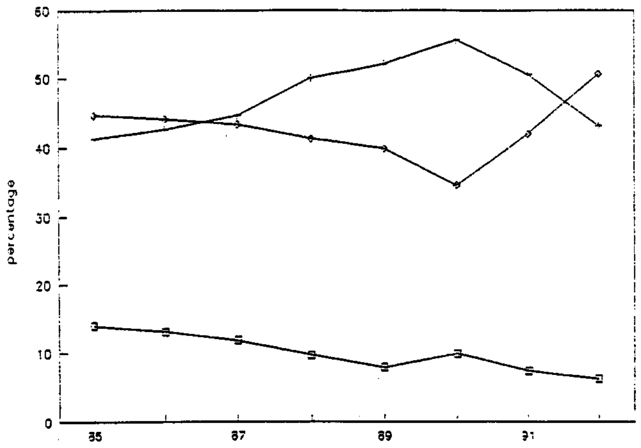

Fig. 1. Use of fuel 1985-1992
□ = coal; + = imported electricity; ◊ = others

Table 1. The use of fuels in 1992
(Converted into standard coal, 10,000 tons)

Region	Diesel oil	Heavy oil	Coal
Luohu	19.15	4.71	1.61
Futian	17.51	4.02	1.41
Nanshan	19.24	44.76	2.81
Baoan	21.08	8.81	6.13
Longgang	20.33	19.81	14.64
Total	97.31	82.11	26.60

We define a stack as a chimney higher than 15 metres and the boilers burning more than 2 tons per hour as a point source: stacks below 15 metres, furnaces in building industries, heating of hotels and houses are included in area sources. Road traffic is designed as a line source.

The fuel of point sources is mainly oil, the contribution of diesel oil and heavy oil to the total consumption of each are 40% and 88%, respectively; the amount of coal versus the total consumption is 39%. The contribution of point sources in energy consumption in Shenzhen is 45 %.

The 478 boilers belonging to point sources are almost equally diveded over four parts in Shenzhen. The urban district including Luohu and Futian, the suburbian districts of Nanshan, Baoan and Longgang account each for nearly 25%. The number in Nanshan is more than the average, 27%, and is concentrated in the Southern Peninsula. The calculation also shows that the total number of boilers, including those belonging to area sources, and the total fuel consumption is the largest in Nanshan. The density of pollutant sources in the Southern Peninsula is very great as its area is only 1.7% of the total area of Shenzhen.

The energy consumption of area sources is mainly based on diesel oil (23%), heavy oil (12%), and coal (62%). The main emissions of area sources are caused by the 448 small furnaces and nearly 15,000 oil-fired ovens used in the food industry distributed in the whole city, by coal-fired brick factories concentrated in both Longgang and Baoan (49%) and by all the ovens used by the residents in the area. The number of households in Shenzhen is 218 100 (by the end of 1992) and the usage of liquefied gas is almost universal.

The annual consumption of diesel oil is 379 700 tons (36% of the total consumption) and that of gasoline is 142 600 tons (nearly 100 percent of the total consumption). The total length of the roads built of the end of 1992 is approx. 900 km and within the special zone 299 km [2]. Over the years 1980-92 the number of vehicles has increased very rapidly, (Table 2); the average flow of vehicles in 1992 is 2 533 units per hour, and the highest value is 4 470 units per hour [5].

Table 2. The annual number of vehicles in Shenzhen (unit:vehicle)

Year	80	81	82	83	84	85	86	87	88	89	90	91	92
Total	5193	8566	11744	17109	28236	44218	43573	50360	60924	71369	93379	112393	134533

The amounts of the pollutant burden from the three kinds of pollutant sources (excluding fume) are given in table 3 [6]. The reason for not including fume is that the black smoke index is still low even though it has increased somewhat during the past few years because of commercial and industrial development in the area.

Table 3. A general view of the three kinds of pollutant sources

The pollutant	SO2		NOx		Iso-pollutant burden	The ratio of Iso-pollutant burden
Pollutant source	Emission amount (t/a)	%	Emission amount (t/a)	(%)	Pi	Ki(%)
point source	12660	60	7230	25	156700	36
area source	6930	33	3308	11	79280	18
line source	1482	7	19284	64	202720	46
Iso-pollutant burden Pi	140480		298220		438700	100
the ratio of Iso-pollutant burden Ki(%)	32		68			100

$Pi = q_i / C_i$ = standard pollution load index
q_i = the total emission of pollutant i in ton
C_i = concentration limit (mg/m^3)
$Ki = Pi/\Sigma Pi$

The highest ratio of the iso-pollutant burden in table 3 is 46 %, which indicates that the main emissions of pollutants in Shenzhen are caused by line sources. The largest ratio of iso-pollutant burden is for NO_x. It reaches 68 % and this is 2.15 times that of SO_2, so NO_x is the main air pollutant in Shenzhen.

The present air quality and its cause

The air quality in Shenzhen had generally been good since its founding as a special zone but the concentration of NO_x in recent years in the city has been above the recommended limits and shows no tendency to decrease. This condition is most severe near the main road and the maximum concentration are 5.45 times the standard. Inside the city, the average daily concentration of NO_x is 49 % above the limit. The concentration of other pollutants, such as total suspended particles (TSP) and Pb, are different. The average daily value of TSP is approx. 10% above the limit and the average of Pb has never surpassed the limit. The monitoring data of air quality in Shenzhen are shown in Table 4.

1.8 kg extra SO_2 is generated by the combustion of coal compared to the emissions by oil in order to get one ton of steam. If all the present boilers using oil were converted to coal, the amount of SO_2 emission increase by 18,000 tons (49%). Although the contribution of coal to the energy consumption is very low, 78 % of the total amount is consumed in Baoan and Longgang, which are located on the leeward of the prevailing wind of the urban district. In spite of their combined area (84 % of Shenzhen), the influence on the urban district is low. In addition, according to the calculation, to produce the same amount of heat, the emission of SO_2 and NO_x from liquefied gas is only 1/450 and 1/98 of that from coal. As a result, the wide usage of liquefied gas as a domestic fuel has reduced the pollutant

Table 4. The annual air quality monitoring values in Shenzhen (mg/m^3).

Pollutant factor	SO_2		NO_x		TSP		Pb	
II grade standard	0.06		0.1		0.3		0.7	
Year	Annual Average	Exc. of limit (%)	Annual Average	Exc. of limit (%)	Annual Average	Exc. of limit (%)	Annual Average	Exc. of limit (%)
1985	0.009	0	0.036	3.7				
1986	0.010	0	0.046	6.2				
1987	0.019	0	0.047	7.5				
1988	0.016	0	0.053	9.0				
1989	0.016	0	0.071	21.0	0.198	13.5	0.087	0
1990	0.009	0	0.085	29.4	0.119	0.6	0.093	0
1991	0.009	0	0.108	39.8	0.161	7.1	0.126	0
1992	0.016	0	0.119	42.5	0.195	22.4	0.195	0

emissions. The concentration of SO_2 in air in Shenzhen continues to be low due to the type of fuel used and the reasonable distribution of pollutant sources. This is why Shenzhen doesn't have the air pollution characteristics of coal-smog (London-type smog).

A statistical study has been made of the average concentration of NO_x, the total number of vehicles and the average flow value of vehicles in Shenzhen from 1985 to 1992. The result shows that the correlation coefficient r_{xy} of the annual average concentration of NO_x and the total number of mobile vehicles is 0.989, the coefficient r_{xz} of the annual average concentration and the average traffic flow is 0.955. r_{xy} and r_{xz} are significant at the 0.01 level, hence there is a clear positive correlation between the average concentration of NO_x and both the total number of vehicles and the average traffic flow.

Furthermore, the concentration of NO_x in the urban district is higher than that of the Nanshan district, although the number of industrial pollutant sources and the total amount of fuel consumption in the urban area is much lower than that in the Nanshan district. The reason lies in that the traffic in the urban district is much larger than that in Nanshan.

From the above analysis and the contribution of NO_x line sources as indicated in table 3, the conclusion follows that the main cause of the continued increase in the concentration of NO_x in the air in Shenzhen are emissions from mobile vehicles.

Conclusions

The energy consumption mainly relies on electricity and oil introduced during the city development of Shenzhen, which results in the distinct different situation regarding air pollution compared to that of most of other cities in P.R. of China. With the iso-pollution burden and correlation analysis method, the impact of different fuels and sources on air pollutant, on air quality can be assessed. NO_x is the main air pollutant and its rate of iso-pollutant burden is 68%; the mobile vehicles are the main pollutant sources and its iso-pollutant burden ratio is 46 %; the contribution of NO_x is 64 %. Point sources are less significant but are responsible for the SO_2 pollution; area sources have a minor impact.

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CHARACTERISTICS OF SEOUL SMOG

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Abstract - Characteristics of visual air quality in Seoul have been investigated from March 1993 to February 1994. Optical properties, meteorological parameters, and particle characteristics were measured. The data indicate that light scattering by particles is the dominant process in light extinction. Fine particle mass concentration and the fraction of sulfate, nitrate, and ammonium ions in the particles are the major variables which determine the occurrence and characteristics of a smog episode in Seoul.

Introduction

The city of Seoul is a mega-city with the area of 605 km^2 (0.6% of the total area of South Korea) and contains about 25% (11 million) of the total population, 32% of the total vehicles, and more than 40% of the total national production. As a result, severe environmental problems have arisen in Seoul including frequent visibility impairment episodes, commonly referred as smog.

The average prevailing visibility in Seoul during 1993 was about 10.2 km or the total light extinction coefficient, b_{ext}, of $0.384 \times 10^{-3} m^{-1}$. The b_{ext} is the sum of four terms; scattering by particles, b_{sp}, absorption by particles, b_{ap}, scattering by gas, b_{sg}, and absorption by gas, b_{ag}. The b_{sg} is the Rayleigh coefficient and its value is $0.012 \times 10^{-3} m^{-1}$. The b_{ag} can be calculated by a Hodkinson relation (Hodkinson, 1966) from the NO_2 concentration. Thus, b_{ap} can be estimated if both b_{ext} and b_{sp} are measured simultaneously along with NO_2 concentration.

Generally, the contributions from gas molecules to b_{ext} in urban atmosphere are minor compared to that of particles. The fine fraction of particles is mainly responsible for visibility impairment, especially the fraction between 0.1 μm and 1.0 μm. The chemical composition of fine particles is also important since the light scattering and/or absorption capacity of a particle is highly dependent on particle composition (Sloane and White, 1986). Thus, to understand the characteristics of the smog phenomenon in Seoul and to develop control strategies, both optical properties and particle characteristics, especially those of fine particles, should be studied simultaneously.

During 1993-1994, optical properties, b_{ext} and b_{sp}, and particle properties, PM-3 particle mass loading and ionic composition were measured together with meteorological parameters to (1) quantify the degree of visual air quality and (2) identify major variables that contribute to visibility impairment.

Measurements and results

Measurements were conducted from March 1993 to February 1994 at the Korean Institute of Science and Technology and each measurement lasted between three and seven days. A transmissometer (Optec model LPV) and a nephelometer (MRI model 1598) were operated continuously to measure b_{ext} and b_{sp}, respectively, along with ambient temperature and relative humidity (RH). A filter sampler with a 3μm inlet was used to collect fine particles, equipped with a 47 mm teflon filter. Fine particles were sampled by means of a cascade impactor in April 1993.

Measured optical coefficient values show a typical diurnal variation along with ambient temperature and RH, with maximum coefficient values during the morning and minimum values during the afternoon for all measurement periods. An example of this trend is shown in Fig. 1. This indicates that the variation of mixing height is a dominant effect determining the overall visual air quality of Seoul. However, the values of optical properties are clearly different for each measurement period as shown in Fig. 2 in which average values of optical properties are summarized. During April 1993, b_{sp} data are not available as the nephelometer was not properly calibrated in this period.

The relative contributions of b_{sp} to b_{ext} generally fall into two categories, between 50% and 56% for clear (October 1993 and February 1994) and moderately smoggy (August 1993) periods and between 67% and 80% for smoggy periods (March and November, 1993) as shown in Fig. 2. The relative contributions of gas molecules are less than

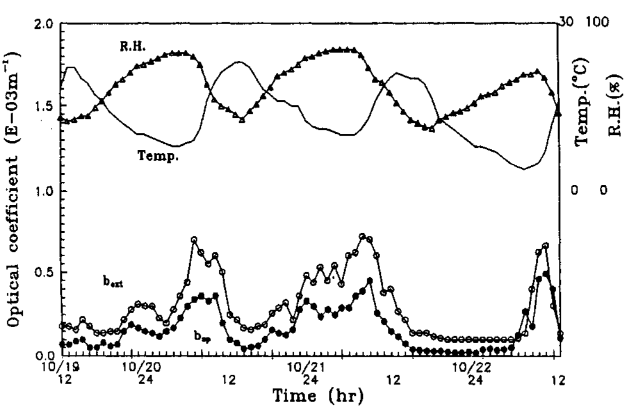

Fig. 1. Meteorological conditions and b_{ext} ( ) and b_{sp} ( ) in October

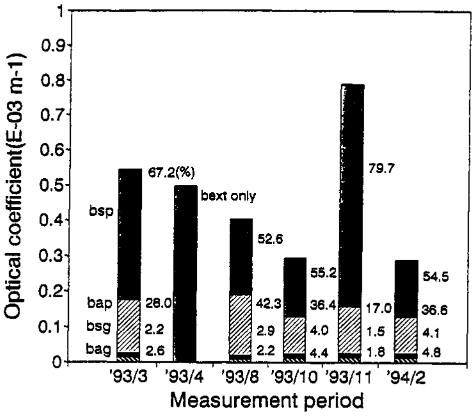

Fig. 2. Seasonal variation of extinction budget (LEB)

10% for all periods, with similar values for all periods. The contribution by estimated b_{ap} values is also shown in Fig. 2. The absolute values of b_{ap} do not vary noticeably for all periods, but the relative contributions of b_{ap} to b_{ext} vary between 36% and 43% for clear and moderately smoggy periods and between 17% and 28% for smoggy periods, respectively. Therefore, the absolute values of b_{ap}, b_{ag} and b_{sg} terms are relatively constant throughout the year while the values of b_{sp} widely vary and thus determine the degree of visibility impairment in Seoul.

The impact of fine particles on visibility is demonstrated by plotting the relationship between b_{sp} and PM–3 mass concentrations as shown in Fig. 3. The line represents the best fit obtained bij linear regression. PM–3 concentration is in close relationship with b_{sp}. A similar tendency has been widely observed by previous studies of Denver (Groblicki et al., 1981), Detroit (Wolff et al., 1982), and Los Angeles, U.S.A. (Larson and Cass, 1989).The data obtained during October 1993 and February 1994 lie below the regression line while other data points lie above the line. This trend can be explained by the amount of ionic species. Trend of PM–3 concentration and ionic composition is shown in Fig. 4. Concentrations of Cl^-, $Ca2^{2+}$, Mg^{2+}, Na^+, and K^+ are relatively small compared to SO_4^{-2}, NO_3^- and NH_4^+, and thus not plotted in Fig. 4. Though PM–3 concentrations during October 1994 and February 1994 are higher than that during August 1993, the amount of ionic species during October 1993 and February 1994, specifically sulfate, is smaller than or close to the amount during August 1993, as shown in Fig. 4. The result is a relatively high PM–3 concentration with small optical coefficients or high visibility.

During this study period, nitrate concentration in PM–3 is high during all periods except in August 1993, and represents more than 50% of sulfate mass concentration. Note that the average nitrate and sulfate concentrations of a previous study, however, were 0.2 μg/m^3 and 9.7 μg/m^3, respectively (Lee et al., 1986), nitrate being only about 2% of sulfate mass concentration. This trend reflects the drastic increase of the number of automobiles and the change of fuel from coal and heavy oils to natural gas and light oils in Seoul.

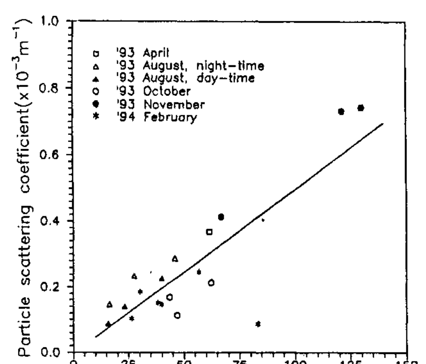

Fig. 3. Correlation between PM–3 and b_{sp}

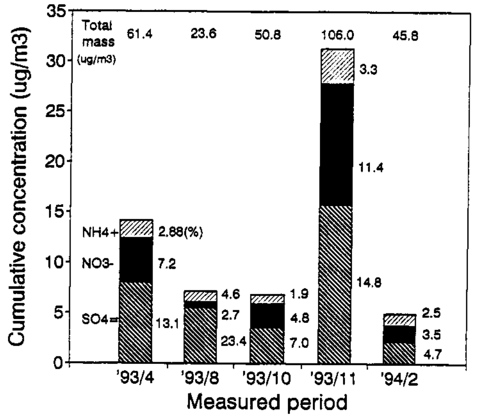

Fig. 4. Seasonal variation in chemical composition of PM–3

Conclusions

Field measurements of the optical coefficients, b_{ext} and b_{sp}, along with meteorological parameters and the fine particle mass concentration and composition were carried out from March 1993 to February 1994. Variations of optical coefficients and RH show a strong diurnal variation pattern, high values during the night and low values during the day, implying that the visibility in Seoul is mainly governed by the diurnal variation of temperature and, thus, mixing height. Light-scattering by particles was the dominant process during the smog episode periods, comprising about 70%-80%, comparing to 50%-60% during clear periods.

The relationship between the concentration of PM-3 and b_{sp} shows good agreement. Concentration of nitrate has drastically increased comparing to the data of the previous 1986-study. A smog episode is characterized by high mass loadings of PM-3 particles and large fractions of secondary particles such as sulfate, nitrate, and ammonium ions in the fine particles.

Acknowledgements

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TROPOSPHERIC OZONE MEASUREMENTS IN CROATIA

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Abstract - The levels of oxidants and precursors have incidentally been monitored for a long period in Croatia and systematically since 1989 in the cadre of the EUROTRAC subproject TOR (Tropospheric Ozone Research). The results of measurements at different locations indicate that the diurnal behaviour of ozone concentrations is dependent on local air pollution. Urban sites show diurnal variations of a factor 10 or more, rural sites of a factor 2 to 5 and less than a factor of 2 is observed above the boundary layer.

Introduction

Measurements of surface ozone in Zagreb, the capital of Croatia, had already been performed by the end of the 19th century, but were analyzed and described only recently [1]. The analytical method, according to Schönbein, was based on iodine paper and an 11 degree colorimetric scale. Measurements were performed twice a day in the period from

1889 to 1990. The first measurements using automatic monitoring equipment took place in the centre of Zagreb during the spring and summer of 1975 [2]. Then the monitor was transferred to the island of Krk for measurements during 1977–78 [3]. Shorter measuring campaigns took place in the Kvarner Bay area [4] and in the city of Split on the Dalmatian coast from April until October 1979 [3]. The level of ozone and some other atmospheric pollutants (NO_x, SO_x, non-methane hydrocarbons, lead and polycyclic aromatic hydrocarbons) were checked for shorter periods over the years 1978–81, because of considerable concentration of industry planned in this region at that time. In the summer of 1985 ozone was monitored on the mountain Medvednica (station Puntijarka) north of Zagreb at an altitude of 980 m and in the summer of 1986 near the town of Sibenik on the Adriatic coast [5]. In 1988 a permanent pollution monitoring station was set up at the Rudjer Boskovic Institute in the northern part of Zagreb on the foothills of Medvednica and this station was included in the European network of stations to study the level of tropospheric ozone over the European continent within the EUROTRAC/TOR project [6]. In 1989 the higher altitude station at Puntijarka got also included in the same network and is being operated almost continuously since then. In the summer of 1989 ozone was monitored at three altitudes: at the Rudjer Boskovic Institute 180 m a.s.l., at Medvedgrad half way up the mountain at 580 m a.s.l. and at Puntijarka [7]. In the summers of 1990 and 1991 surface ozone measurements were taken on several locations along the Adriatic coast (Rovinj, Krk, Iz, Hvar and Makarska) [8]. In addition our team took part in photochemical pollution measurements at other urban and suburban locations of the Mediterranean region: Greater Athens in the summers of 1982–84 [9], in Cairo in March 1990 and in Greater Thessaloniki in September/October 1991.

Long-term ozone measurements provide information on its concentration in a particular region and eventually on the trends. Indeed one of the aims of the EUROTRAC/TOR project is to assess the levels of ozone in the lower troposphere over Europe by collecting data from some 20 stations in a data bank for subsequent detailed analysis by intercomparison and modelling. The data obtained at the stations in Zagreb and Puntijarka [10] are included in that data bank. Sometimes particularly interesting events can be identified such as a case of stratospheric intrusion all the way to the earth surface as observed in Zagreb on 6 February 1990.

The concentration of ozone or more appropriately its mole or volume fraction in ambient air is a function of many factors: emissions of precursors especially nitrogen oxides and hydrocarbons, solar irradiance, wind direction and wind speed, temperature, etc. Usually only a few of these can be measured and one is forced to draw conclusions on the basis of a very limited data set. The following is a description of the methods we found most useful during our 20 years of experience in analysing the ozone data in Croatia and some other locations in the eastern Mediterranean region.

Experimental

Early measurements (in the seventies and early eighties) were performed by a Bendix ozone analyzer (Model 8002) based on the chemiluminescent reaction of ozone with ethylene. Later measurement employed Dasibi 1008 AH and 1008 PC, as well as Environment SA41M monitors based on UV absorption. The Dasibi instruments have a reliable internal calibration system and the Bendix instrument was calibrated against a neutral potassium iodide method, by an optical method [11] and later against the Dasibi instruments.

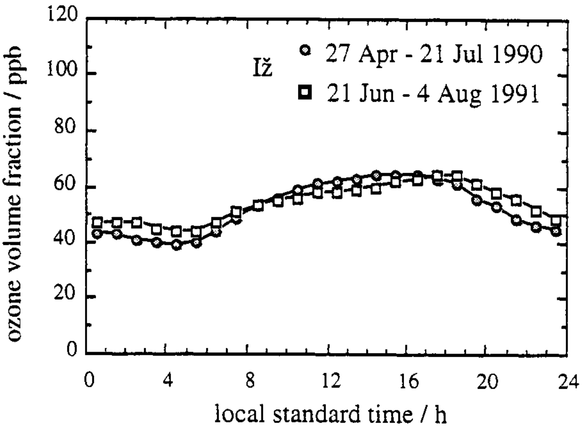

Fig. 1. Average diurnal behaviour of ozone volume fractions on the island of Iz, central Adriatic, for two summer seasons

Results and discussion

As opposed to many other pollutants the fraction of ozone in ambient air varies strongly over 24 hours of the day. An average ozone volume fraction therefore does not represent useful information on the state of atmospheric pollution. The average diurnal behaviour may be rather different at two sites having the same average ozone volume fraction and such diurnal behaviour provides more information on the status at a particular site.

Urban stations have very pronounced average diurnal variation even when it is obtained by averaging over a considerable length of time such as the summer season (e.g. in Athens and Zagreb [5]). Measurements at elevated sites show hardly any diurnal variation (e.g. at Immitos [5] and Paros in Greece [8]). In rural sites the variation is relatively weak, yet still reproducible from season to season as seen in Fig. 1 for the island of Iz. An even better presentation of the measurement values is obtained by plotting the median, first and third quartiles as a box and say 10th and 90th percentile as bars as well as the minimum and maximum values for each hour of the day (fig. 2). Each hour is then represented by 7 values instead by a single mean value and interesting conclusions can be drawn, especially if the distribution of values is highly asymmetric about the median. The variation of the median is almost identical to the average behaviour and the black squares for the median in Fig. 2 show the characteristic behaviour for an urban site in Zagreb and an elevated site at Puntijarka.

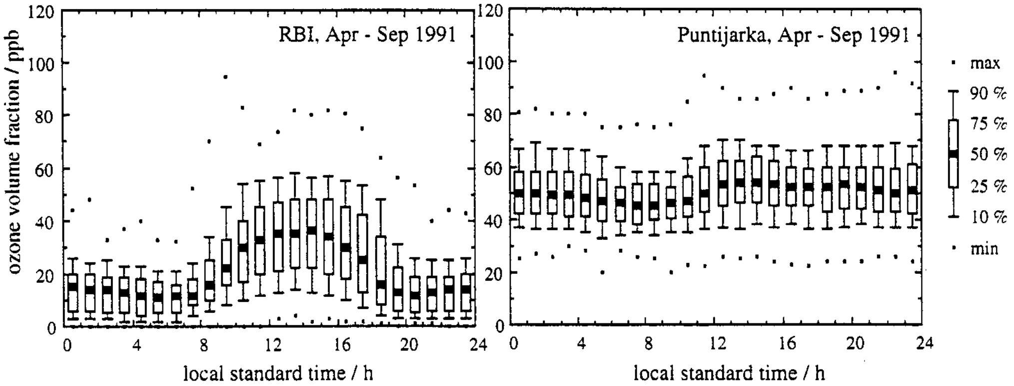

Fig. 2. Diurnal behaviour of ozone volume fractions in Zagreb (RBI station) and on the mountain Medvednica (Puntijarka station) for the growing season in 1991.

The explanation of diurnal behaviour of the ozone volume fraction, however, requires a better understanding of the phenomena involved in the formation and destruction of ozone. We therefore tried to find a parameter which would contain more useful information than the average value by reflecting some aspects of the diurnal variation.

Clearly the ratio of the maximum to minimum value in the type of plots shown in Fig. 1 yields an insight on the wavy diurnal variation, but a more sensitive index is obtained by taking the ratio of the maximum to the minimum hourly average ozone volume fraction for each individual day and calculate the average value of such ratios for a longer period of time. For urban sites with heavy photochemical pollution this index has a value of over 10, above the boundary layer it is less than 2, whereas in less polluted urban and suburban sites as well as in some rural locations it will be of the order of 2 to 5. Since most of the present day monitors have a detection limit around 1 ppb for ozone, hourly average values can sometimes be zero and these are given the value of 0.4 ppb for the purpose of calculating the index in order to avoid division by zero. Such indices calculated for different sites are given in Table 1. It remains to be seen whether they represent a useful single value indicator for the state of photochemical pollution at a given site, without additional information.

Table 1. Indices characterizing the level of photochemical pollution for several sites

Site (altitude)	Period	Pollution index
Athens	summer 1985	16.0
Paros (800 m)	summer 1985	1.3
Cairo	March 1990	5.5
Zagreb	summer 1990	5.3
Puntijarka (980 m)	summer 1990	1.5
Iz	summer 1991	1.8
Rovinj	summer 1991	4.8

The average diurnal behaviour at a site can be taken as typical for that site and large deviations from such behaviour can be searched for automatically and examined with respect to other available parameters. For instance, by plotting the average deviations as a function of wind direction the direction of strongly affecting winds can be identified.

Conclusion

Although the general level of boundary layer pollution by ozone in the various sites in Croatia is not alarming, every summer season and on many sites the usual air quality standards (80 to 100 ppb hourly average) are exceeded on several days even in some rural areas. The modern measurements were taken for too short a time period for any conclusions about the trends to be drawn, but the late 19th century measurements indicate that the average ozone levels in the city of Zagreb might have doubled over the past 100 years.

Acknowledgement

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LOCAL AIR POLLUTION PROBLEMS IN KOREA

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Abstract - During the past three decades, rapid economic development has taken place in Korea and the quality of air has deteriorated substantially, especially in large cities and industrial complexes. In the past the major source was the combustion of fuels, the amount of which rapidly increased with economic development and industrialization, and sulfur dioxide was the major pollutant in the air. However, as the number of automobiles have increased in recent years, automobile exhausts have become the main source of air pollution. Increasing public awareness leads to a consensus of sustainable development in Korean industries. The Government is formulating abatement policies and forces industry to comply to these measures. Investment in the facilities and R&D on environment should be increased, and international cooperation accelerated.

Introduction

Since 1962 the Korean economy has developed with an average annual growth rate of about 8%. During this period of rapid economic development and industrialization the population moved from rural areas to cities and industrial complexes, and at present more than 85% of the population of 42 million of Korea live in large cities. In the city of Seoul alone there are more than 10 million people, equivalent to 25 % of the whole population. Here environmental problems, especially air pollution problems mainly arise.

The quality of air began to deteriorate from the mid-seventies when the industrialization in Korea accelerated, but during this period, the main concern was economic development and industrialization, and the attention to environmental problems was minimal. However, as the quality of air continued to deteriorate rapidly, people began to be concerned about air pollution. The government started to take measures to control air pollution problems in the 1980s and some improvements in the quality of air have been achieved. However, as sources of air pollution are very diverse, and as the quantity and diversity pollutants increase with the industrialization, air pollution problems have become very serious and important problems to tackle.

Efforts to improve the quality of air have been accelerated with the establishment of the Ministry of Environment and the enactment of the Air Environment Preservation Act in 1990. As the public awareness of the preservation of environment is increasing, and the consensus on the environmentally sound and sustainable development (ESSD) is emerging, more strictly enforced policy measures are anticipated to improve the quality of air in Korea.

Present status of air pollution

Sulfur dioxide

Figure 1 shows annual average concentrations of sulfur dioxide in several large cities in Korea since 1980.

In an effort to improve the quality of air in large cities, several steps to improve the quality of fuel have been taken since 1980. Low sulfur fuel oil was first supplied in 1980 in Korea. The use of coal for heating commercial building and apartment complexes was regulated in 1984 and the use of LNG was required for these facilities in 1988 in large cities. The gradual decreases in the concentration of sulfur dioxide in Seoul and Pusan shown in Figure 1 are the results of these efforts. In the case of Seoul, the concentration of sulfur dioxide was 0.094 ppm in 1980, but it decreased to 0.062 ppm in 1988. It further decreased down to 0.043 ppm in 1991. This was the first time when the concentration of sulfur dioxide in Seoul was recorded below the level of 0.051 ppm (the Korean Ambient Air Standard since 1980. The concentration of sulfur dioxide in Seoul further decreased to 0.035 ppm in 1992.

TSP

The standard for TSP was first established in 1984, and measurements were taken from April 1984.

Figure 2 shows the content of TSP in the air in Seoul since 1984. TSP in Seoul was 210 μg/m^3 in 1984, but it decreased to 97 μg/m^3 in 1992 which is below the standard level of 150 μg/m^3. Levels of TSP in other cities in 1992 were also below 150 μg/m^3. There are seasonal variations in the level of TSP, showing higher levels of TSP in spring. Any noticeable reduction of TSP is not to be realized in the near future as the number of automobiles increases and the large-scale construction works of subways and apartment buildings continue in large cities.

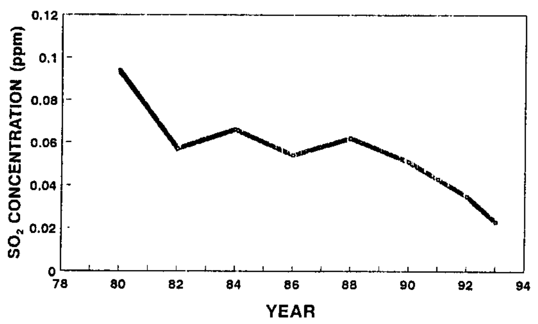

Fig. 1. Annual average concentrations of sulfur dioxide in several large cities in Korea

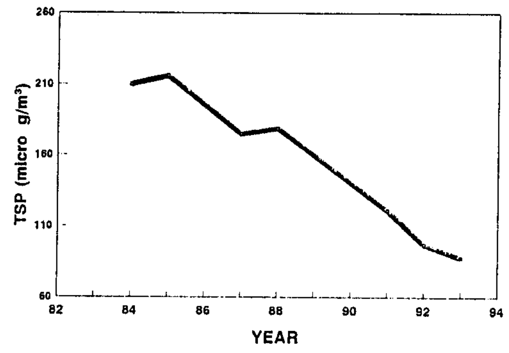

Fig. 2. The content of TSP in the air in Seoul

Acid rain

When the value of pH in the rain is lower than 5.6, the rain is called acid rain. The acidity of the rain was measured in Korea since July 1983 at 42 sites in 30 cities. Table 1 shows the measurements of acidity of the rain in large cities since 1986. It shows that in 1992 limited deposition of acid rain occurred in Seoul and Pusan. Like the concentrations of sulfur dioxide, there are seasonal variations in the acidity of the rain, showing higher acidity in the winter time.

Other pollutants

Standards for NO_2, O_3, HC and CO were established in 1983, and thereafter measurements for these pollutants have been taken at 78 stations in 31 cities. Figure 3 shows concentrations of these contaminants in Seoul. At present, these contaminants in Korea are below the environmental standard levels, but as the number of automobiles increases rapidly in recent years, it is anticipated that these pollutants will soon become major pollutants in the air, especially in large cities.

Table 1. Annual average of acidity rain in several large cities in Korea

UNIT: pH

CITIES	1986	1987	1988	1989	1990	1991	1992
SEOUL	5.3	5.1	5.7	5.6	5.0	5.4	5.3
PUSAN	5.2	5.4	5.2	5.2	5.2	5.1	5.2
TAEGU	5.4	5.3	5.6	5.3	5.7	5.9	5.6
KWANGJU	6.1	5.8	5.7	5.7	5.5	5.5	5.7
TAEJEON	5.4	5.5	5.7	5.8	5.4	5.6	5.7
ULSAN	5.2	4.9	5.1	5.6	5.6	5.7	5.6

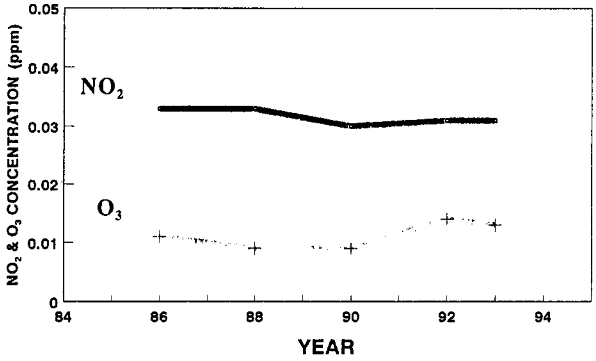

Fig. 3. The variation in the concentrations of NO_2 and O_3 in Seoul

Air pollution strategies and measures

Sulfur dioxide

As described before, due to measures taken in the quality of fuel, the concentration of sulfur dioxide has decreased in Seoul and Pusan. However, in some industrial complexes and cities where the obligatory use of low sulfur fuel oil and LNG has been delayed, the improvement is minimal. In order to reduce sulfur dioxide further, the government is planning to expand the compulsory use of low sulfur oil and LNG to wider areas. The level of sulfur content in fuel oil will be decreased further, and in order to meet the increased demand of low sulfur fuel oil, the major refineries were asked to employ desulfurization facilities in 1993. The government is planning to continue to discourage the use of coal, and to supply coal with a low content of sulfur.

Emissions of automobiles

The main single contaminant of air in Korea has been sulfur dioxide from the combustion of fuel, but as the number of automobile increases, it is anticipated that automobile exhaust gases will become the major pollution source.

There are more than 6 million automobiles in Korea in 1994. This is an increase of a factor of 150 within 30 years, compared is the total number of automobiles of 40 000 in 1965. In 1992 the total amount of air pollutants was estimated to be 760 000 metric tons, with a contribution of 460,000 metric tons from automobile exhaust gases. At present the concentrations of NO_x and CO in the air in the major cities in Korea are not higher than in the developed countries, but it is certain that this type of pollutant will increase with the number of automobiles, causing more frequent smog and visibility problems. In an effort to reduce the air pollution from automobile exhaust gas, an automobile emission standard was set and put into force in 1980. Strict emission standards for new gasoline and LPG vehicles were set in 1987. According to the standard, from 1988 on all newly manufactured passenger cars using gasoline are required to be equipped with catalytic converters. As a result, in 1992 all gasoline passenger cars and 90 % of LNG passenger cars are equipped with catalytic converters. In 1993 the sale of leaded fuel was stopped, and the use of phosphorus was restricted in gasoline as a catalytic medium. Further regulations and measures are planned to encourage the change of fuel in small cars from diesel to gasoline. The engine power of city commuter buses will be raised from 185 Hp to 230 Hp to reduce smoke. 50 % of the buses will be equipped with the more powerful engine by 1996. Standards for the quality of gasoline will be upgraded. Stricter controls of automobile emission gases for newly manufactured automobiles as well as existing automobiles are also planned.

TSP and noise

The government plans to prepare realistic programs to reduce TSP in 1994.

Noise in large cities is already a serious problem. Measurements of the noise level in cities due to city traffic are under way in 1994, and will influence new regulations to control noise. Also in 1994, standards on the noise and vibration due to trains and airplanes are being prepared.

Air-monitoring network

In 1992 there were 78 air-monitoring stations in 31 cities in Korea measuring automatically six major ambient air pollutants (TSP, sulfur dioxide, ozone, lead, and hydrocarbons) along side meteorological parameters. The number of air-monitoring stations will be increased to 112 in 47 cities by 1996. In addition to these stationary monitoring stations, major cities also operate mobile monitoring stations.

The stack monitoring network has been operated as part of an overall program to improve air quality and to control emissions. Since 1989 in the Ulsan industrial complex, about 170 stacks are monitored. It is planned to install continuous monitoring systems to most of the stacks in 1994.

Acid rain monitoring network

Acid rain monitoring stations have been operational since 1983, and as of December 1992, there are 42 stations in 42 cities. The number of stations will be increased to 65 in 45 cities by 1996.

Research and development

The Government-sponsored National Environmental R&D programs were launched in 1985 as a subprogram of "technology development for public welfare" of the Ministry of Science and Technology. In 1992 the more comprehensive National R&D programme on Environmental Science and Technology was formulated which will be carried out with inter-ministerial coordination of the Ministry of Science and Technology, the Ministry of Environment and the Ministry of Commerce and Resources. Major research institutes in Korea such as the Korea Institute of Science and Technology (KIST), the National Institute of Environmental Research (NIER), the Korea Research Institute of Chemical Technology (KRICT), the Korean Environmental Technology Research Institute (KETRI) and the Seoul Metropolitan Institute of Public Health and Environment, and many universities are collaborating in these projects.

The environmental market in Korea is expected to grow rapidly, and, consequently, technologies for environmental protection and pollution abatement have become important. Recently, most of engineering subsidiaries of Korean conglomerates and many specialized environment companies have started to invest more in environmental R&D to meet the expanding market.

International cooperation

Korea is participating in many international environmental institutions. As for UNEP and WHO, Korea actively participates in the Global Environmental Monitoring System (GEMS) and the INFOTERRA program. In close cooperation with UNDP and ESCAP, Korea is actively pursuing exchange of information and development of human resources and promotion of cooperative programmes. Korea plans to actively participate in the East-Asia/North Pacific Region Project of IGAC and the PEM-WEST Project of NASA to investigate problems of air pollution, transport of pollutant, and acid rain over a large area.

Korea has also been conducting series of bilateral cooperation programmes with USA, Japan, Russia and Australia since 1987 to enhance the nation's capability in handling environmental problems. Such international cooperation will be more actively pursued in the future.

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THE APPLICATION OF ACCELERATOR MASS SPECTROMETRY (AMS) IN THE STUDY OF SOURCE IDENTIFICATION OF AEROSOLS IN CHINA*

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Abstract - Accelerator Mass Spectrometry (AMS) is a new physical technique and it was successfully established in China in 1992. This paper describes the application of AMS in source identification for atmospheric aerosols which was part of the national project of AMS application in environmental research. For comparison, sources were studied using multivariate analysis models such as correspondence factor analysis, principal factor analysis and pattern recognition analysis. The results of the samples collected in suburb of Beijing, analysed by factor analysis, showed that the predominant TSP source was soil which contributed more than 50% to atmospheric particles. However, the AMS results demonstrated that carbonaceous aerosols have quite different emission sources. For carbonaceous aerosols of Beijing, Hunan and Shandong, the contribution to ambient particles from fossil fuel was nearly 2/3, and as human activities (coal-burning, etc.) increases, the fossil part contributes more. Therefore, it is significant to combine the method of factor analysis and AMS in the study of atmospheric aerosols.

Key Words: AMS, factor analysis, aerosol, source identification

Introduction

Aerosol is one of the most important atmospheric pollutants, serious particulate pollution is characteristic of the atmosphere in China, and was long been of concern. Therefore, research on aerosol particles has been undertaken over a long period. This research mainly focussed on size distribution, chemical composition and the origin of aerosols (Xu Weiguang, 1981; Wang Mingxing, 1985; Zhang Yuanhang, 1987). A number of multivariate analysis methods were developed to study the origins of aerosol, most of them shown to be useful for obtaining information. However there are two main limitations for factor analysis (Herry, 1987);
(1) The basic hypothesis of factor analysis theory is that all factors are independent and uncorrelated, but the hypothesis is only partly true, which is the main problem for determining the actual source apportionment of aerosols;
(2) Uncertainty stems also from the unequivocal character of trace element compositions from different sources. For example, the aerosols originating from soil and coal-burning have similar source profiles and it is hard to identify the two most important aerosol sources in China.

Thus, in order to obain more information about aerosol sources, some new techniques have been employed in research of this field. As ^{14}C was an unique tracer for biogenic sources, accelerator mass spectrometry (AMS) stands out as an important tool for source identification for aerosols and other species.

AMS allows a reduction of sample size to milligram level (Liu Yuanfang, 1994). Therefore, AMS makes it possible to use the information of important isotopes in environmental research. From 1993, a national project was started for this kind of research in China, planning to employ AMS in the study of source identification for atmospheric methane and aerosols.

In this paper, the methods of factor analysis and AMS will be combined for source identification of aerosols in China, and by comparison and assessment of the two methods, a new approach is investigated to obtain more reliable information on aerosol sources.

Experiments

(1) Field sampling

From August to November of 1993, two large volume TSP collectors were used for field sampling in Zhongguancun region, a suburb northwest of Beijing, for factor analysis and AMS method respectively. The samples for the two methods were collected at the same time; each sample needing nearly 24 hours to collect. In total, 50 samples were collected for each method.

To test the composition of carbonaceous aerosols in China, a few samples were collected in downtown Beijing, Shandong, a coastal province and Hunan, a terrestrial province of China. The range of mass concentration was 0.36 - 0.42 mg/m^3 for samples from suburb of Beijing, and 0.44 - 0.57 mg/m^3 for urban samples of Beijing.

(2) Graphite target preparation
The first step to apply AMS in environmental studies is to convert the ambient samples to graphite targets. A vacuum line was set up for AMS graphite target preparation from aerosol samples (Fig. 2). The line consists of four parts: vacuum pump, combustion, CO_2 purification and reduction. It needs 6–8 hours for our conversion line to make one graphite target from aerosol. The accuracy of the overall process has been tested by the conversion of archaeological samples whose ages were determined (Table 1).

(3) Trace element analysis
The trace elements composition of each sample for factor analysis were measured with ICP in the Research Center of Ecological Environment, Chinese Academy, the measured elements were totally 21 species: Ba, Ca, Co, Cu, K, Mg, Pb, Sr, Zn, Mn, Al, Be, Li, Fe, Na, Ni, Ti, Cr, P, S and V.

Table 1. AMS measurement on standard archaeological samples

Sample	Actual age (BP*)	Age measured by AMS(BP*)
Charcoal 1	2120 + 90	2280 + 160
Charcoal 2	10510 + 270	10660 + 370

(BP*: before present)

Table 2. PFA results of Zhongguancun TSP

Factor	1	2	3	4	5
Source	Soil Coal-burning	Metallurgical source	Oceanic source	Secondary sulphate	Oil burning

Results and discussion

(1) Multivariate analysis results
As a traditional method, multivariate analysis models have been widely used in the source identification of aerosols. In this paper the samples from Zhongguancun region were analyzed by correspond factor analysis, principal factor analysis and target recognition analysis methods. The theory of these models can be seen in the papers of Herry(1984), Dai Shugui (1986) and Zhang Yuanhang (1987).

Correspondence factor analysis (CFA) is a simple model to reveal the relationship among samples and also trace elements in the samples. We find by CFA that the trace elements can be distinguished by four groups, which are represented by Ca, Fe, Zn; Mg, Al, Ti etc.; Na, K; and S respectively, and samples constitute clear clusters.

The CFA results can be further evaluated by Principal factor analysis (PFA) calculation. We obtained 5 factors by PFA which are listed in Table 2.

For source identification, target transformation factor analysis (TRFA) is a quantitative analysis method. We obtained 4 factors by TRFA. Comparing the calculated profiles with actual profiles we measured on samples from various sources, the four factors were determined to be soil and coal-burning source, oceanic source, metallurgical and oil-burning combined source and secondary sulphate source, which contribute 57%, 23%, 7%, and 13% to atmospheric aerosol respectively.

Therefore, the conclusion is that the results from CFA, PFA and TRFA are similar. These calculation shows that for the TSP samples of Zhongguancun, suburb of Beijing, the most important source is soil and coal-burning, which contributes more than 50% to atmospheric aerosol, the next origins can be listed as oceanic, metallurgical, oil-burning origin and secondary sources. Compared with historical data, though economic development increased in Beijing, the TSP and the contribution from anthropogenic sources showed tendency to decrease in recent years.

(2) Application of AMS
^{14}C is a special "fingerprint" for tracing biogenic species. The atmospheric ^{14}C used as a tracer was seen in atmospheric CO_2, CH_4 and aerosols studies (Currie, 1984). Trace elements and carbon account for similar percentages in mass concentration in aerosol (Fig. 1).

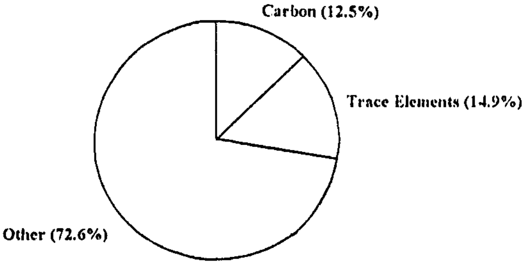

Fig. 1. Mass percentage of trace elements and carbon in aerosols of Beijing

Al and Pb were taken as representative elements from soil and vehicle exhaust, K/Al ratio is a biogenic tracer when lower than in crust material. For Beijing TSP samples, Al, Pb and total carbon (TC) vary similar to TSP, only ^{14}C has

Table 3. Source contributions from biogenic and fossil source to carbonaceous particles

(a) Beijing Suburb

	No-Heating Period								Heating Period		
Source	1	2	3	4	5	6	7	8	1	2	3
Biogenic	32	31	34	30	23	25	34	27	36	20	19
Fossil	68	69	66	70	77	75	66	73	64	80	81

(b) Downtown Beijing, Hunan and Shandong

	Downtown(NH)*			Downtown(H)			Hunan	Shandong
Source	1	2	3	1	2	3		
Biogenic	16	15	13	2.3	3.5	4.2	32	27
Fossil	84	85	87	97	96	96	68	73

* NH: No-Heating H: Heating

reverse variation with TSP. K/Al ratio has equivocal correlative variation with TSP or ^{14}C. So ^{14}C can be regarded as a reliable biogenic tracer for aerosols.

The quantitative calculation of the contribution of natural and anthropogenic sources to ambient particles can be obtained from the 14C abundant measurement on atmospheric samples and sources. 14C was measured in 11 samples in Beijing suburb region, 6 samples from downtown Beijing and 2 samples from Hunan and Shandong province (Table 3).

Multi variable analysis was performed on the 8 samples collected in no-space heating period in Zhongguancun region, which were simultaneously collected with the samples as above. The biogenic sources contribute nearly 1/3 to atmospheric aerosol, and in the winter period, the biogenic part is reduced slightly. The results of Hunan and Shandong do not show much season variation. But for samples of downtown Beijing, when coal consumption increases in space heating period, the biogenic contribute falls sharply, and fossil sources exceed 95%.

According to multivariate analysis, soil was most important source of trace elements in aerosols. The contribution of soil to total carbon, biogenic carbon and anthropogenic carbon in carbonaceous aerosols, were estimated to be 9%, 19% and 5% respectively. The contribution of the soil to carbonaceous aerosols was not so important.

Conclusion

The application of AMS in source identification of atmospheric aerosol in China is at an early stage. However, it can be concluded that trace elements and carbonaceous material contribute similar to ambient particles, but their origins differ greatly. It is necessary to combine the two methods in the study of atmospheric aerosols, to effectively study the source apportionment of aerosols.

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PHOTOCHEMICAL OXIDANT PROBLEMS AT YEOCHUN AND DONGKWANGYANG AREA, KOREA

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Abstract - Analysis of the trends in oxidant concentration indicates that increased emissions of precursors near Yeochun causes more frequent exceedence of the allowable limit of oxidant concentration. This increase of oxidant concentration is aggravated by local meteorological conditions.

Introduction

The Yeochun, and Dongkwangyang area is located in the southern part of the Korean Peninsula as shown in Figure 1. This area is characterized by high emissions along Kwangyang Bay. The bay features the single biggest steel-making plant in the world, over 35 petrochemical plants, and two fossil fuel powered electric stations.

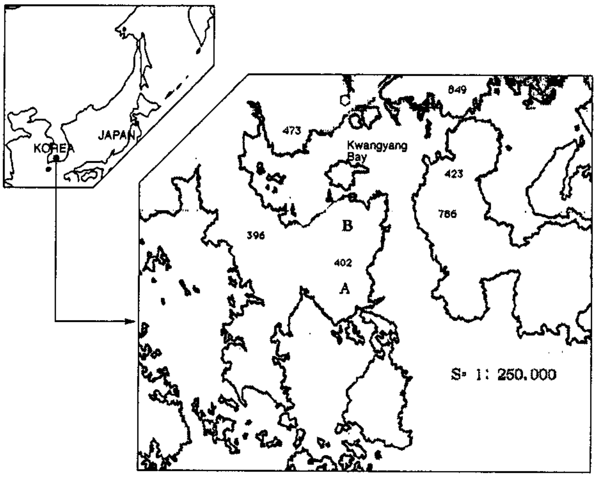

Fig. 1.
Location of sites used in this analysis.
A: Yeosoo, B: Yeochun, and C: Dongkwangyang.
Numbers in the map denote the elevation above sea-level in meters.

The steel-making company, POSCO, which is the second largest steel-making company in the world, produces approximately half of its product at one Dongkwangyang plant. It started its production in 1987, and further expansions were completed in 1990 and 1993. The petrochemical industries in this area have continously increased their production until very recently. Major expansion of the steel and petrochemical industries is planned for the future. The emissions of air pollutants have consistently increased since the establishment of the Yeochun industrial complex in 1969.

The distance between the steel-making plant located at the northern part of the bay and the petrochemical complex located at the southern part of the bay is about 5 - 20 km. The entrance to the bay is just 2 km wide and the topography surrounding the bay is largely composed of mountains and hills. This unique situation has been cause of much concern to local people and the Korean Ministry of Environment. The annual average oxidant levels in this region are the highest compared to data of all monitoring stations operated by the Ministry of Environment, and the level has noticeably increased since the early 1990s.

Oxidant trend analysis

Figure 2 shows the three-year (1990-1992) trend of oxidant levels at the Yeochun area. There is a definite increase in oxidant levels during the three years shown in this plot. The average oxidant concentration is a little bit lower in 1993 than 1992. Similar trends are also observed in other nearby monitoring stations, namely Yeosoo and Dongkwangyang.

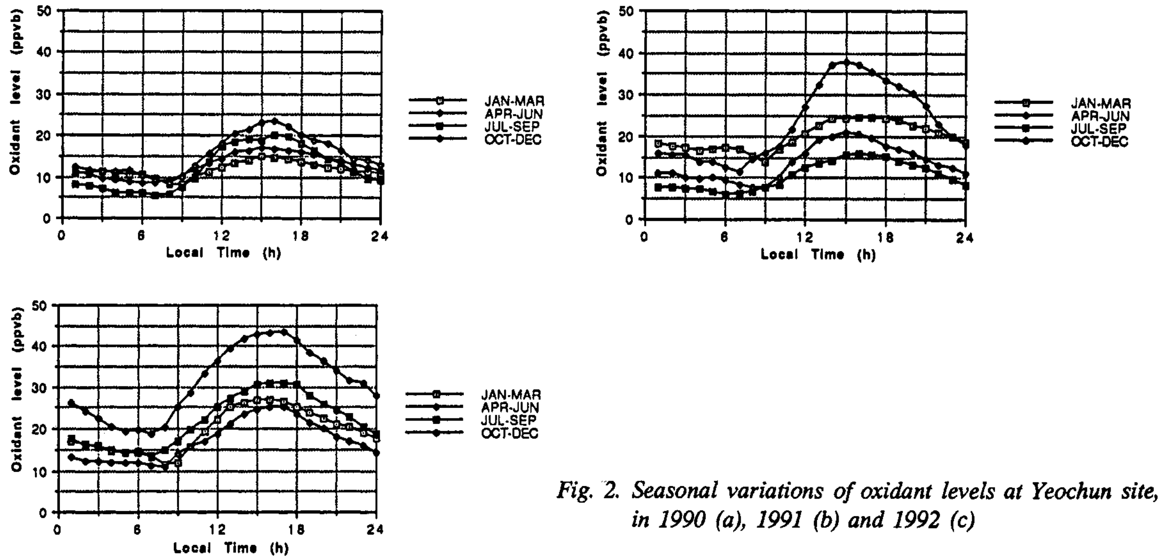

Fig. 2. Seasonal variations of oxidant levels at Yeochun site, in 1990 (a), 1991 (b) and 1992 (c)

The 24 hour average concentration in this region has a maximum in spring. This maximum is attributable to the vertical motion of the air related to anticyclones in the Northern Hemisphere and solar radiation intensity. The springtime oxidant maximum has been observed at Kosan, Cheju Island, Korea (K.Y. Park, 1993) and in other background monitoring sites in Japan. Monitoring data at the Kosan site shows very similar seasonal variations and concentration levels to those at Norikuradake (2876 m high above sea level), and Happou One (1940 m high above sea-level) in the central mountainous region in central Japan, and Hakkoudasan (1324 m high above sea-level) in the most northern part of the main island of Honshu in Japan (H. Ueda, 1993). The characteristics and behaviour of background surface ozone concentrations at 10 of the background surface ozone stations in Japan were analyzed by Sunwoo et al. (1993).

The daily pattern showing a maximum in the afternoon at the Yeochun site is shown in Figure 3. It is generally believed that the daily oxidant maximum will normally be observed during early afternoon hours due to photochemical effects. However, a night-time oxidant maximum was often observed at this site. The reason for the night-time oxidant peaks is not well-known. The vertical transport of oxidants present at high elevations and precursors of oxidants due to local meteorology is the most plausible explanation. The possibility of horizontal transport of oxidants is unlikely, since the area is far from major urban or other industrial centers and the immediate surroundings of the bay have a rural character.

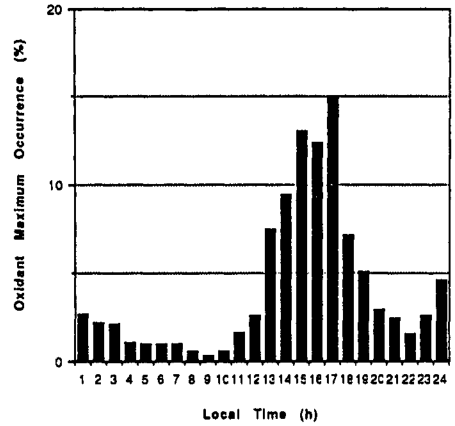

Fig. 3. Distribution of maximum O_3 concentration over 24 hours.

Table 1. The trend of exceedence of limits

Year	Hours of exceedence	Days when exceedence is observed
1990	18	9
1991	1	1
1992	22	10
1993	8	5
1994	27*	14

* until June, 1994

The oxidant concentrations measured at three air quality monitoring stations maintained by the Korean Ministry of Environment never exceeded the Ambient Air Quality Standard for oxidant (100 ppbv averaged hourly) until 1993. In 1994, non-attainment of oxidant was observed for the first time since monitoring was started in this region. The number of high oxidant hours, defined as hours when hourly averaged oxidants levels are over 80 ppbv, has increased over the past few years. (Table 1)

This study confirms that high wind speed and cloud cover hinder the occurrence of high oxidant episodes, while the passage of slow-moving high-pressure systems through the area favors the occurrence of high oxidant episodes. The effort to forecast the occurrence of high oxidant episodes by analyzing the meteorological variables was not very successful, probably because of the complexity of the air flow in this area.

Conclusion

The oxidant monitoring data at Yeochun and Dongkwangyang have been analyzed. The seasonal variation shows a spring maximum. The oxidant level in this area has been increasing since the 1990s.

It is thought that local circulation coupled with synoptic scale meteorology is a crucial factor in determining the occurrence of high oxidant episodes in this area. The effect of sea-land breezes and mountain-valley circulations make the distribution of air pollutants complex. Pollutants emitted from both sides of the bay can be trapped in the Bay, causing high oxidant episodes in this region. In order to clarify the causes of the occurrence of high oxidant episodes, more complete observations and modeling studies are needed.

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LOCAL AIR POLLUTION PROBLEMS IN INDIA

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Abstract - The Indian megacities have achieved the dubious distinction of being some of the most polluted cities of the world and leading the list is the national capital Dilli. Exponential increase of the number of automobiles, particularly two- and three-wheelers, a number of industries and thermal power plants in the proximity of cities, the high population growth rate, poverty, unawareness and general apathy to the needs of environmental safety measures are mainly responsible for the current scenario. Considering the menace of air pollution which is new compared with other pressing problems such as those related to sanitation, drinking water etc., a significant amount of air pollution monitoring has taken place during the last one and a half decade. Needless to say, that a lot has to be done yet, but at the same time it must be added that currently serious efforts are being made on both government and public levels to meet the challenge of air pollution problems in India.

Introduction

The menace of air pollution in India, largely confined to urban areas, is rather new compared with the problems of poverty, population explosion, malnutrition, sanitation and quality of drinking water. With 27% of the Indian population living in urban areas, it is often proclaimed that India lives in its villages. However in terms of absolute number, 250 million urban residents would constitute one of the largest countries in the world. Further, the population growth rate in the larger cities is much higher than the already large Indian average. Some of the Indian metropolitan cities unfortunately qualify as being among the most polluted in the world and leading the list is our national capital - Dilli.

The rapid but not very well planned industrial growth during the recent past, the close proximity of industrial complexes and thermal power plants to the cities and residential areas, automobile exhausts continuously spewing toxic gases and the fast degradation of the forest cover - all have contributed to the increasing detriment of the environment [1].

The stress on life and environment brought about by pollutants and a general apathy and indifference to the need for environmental safety measures have led to disasters such as the December 1984 Bhopal tragedy, which claimed thousands of lives and created serious and adverse problems to many more [1]. The damage caused by the emissions from the automobiles and neighbouring industries to historical buildings and monuments like the Taj Mahal in Agra, Belur Math and Victoria Memorial in Calcutta, to name only a few, does not require an expert to be recognised.

Population, poverty and pollution

The total population of our planet 10 millennia ago was about 10 million. People in olden days were also polluting air by burning soft coal and wood; there were oxen and carts, horses and buggies, famine, starvation and water contaminated with microorganisms. But the people were too few and the land so vast that these insults could be absorbed without any serious consequence. Today the daily needs of about 5.5 billion people of whom many are maintaining a higher standard of living using more energy and products than ever before, have resulted in more toxic wastes. The enormous industrial growth, a measure of development and mainly responsible for the high standard of living, is greatly exploiting the natural resources and is the major contributor to the pollution loads in the world [2,3].

Currently the net addition to the global population is mostly in the developing countries which already have to provide habitats for about 80% of the people of the world. India with its present population of 900 million, occupies the first place in terms of the total increase in the number of children per year. It has 20 cities with over a million people each and a couple with over 10 million. In addition, there are several thousand cities with populations of more than 100 thousand. These numbers are likely to increase much more in the near future and by 2015 over 50% of the Indian population will be living in urban areas.

It is a known fact that the population growth, development and productive environment form the three points of a triangle [4]. Progress can hardly be made in one area unless progress is made in other two also. Further, poverty and higher population growth rate are closely related. Without the eradication of poverty and the provision of adequate women's education the "replacement level" fertility rates cannot be achieved [4].

The growth of the world population has in the past been accompanied by a steady increase in the world's capacity to provide for the necessities and amenities of human life. The problem, therefore, is not simply only of numbers. The problem has been the widening disparity in consumption and life styles between the rich and the poor. A child born in a rich industrialized country or in a rich family in a developing country, where the per capita consumption of energy and materials is high, places a much greater burden on the planet than the child born in a poor country/family [4,5,6].

Two groups in particular are responsible for a disproportionate share of the consumption of resources and environmental degradation; the world's billion richest and billion poorest. Those at the top consume the largest slice of the Earth's resources and generate an enormous quantity of waste. Those at the bottom have the highest fertility rates and their quest for survival is responsible for a disproportionate amount of environmental destruction [7]. The Indian subcontinent is unfortunately credited with having a large number of people in the latter class.

Local pollutants and their monitoring

Urbanisation, while having a positive impact on economic development, has over the years led to the overall deterioration of the quality of the environment, with the larger cities reaching saturation point and unable to cope with the increasing pressure on their infrastructure. Indian cities, while contributing nearly 60% of the national income, are also inherently unsustainable in environmental terms. The single most important factor responsible for the degradation of air quality in cities is the exponential increase in petrol and diesel fuelled vehicles. Between 1986 and 1991, the number of vehicles on Indian roads increased from 11 million to 21 million. About 20% of the total vehicular population in India is concentrated in about half a dozen major metropolitan cities.

Another distinctive feature of the vehicular population in India is the fact that nearly 70% of the vehicles are two- and three-wheelers which are mostly driven by inefficient fuel burning two-stroke engines. The number of two-wheelers has been growing at the rate of 20% a year and there will be around 36 million such vehicles by the turn of the century, as against 7 million in 1987. The two- and three-wheelers are likely to constitute 80% of the vehicles in 2000 AD, and most of these will operate in urban areas [8].

Although the total vehicular population in India is low compared with rich Northern countries, Indian megacities are highly polluted. Apart from the heavy concentration of vehicles in urban areas, factors like types of engines used, age of the vehicle, congested traffic, poor road conditions and outdated automotive technology also accentuate the problem, making the situation grave.

An estimate of the total pollution load in major cities made by the Central Pollution Control Board (CPCB) during the year 1991 shows that Dilli tops the list in pollution load, followed by Bombay [Fig 1]. Among the pollutants, CO emission was found to be the largest. Two-stroke vehicles were found to be the major contributors of CO emissions. Hydrocarbons and oxides of nitrogen together constitute a substantial portion of the total vehicular emission.

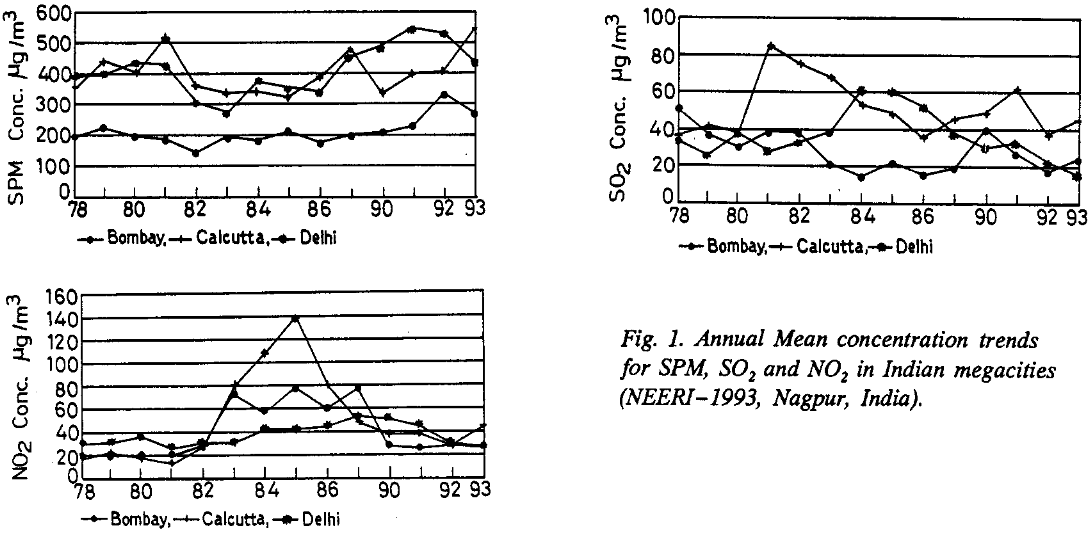

Fig. 1. Annual Mean concentration trends for SPM, SO_2 and NO_2 in Indian megacities (NEERI-1993, Nagpur, India).

Monitoring by CPCB at different traffic intersections in Dilli shows that ambient CO and NO_x exceed the prescribed limit. Further, a study by the CPCB on the ambient noise levels in the metropolitan cities has shown that the noise levels exceed the standard and that the vehicles are the major sources of noise.

Pollutants emitted from the thermal power plants, particularly if located in the urban neighbourhood, also need special mention. A coal-based thermal power plant pollutes the atmosphere by gaseous emissions of SO_2, NO_x, large amount of solid wastes, fly ash and bottom ash. A super thermal plant using even normal or low-sulphur coal will emit about 100 tonnes of sulfur dioxide a day.

The first organized effort to record comparable, continuous and concurrent data on gaseous and particulate pollutant levels in the ambient air was initiated in the late 1970s in ten cities by the National Environmental Research Institute (NEERI), Nagpur as the National Air Quality Monitoring Programme. These cities include Ahmedabad, Bombay, Calcutta, Kochi, Dilli, Hyderabad, Jaipur, Kanpur, Madras and Nagpur. The data have established long term air quality trends for health related critical pollutants such as : Particulate, Suspended Particulate Material (SPM), SPM<100 μm, Respirable Suspended Particulate Material (RSPM), RSPM<10 μm), SO_2, NO_x, NH_3, H_2S and Polycyclic Aromatic Hydrocarbons (PAHs). The PAHs and toxic trace metals are concentrated in the respirable size fraction i.e. less than 10 μm size aerosols in urban airsheds. The analysis indicated that RSPM in the Indian Urban environment during 1991 and 1992 accounted for 30 to 35 % of the total SPM. The industrial sites have shown higher concentration profiles for RSPM ranging from extreme concentrations of 53 $\mu g/m^3$ (Hyderabad) and 232 $\mu g/m^3$ (Calcutta).

In addition to this there have been studies related to the analyses of wet and dry deposition processes prevailing in the atmosphere with reference to industrial, commercial and residential sampling areas to enable evaluation of the acid rain, characterization and specification of aerosols in various size fraction (<100 μm and <10 μm) for toxic trace metals such as Al, As, Cd, Cr, Cu, Fe, Pb, and Zn; analysis of organic fraction of SPM, and evaluation of cationic and anionic species in wet and dry deposition of air pollutants. Higher sulfate contents in rain water have been recorded in industrial zones of Ahmedabad, Kochi, Kanpur and Madras. Conductivity of rain water was maximal in the first rain event being the highest at Kochi [415 μ mho/cm.] at the lowest pH (4.8) during 1992-93 indicating the built-up of pollution due to anthropogenic activity.

For the sake of completeness a few words may be added with regard to other important pollution problems in the Indian context.

During summer, in many parts of the country, there is an acute scarcity of water in general and potable water in particular. Until recently almost all the towns and cities located on the banks of rivers have been dumping their untreated effluents and wastes directly to the rivers. Even the ground water is being polluted by injecting the untreated discharge directly to the water table by many factories. This aspect, along with the soil degradation and the problem of the disposal of waste, needs to be more carefully investigated.

Concluding remarks

It has long been recognised that poverty is one of the greatest threats to the environment. In the developing countries, many choices that degrade the environment are made because of the imperative of immediate survival and not because of a lack of concern for the future. Economic deprivation and environmental degradation have thus come to reinforce one another in a vicious cycle that perpetuates destitution. Top priority for the world community will have to be in the agreement on ways and means - which fortunately are known - to stop this cycle [4]. Environmental degradation in general is a global problem and can be tackled only by the joint efforts of the whole world [9].

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SUMMERTIME PHOTOCHEMICAL POLLUTION IN BEIJING

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Abstract - The large increase in traffic density in Beijing has created problems regarding photochemical smog. Data from monitoring stations show increased exceedence of the maximum allowable concentration of 80 ppb. Trajectory analysis during photochemical smog episodes show that highways and areas characterised by dense traffic contribute significantly to this problem.

Introduction

Since the 1980s, rapid economic growth in China has caused an enormous increase in the number of vehicles in large cities, such as Beijing, the capital of China. This has led to a large increase in the summertime photochemical pollution in the city area, which damages vegetation and affects human health. For the assessment of the current situation and predicting future development of photochemical pollution in this area, field measurements associated with meteorological observations were conducted in 1986, 1987 and 1993, and a numerical model for predicting the ozone concentration in ambient air was developed. It was found that the surface ozone concentration frequently exceeded the national air quality standard, and that photochemical smog pollution has become an acute problem in the Beijing area.

We report here the observations of field measurements within the Beijing area, the comparison of three year's data, and the application of trajectories for source identification. The prediction of potential ozone ambient air concentrations for this area in 2000, 2005 and 2010 will be reported in another paper.

Field observation

Beijing area is located in the north-west part of North China Plain with an area of 16808 km2. The north east, north, and west part of this area are surrounded by mountains, but the south east part is in a plain slightly sloping down to Bohai Bay. The meteorological conditions in this area are characterised by southerly winds in the afternoon and northerly wind at midnight. The minimum wind speed appears mostly in summertime and in early morning, but the maximum wind speed is at 15.00-16.00 hour in the afternoon.

The location of monitoring sites for the measurement of ozone and its related species, shown in figure 1, have been chosen according to the previous records of ozone ambient air concentration, the major wind field data and the location of possible pollution sources. Three field measurements were conducted in July 8 to 17 in 1986, June 2 to 11 in 1987 and June 10 to 24 in 1993, simultaneous with meteorological observations. The ambient air concentration of O_3 ,NO_x, total hydrocarbons, individual C2–C10, and HNO3 etc. have been measured by using the standard analytical methods published by Chinese National Environment Protection Agency.

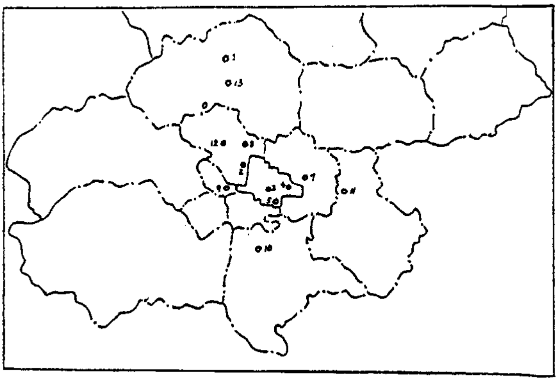

Fig. 1. Map of monitoring sites in Beijing area

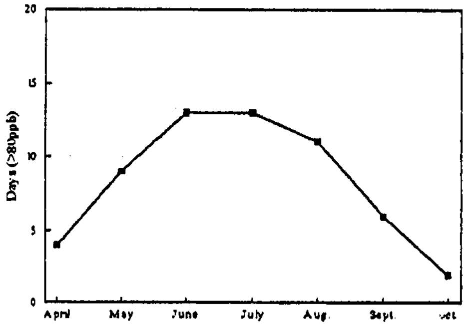

Fig. 2. Monthly variation of number of days exceeding 80 ppb of ozone (1985–1988)

Results and discussions

1. Ambient air concentration of ozone in Beijing area

Data for ozone, collected from the monitoring network of Beijing Municipal Monitoring Station, show that high ozone concentrations appear usually from May to September, and reach its highest level in June, July and August. Figure 2 shows the monthly variation of days in which the ozone ambient air concentration exceeds 80 ppb, the second level of National Air Quality Standard, during 1985–1988. Figure 3 gives the diurnal variation of averaged ozone concentration observed in June of 1987 and 1993. It indicates that in summer the ozone concentration is increased from 10 to 20 o'clock in 1987 and 8 to 20 o'clock in 1993. The ozone peak appears not only earlier, but is also higher in 1993 than that in 1987. These variations are closely related to the higher temperature and solar intensity in Beijing area during this period.

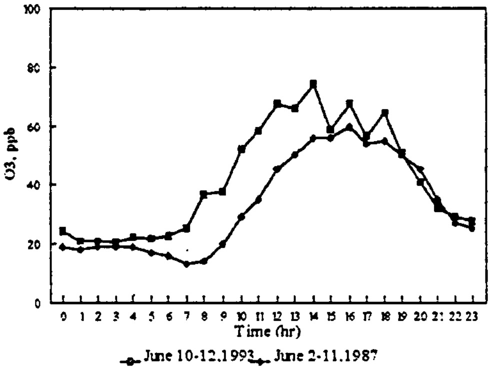

Fig. 3. Diurnal variation of average ozone concentration

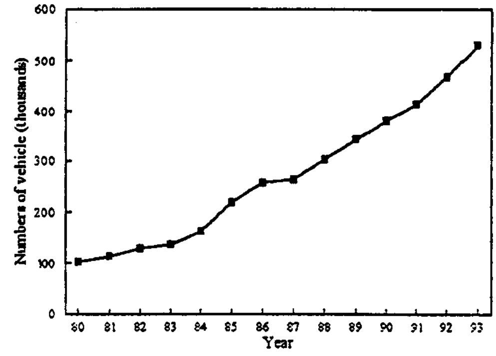

Fig. 4. Increase of the vehicle movements in Beijing area (1980–1993)

The spatial distribution of ozone in summer in Beijing area is reflected also by the days exceeding 80 ppb. From table 1 and Fig. 1 it can be seen that the north-western part and eastern part of Beijing are more polluted by photochemical oxidants and that pollution enhanced greatly from 1987 to 1993, especially in the south urban area (station No. 5). The enhanced photochemical pollution mainly depends on the increase in emission of pollutants and meteorological conditions in these years.

Table 1. The number of days exceeding 80 ppb of ozone in June 2-11, 1987 and June 10-24, 1993

Station	No. 1	No. 3	No. 5	No. 8	No. 9	No. 10	No. 11	No. 12	No. 13
1993	7.1	0 2	0.9	4.8	11.8	18.5	41.1	31.1	35.6
1987	3.5	1.3	4.5	3.5	7.4	9.2	15.4	18.0	11.6

2. The relation with vehicle emission

Table 2 shows the trend of ozone concentration changes in the summer of 1986, 1987 and 1993. The ambient air concentration did not show much difference between 1986 and 1987, but the frequency of exceeding 100 ppb in 1993 is around 4.5 times higher than observed in 1986 and 1987. The increase of the amount of vehicles in Beijing area from 1980 to 1993 shown in Fig. 4 shows the same trend.

Table 2. Ozone concentration in summer time (hourly average)

No. Year	Summertime (ppb) meas.	Avg	Max.	Frequency of exceendence in % > 60 ppb	> 80 ppb	>100 ppb
1986	1689	37	135	16.2	5.5	1.6
1987	2281	36	163	16.2	4.7	1.6
1993	1614	46	161	30.0	15.4	7.2

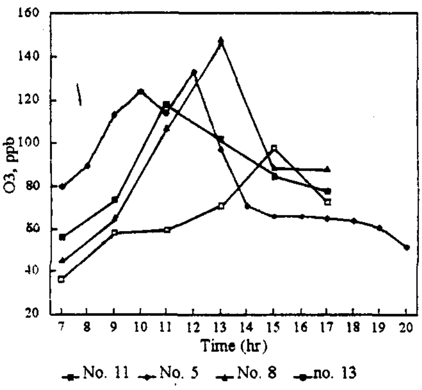

Fig. 5. Daytime variation of O_3 (June 15, 1993)

It is obvious that the enhanced photochemical pollution in Beijing is closely related to the rapid growth of transportation in this area. Beijing is a hub of transportation for whole China, with a yearly increase of vehicles of 13.8% on average. If this rate continues, more than two million vehicles in Beijing could be expected in 2015. Another problem is that the emissions of CO, hydrocarbons and NO_x per car are in China respectively 1.3 to 3.3., 4.4 to 8.2 and 1.5 times the emission rate per car in the USA. According to the emission inventory information in 1992, the emission of photochemical precursors hydrocarbons from vehicles contributed 84% of total HC emission in Beijing, and the NO_x contribution of vehicles to the total NO_x emission increased from 7.2% in 1986 to 13.2% in 1992.

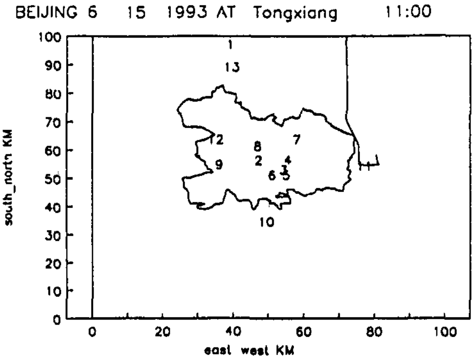

Fig. 6. Trajectory

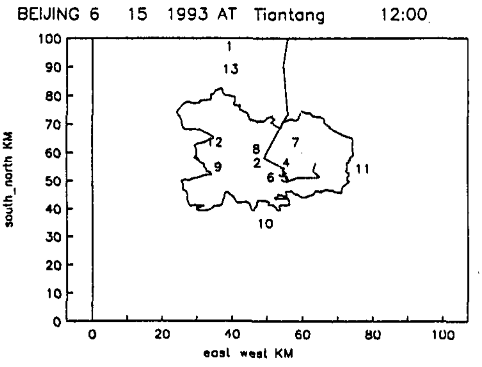

Fig. 7. Trajectory

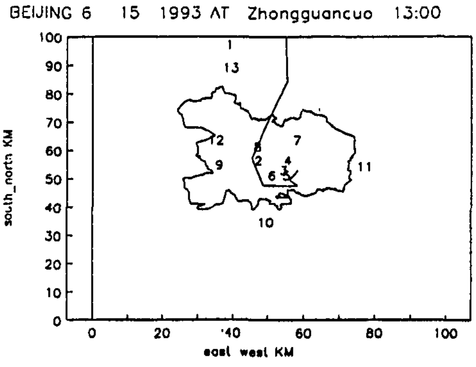

Fig. 8. Trajectory

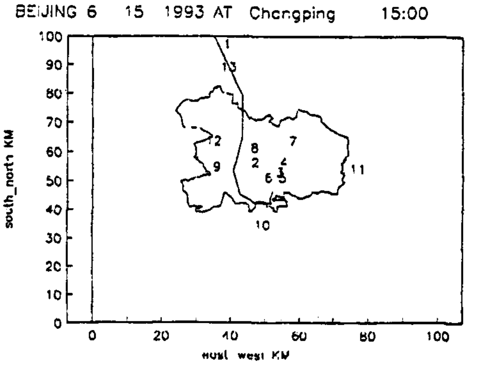

Fig. 9. Trajectory

3. Wind trajectory

In order to understand the relationship between the elevated ozone concentration and the emission sources, the transport of pollutant has been modelled by use of the data from 10 meteorological stations in Beijing area. Most of the results show that the trajectory of air mass with high ozone concentration originated from busy highways or areas of streets with dense traffic. Examples are shown in Fig. 6–9.

Fig 5 illustrates the daytime variation of hourly average ozone concentration at four measuring sites on June 15, 1993. where the high ozone concentration have been observed. Fig. 6–9 shows the air mass trajectories from 06:00 a.m. to 18:00 p.m., which passed through these four stations at certain time. In Fig. 6, the air mass passing station No. 11 originated from the very busy express way to the airport, and an ozone peak occurs at early noon.

In the case of station No. 5 and No. 8 (Fig. 7 and 8), the sources are located from the east urban area with prosperous market streets. Because of the downwind location of station No. 3 (Fig. 9), the highest ozone peak appeared in afternoon while the air mass has accumulated more pollutants.

EMISSIONS AND AMBIENT AIR QUALITY TRENDS, CALCUTTA CITY: 1973–1993

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Abstract – Traffic emissions in Calcutta have increased sharply and the resulting impact is threatening human health and damaging buildings such as the Victoria Memorial Hall in Calcutta. Ambient concentrations have been monitored around this building and a model has been developed which describes concentration and deposition patterns as function of traffic emissions and abatement measures. Planting a green belt is the most effective counter measure to abate the impact of local emissions on Victoria Memorial Hall.

Introduction

With the growth and expansion of the city and progressive industrialization of the areas on both sides of the river Hoogly, the population of Calcutta had been increasing rapidly since the beginning of this century. The 12.2 million inhabitants, as per the 1991– census, is expected to be 16 millions by the year 2001. More than 35% of the residents are classified as slum dwellers (1).

The paper presents the projection of air pollution aspects of Calcutta in the perspective of population dynamics, economic development and existing air quality status in relation to the health-related parameters as monitored under the National Air Quality Monitoring programme by the National Environmental Engineering Research Institute (NEERI) on a regular, long term basis (2,3,4,5,6,7).

The city proper has an area of about 104 km^2 while the Calcutta metropolitan District measures 1,295 km^2. Calcutta has a characteristic tropical climate: hot and humid with more than 2000 mm of annual rainfall. Temperatures range from 10°C (in winter) to 40°C (in summer). Moderate northwesterly winds prevail for most of the year with a high frequency of calms. In this period evening smog often occurs due to night–time inversions. The pre–monsoon and monsoon seasons are dominated by strong southwesterly winds which favour transport and mixing of pollutants.

In the heart of Calcutta city there is a marvellous structure, one of the privileged historical and cultural heritage of modern architecture: Victoria Memorial Hall (VM).

Soft coke, wood, kerosene, charcoal, LPG and electricity are the major fuels in the domestic sector. The coal supply to the domestic sector indicates that coal still is the most important fuel for cooking due to its cheapness and readily availability around Calcutta city (8).

The transport system in Calcutta consists of buses, local trains, metro, trams, taxies, autorickshaws and ferry services in the inland water system, coupled with slow moving traffic like rickshaws pulled by human beings, bicycles and pedestrians. To meet the rising transport requirement, there has been a rise in the total number of vehicles registered in Calcutta municipal city. The growth of two–wheelers, four–wheelers, taxies and contract carriages during 1980–1990 has been 50%, 25%, 200% and 350% respectively (9).

Study area and methods

Air pollution in Calcutta city has been categorised under domestic, transport and industrial sectors. The contribution from the domestic sector has been quantified on the basis of type of fuel and per capita consumption of the inhabitants. Emissions of line sources are calculated on a yearly basis by means of the number of the registered vehicles by transport authorities and through actual vehicle count surveys at the traffic centres around VM for the following categories. Light duty gasoline, heavy duty gasolene and light duty diesel. Three main roads viz. Hospital, Cathedral and AJC Bose (all double lane roads approximately 200m, 200m and 300m long) define the VM boundary for GLC calculation.

NEERI has been operating three ambient air quality monitoring stations in Calcutta city since 1973 for suspended particulate matter (SPM) on a 24 hourly basis up to 1987 and an 8 hourly basis from 1990 onwards using a Hi-vol-sampling technique. Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are monitored by standard methods on a 4 hourly basis (10). The data are processed for statistical analysis using EPA methodology including storage and retrieval of aerometic data. These air monitoring stations representing industrial, commercial and domestic ativities are also identified as Global Environmental Monitoring Stations (GEMS-AIR) by UNEP, WHO.

To evaluate the impact of pollution on sensitive receptors, a versatile air quality model PAL–a UNAMAP package of air quality simulation modelling algorithm with certain modifications for local application, is employed. In order to assess the pollution impact on the monument, GLCs (Ground Level Concentrations) were predicted for SO_2, NO_2, HC and CO all over the VM campus which comprises 64 acres of land selecting a minimum grid of 25 meters. Predictions were made for all three seasons using a 30 years average of meteorological parameters obtained from the Indian Meteorological Department.

Various protection strategies were proposed for VM. A plantation scheme creating a green belt (GB) to mitigate pollution impact is the most appropriate and feasible sollution.

According to the NEERI:GREEN package (11) based on certain basic algorithms evolved using a Gaussian Diffusion approach and settling (depositions) rate concepts of dry deposition of pollutants, the pollution attenuation factor (Af) for sources releasing at ground level is given by:

$$Af = \frac{Q_{WB}}{Q_B}$$

Af = ratio of mass flux of pollutant reaching at distance X1 and X2 in the absence of GB (Q_{WB}) to the mass flux reaching at the same distance in the presence of the GB (Q_B).

Results

The total vehicular pollution load within the Calcutta Municipal city was 311.5 tonne/day during 1990. The major pollutants emitted from vehicles are carbon monoxide, hydrocarbons and oxides of nitrogen contributing approx. 65%, 15.76% and 17.3%, respectively of the total vehicular pollution load.

The actual pollution load is probably much higher in Calcutta city than the calculated load due to frequent traffic pile-ups, crawling speed of the vehicles, poor-maintenance and erratic driving patterns coupled with the presence of high rise buildings, slow wind patterns, high temperatures in the city (relative to the outskirts) and high humidity.

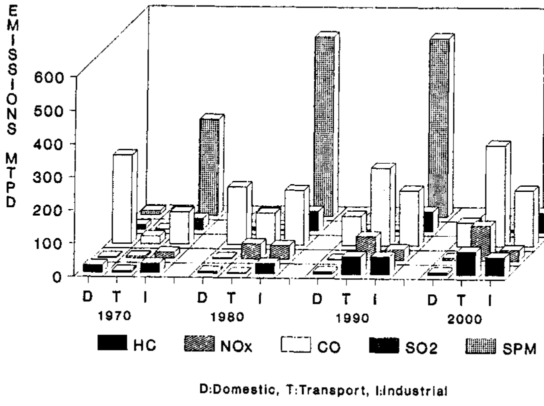

Fig. 1. Pollution Load in Calcutta city

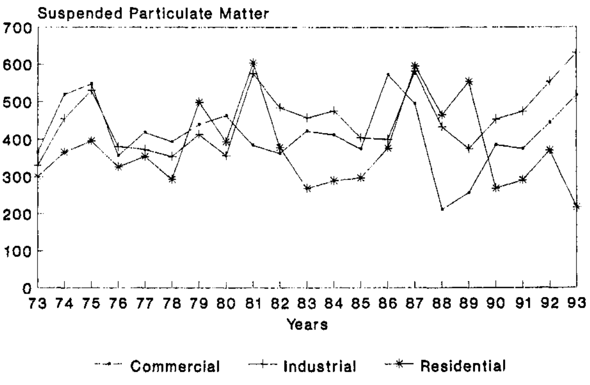

Fig. 2. Ambient Air Quality: SPM Calcutta in $\mu g \bullet m^{-3}$

An industrial survey (1990) of emission inventories projects that 77% of the total business categories fall under heavy industry and the rest under manufacturing and repair services. Heavy industries are located the surrounding areas of Calcutta city which include two coal-based thermal power plants, coal mining, iron, steel, manganese and mica refining. Medium- and small-scale industrial units accounting for more than 1,90,740, include glass and ceramics, machinery and tool fabrication, chemicals, rubber vulcanization and goods manufacture, foundries, jute, paper, hydrogenated oil etc. Coal with 0.3–0.7% 'S' content and 25–40% ash content is the major energy source for all these activities.

The major industrial pollutants in Calcutta are SPM and SO_2 (12). Fig. 1 projects the contribution of total pollutants, SPM, SO_2, NO_2, CO, HC from 1970 to 2001 AD from industrial, commercial and domestic sectors.

Ambient air quality

The ambient air quality status for SPM, SO_2 and NO_2 are shown in Figs. 2, 3 and 4. The SPM levels of the annual average concentrations are clearly exceeding the WHO long-term guidelines in all monitoring stations in all years. The annual average concentrations of SO_2 are below or around the WHO guidelines. The annual trend shows a marked seasonality with lowest daily average SPM and SO_2 in the monsoon period.

Air pollution impact analysis on a sensitive receptor

The overall predicted GLCs at VM of SO_2, SPM, NO_2, CO, HC for the winter season are shown in Fig. 5. The maximum predicted GLC at VM of SO_2, NO_2, HC, CO, SPM for post-monsoon were 23.5, 106, 806.7 and 19 $\mu g/m^3$, respectively. The GLC of NO_x pollution alone exceeded the prescribed Central Pollution Control Board standard value

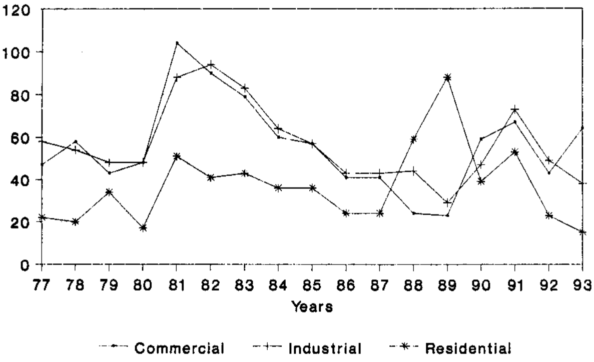

Fig. 3. Ambient Air Quality: SO_2 Calcutta in $\mu g\ m^{-3}$

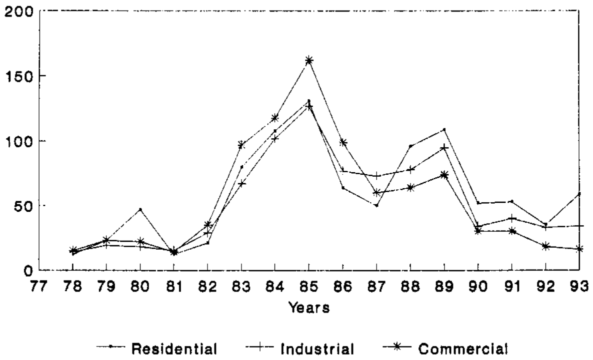

Fig. 4. Ambient Air Quality: NO_2 Calcutta in $\mu g\ m^{-3}$

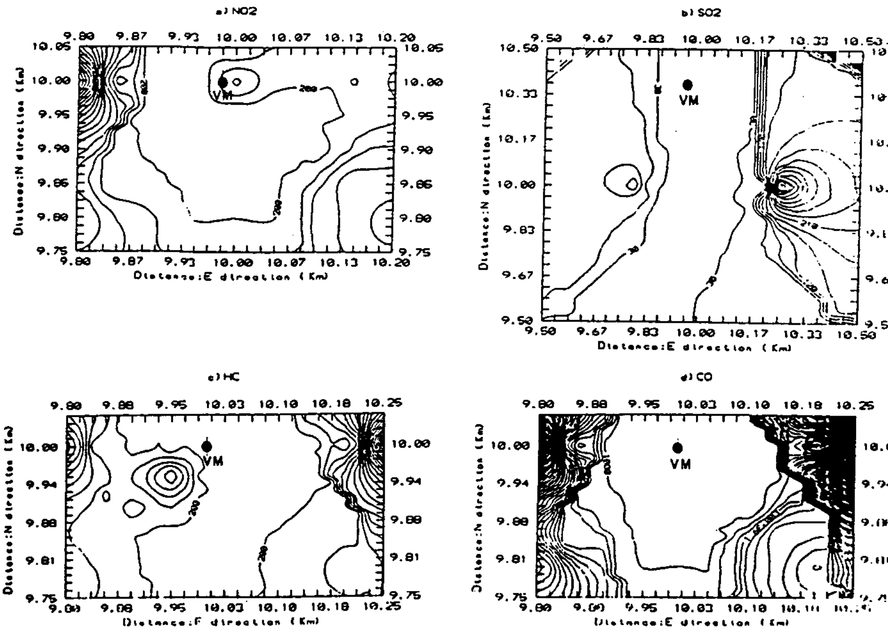

Fig. 5. Predicted GLC Isopleths: a) NO_2; b) SO_2; c) HC; d) CO

of 80 μg/m^3 for residential and commercial areas around VM. The predicted GLC values for winter and summer are lower than those of the post-monsoon period because of predominant ground level sources and existing meteorological conditions. Among all the three sources, it is apparent that the main contribution of pollution load at VM are traffic emissions from the surrounding roads.

The excessive pollution built-up around VM far exceeds the threshold of the urban air environment and consequences are reflected in deterioration of human health, vegetation damage and hastened decay of otherwise non-degradable building materials.

Table 1. Attenuation of pollutants after green belt development

Pollutants	Concentration (μg/m^3)		
	Hospital Road	Cathedral Road	AJC Bose Road
SO_2			
(Before GB)	19.00	51.80	25.08
(After GB)	2.95	8.06	4.00
NO_x			
(Before GB)	249.00	270.00	347.70
(After GB)	39.46	42.78	55.10
HC			
(Before GB)	204.00	412.00	225.60
(After GB)	1.67	3.37	1.84

Table 2. Results of green belt optimization model: NEERI-GREEN

	Pollutants		
	SO_2	NO_x	HC
Distance of GB from Road (m)	40	40	40
Width of GB (m)	20	20	20
Height of GB (m)	5	5	5
Attenuation Factor	6.42	6.31	122

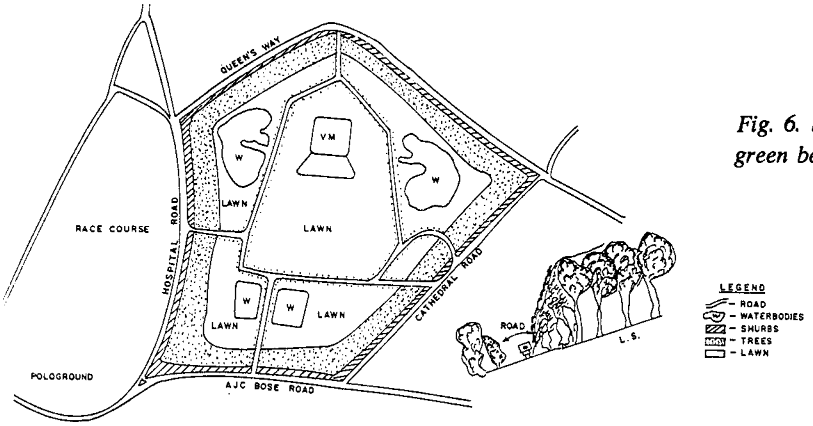

Fig. 6. Schematic representation of green belt around Victoria Memorial

The most appropriate control device to abate the pollution impact in this case is developing GB around the national monument. GB will serve two purposes: i) pollution attenuation and ii) aesthetic enhancement of the area as this is the monument of cultural heritage on one hand and the centre of tourist attractions at Calcutta on the other.

The parametric evaluation of GB sensitivity analysis carried out around VM indicates that the green belt is more effective in attenuating pollution under conditions of higher atmospheric stability because of restricted vertic dilution and smaller distances between the source and GB. Tables 1 and 2 show the results of a GB optimization model for stability class A. The schematic of plantation around VM is depicted in Fig. 6.

Conclusion

Human activities in general are the major threat to Calcutta's ambient air quality. The growth in population in this urban centre is the basic cause of air pollution. Coal supply to the domestic sector indicates that coal-based cooking still remains as a major pollution source. The transportation activity has increased to meet the increasing public demands and its contribution to pollution increased from 5% to 30% during 1970 to 1990. Though it has a large industrial base, it is expected that the pollution load contribution from industrial sources will remain constant in the next decade because of the state policy of locating new industrial units away from the city centre in an identified zone. However, the existing pollution load is quite high. The ambient air quality has shown that SPM concentrations are uniformly high and above WHO and CPCB long-term guidelines while fluctuating trends for SO_2 and NO_2 are observed. The impact of pollution on a sensitive receptor like VM has been evaluated and GB concept proposed to attenuate pollution impaction taking into consideration the uptake of pollution of indigenous flora to protect the monument.

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STUDY ON MASS CONCENTRATION OF AIRBORNE PARTICULATE CAUSED BY TRAFFIC IN BEIJING

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Abstract - The use of coal as fuel was, until recently, by far the most important source of particulate matter in Beijing. Increased intensity of traffic contributes to the emission of especially smaller particles at an increasing rate. The fraction of inhalable and respirable particulate matter in the total amount of suspended particulate matter has increased substantially.

Introduction

In the twentieth century, with the rapid development of modern industry, tremendous amounts of smoke, dust and poisonous gases are discharged into the atmosphere every year, causing direct impairment to human health and lives.

In the past ten years, with the development of industry and agriculture in China, increasing population, expanding cities, increasing energy consumption and destruction of forest and vegetation, the atmospheric environment, especially urban air quality, is getting progressively worse. Particulate pollution in China is quite severe now. Air pollution monitoring of four major cities in China using the Global Environment Monitoring System in 1981 showed that the suspended dust concentrations of both the northern and southern cities were rather high. The mean concentrations of all monitoring sites were higher than the recommended standard for suspended dust recommended by the World Health Organization in 1979.

One reason for the suspended particulate matter pollution in China is an uneven pattern in urban development. The density of population and the increase in construction, economic development and vehicle use are very high in big cities. The pressure on the environment is high, leading to serious pollution. Fine particles are characterised by their etiology, their ability to remain suspended in the air and to carry material which is absorbed on the surface. The smaller the particle diameter is, the longer it remains suspended in the air and the more hazardous it is. Suspended particles smaller than 1 μm can enter human lungs easily, causing pathological changes in lung or silicosis, even lung cancer. In addition, airborne particle pollution causes a decrease in air visibility and abnormal changes in vegetation.

Table 1. Data sheet

	#1	#2	#3	#4	#5	#6
Sampling Time (s)	20	20	20	20	20	20
Traffic (vehicles per hour)	3286	2200	1900	1440	1490	1700
TSP (mg/m^3)	0.212	0.156	0.098	0.051	0.069	0.071
IP (mg/m^3)	0.162	0.132	0.076	0.043	0.055	0.064
RMC (mg/m^3)	0.062	0.047	0.027	0.016	0.021	0.022
RMC/TSP	0.29	0.30	0.30	0.32	0.31	0.31
RMC/IP	0.38	0.36	0.36	0.38	0.38	0.34
IP/TSP	0.77	0.85	0.84	0.84	0.81	0.91

* Values of Traffic are estimated **Sampling data of each site is the mean of ten data

Table 2. Mass distribution data

	MMD(μm)*	GSD**	<1μm(%)	<3μm(%)	<10μm(%)
#1	4.73	2.105	2.6	23.3	79.1
#2	4.50	1.856	2.0	22.4	89.4
#3	4.78	2.145	3.1	27.1	87.2
#4	4.78	2.068	3.3	26.8	89.0
#5	4.58	2.028	4.3	25.8	86.7
#6	4.71	1.820	4.5	22.7	94.8

* MMD is mass median diameter. ***The percentage value is calculated from mass spectrum.
** GSD is the geometric standard deviation of MMD.

Mass concentration, an important characteristic which is frequently used in airborne particle research, can be described according the three definitions below: Total Suspended Particulate Matter (TSP), Inhalable Particles (IP) and Respirable Mass Concentration (RMC). IP is equal to PM10 which is one of the pollution indices of EPA. RMC gives the mass concentration of the fraction of the particles which is respired and deposits in the different parts of the respiratory system. According to the definition of RMC made by ACGIH (American Conference of Governmental Industrial Hygienists), RMC is different from IP. IP includes all the particles whose diameters are smaller than 10 μm, while RMC gives the deposited fraction of different sized particles. Therefore, RMC more accurately reflects the effect of particles on human health.

Sampling and results

In order to survey the air pollution due to traffic in urban areas, especially with regard to the human health effect, an APS (Aerodynamic Particle Sizer) was used to measure TSP, IP and RMC at six roadside sites in Beijing (Fig. 1) in the spring of 1994. The APS 3310 (TSI Inc., St. Paul, Minnesota, USA) is a well documented instrument for real-time measurement of the aerodynamic diameter of airborne particles. The size range of the instrument is from 0.5 μm to 30 μm. The instrument measures the time of flight (TOF) of the particles in an accelerated airflow. This is done by focusing two laser beams in the aerosol flow, thus generating a light scattering pulse both when a particle enters and

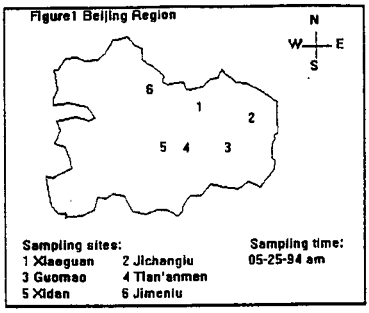

Fig. 1. Beijing Region

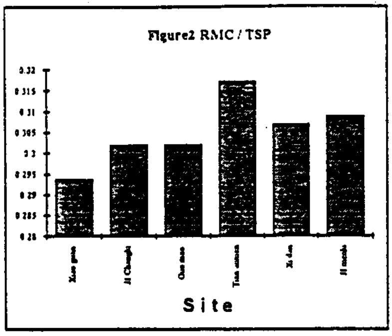

Fig. 2. RMC/TSP

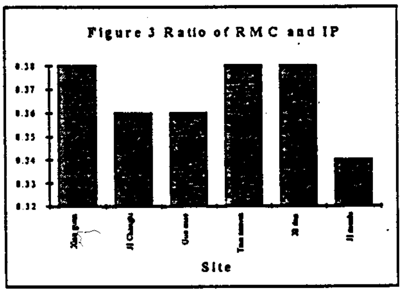

Fig. 3. Ratio of RMC and IP

leaves the measuring volume. By means of the instruments' calibration curve, the time of flight is converted into the aerodynamic diameter. At the same time, the mass distributions of the particles can be calculated.

The results show that: the mass concentration range of TSP($Dp<30\mu m$) is 0.051-0.212 mg/m^3; IP is 0.043-0.162 mg/m^3; RMC is 0.016-0.062 mg/m^3; MMD (Mass Median Diameter of TSP is 5.570-6.067 µm. The ratio of RMC and TSP is about 30% of RMC and IP about 37% and of IP and TSP about 83% (Fig. 2 and Fig. 3).

A typical mass distribution is given in figure 4 and 5.

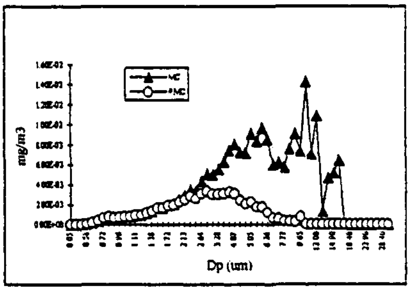

Fig. 4. Mass distribution-#1

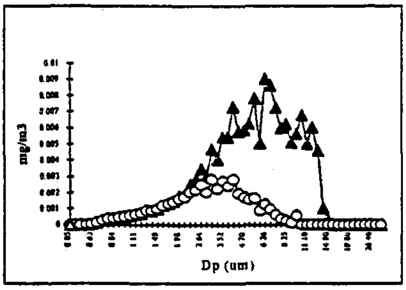

Fig. 5. Mass distribution-#2

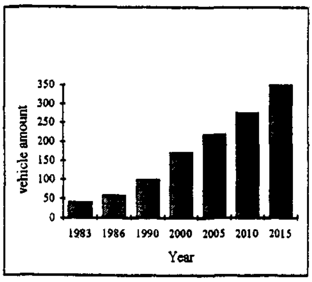

Fig. 6.

Conclusions

Compared with the data of the 1980s, the TSP values are a bit smaller, while the ratios of IP and TSP are much bigger. TSP daily means of the three limits in "Ambient Air Quality Standards" GB 3095-82 are 0.15, 0.30 and 0.50 mg/m^3 respectively. PM10 daily means are 0.05, 0.15 and 0.25 mg/m^3 respectively. The TSP daily mean recommended by WHO is 254 µg/m^3. Pollution has changed during the urban development. Appropriate pollution control technology is needed. In China there are now many high efficiency dust collectors and other similar equipment.

Urban air pollution in Beijing is mainly caused by coal burning. This situation will be improved with the introduction of high efficiency dust collectors. However, the main effect will be on the TSP value and the removal of the large particles. From a health point of view, therefore, the remaining particles are more hazardous than before, because the fine particles account for a bigger fraction of the total quantity. Exposed people undoubtedly suffer from the fine particles in the traffic exhaust; their total exposure to IP depends on the nature and strength of road sources of IP. Traffic airborne particulate includes suspended soil, resuspended dust, combustion smoke and ash.

The mass concentration of particles is closely related to the traffic density, traffic speed, road conditions and car types. In a traffic jam the health risk from respirable particles is much higher. With the rapid and continuous development in the national economy, the public transport industries are expanding rapidly. The air pollution on roads caused by vehicles is quite serious. Pedestrians and cyclists are particularly close to vehicles on the roads. Research results show that the main factor in the health effect assessment of particulate pollution is RMC. Accordingly air pollution by traffic must be allotted a high priority in research in rapidly developing countries. There were about 300 000 vehicles in Beijing in 1983. The average annual increase is 13.8%. Figure 6 is a projection of the future trend.

Since particle composition is a major determinant of toxicity, it is difficult to justify mass concentration limits for particle matter without reference to composition. According to the experiences from some developed countries, the enforcement of PM has almost certainly had beneficial effects on public health. The implement of PM concentration reductions has led to significant reductions in ambient concentrations of carbonaceous and metal oxide aerosols, many of which are toxic and/or carcinogenic. As China is a developing country and Beijing is a rapidly developing city, it will be very difficult to handle the conflicting interests of development and environmental protection. Research on urban particle pollution is beneficial for sustained development. Accordingly, air pollution by traffic must be allotted a high priority in research.

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LOCAL AIR POLLUTION AND COUNTERMEASURE IN GUIYANG

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Abstract - An assessment of pollution, regarding SO_2 and TSP in Guiyang is made. This assessment will induce and other abatement policies which will effectively improve air quality in Guiyang, based on the monitoring data in recent years. The result is that air pollution control in Guiyang should be focussed on area sources with an average height of chimneys of 28m, and that the use of fuel must be changed. Industrial briquet with low sulfur content will be burned in boilers, with a capacity below 4 tons of coal per hour.

Keywords: SO_2; TSP (Total Suspended Parameter); Countermeasure; Guiyang

The air pollution condition in Guiyang

Guiyang, as the capital city of Guizhou province, is one of the seriously air polluted cities in China. The main fuel in Guiyang is coal, accounting for 99.3% of the energy consumption. Coal burning leads to large emissions of sulfur dioxide and smoke, resulting in serious air pollution. The monitoring data from 1985 to 1989 in Guyang shows that, S02 and TSP in Guyang exceeded the national standard seriously.

The social and economic factor

The coal used in Guiyang contains 5% sulfur. Coal consumption is about 1.4 ton/year per person. This is 2.3 times as much as the average level in China.

Table 1 and table 2 show that SO_2 emissions from households, small boilers and furnaces chimneys of an average heights average of 5m account for only 24% of the whole city, the area source Pollution Concentration Burden (PCB), specific contribution of a catagory of emissions to local concentration, is 51% and 42% of the whole city respectively in winter and summer. Tables do not include data for summer. In the highest polluted region Da Shi Zi, the area source PCB is up to 73% and 62.7% respectively in winter and summer. Therefore, air pollution control in Guiyang should be focussed on small boilers, kilns and furnaces etc.

Table 1. SO_2 emission amount and percentage in various sources in winter

			area sources	
		5 m	15 m	28 m
controlled area	emission amount (kg/h)	10026	6528	9381
	percentage (%)	24	16	22
highest polluted area	emission amount (kg/h)	4647	2283	1753
(Da Shi Zi)	percentage (%)	48	24	18
industrial area	emission amount (kg/h)	989	142	2306
(Tai ci Qiao)	percentage (%)	5.7	6.0	13.3
industrial area	emission amount (kg/h)	642	635	1879
(Guiyang Iron & Steel Works)	percentage (%)	20	20	56
industrial area	emission amount (kg/h)	223	568	392
(Ma Wang Miao)	percentage (%)	8.9	48	33.1
light polluted area	emission amount (kg/h)	3524	1999	3052
	percentage (%)	33	19	29

Most of the industrial boilers in Guiyang are old and do not adhere to regulations regarding efficiency and pollution. Table 2 shows that the SO_2 PCB emission from boilers and furnaces with an average height of 15 m and 28 m are 25% and 21% respectively in winter, the total is 46%, and contribute 20.3% and 31.8% respectively in summer, totally 52.1%. Therefore, the boilers and furnaces with an average height of 15 m and 28 m are important pollution sources in our city, which should be controlled.

Table 2. SO_2 area sources PCB in winter (%)

	area sources				area sources		
	5 m	15 m	28 m		5 m	15 m	28 m
controlled area	51	25	21	the area between Da Shi Zi and Tai Ci Qiao	59	19	21
highest polluted area (Da Shi Zi)	73	17	6	the area between Da Shi Zi, Ma Wang Miao and Tai Ci Qiao	60	27	11
industrial area (Tai Ci Qiao)	43	27	25	light polluted area (the area in the north edge)	54	25	18
industrial area (Guiyang Iron steel work)	56	29	21	light polluted area (the area in the southwest edge)	47	26	23
industrial area (Ma Wang Miao)	54	37	8	light polluted area (the area in the southeast edge)	31	23	42

The industrial distribution is unfavorable. Over 80% of the boilers are located within the city proper. Important sources are the Guizhou cement works, Guiyang cement works and Guiyang power plant located in Tai Ci Qiao region, southwest of the city. Guiyang iron and steel works are in You Zha region in the southeast of the city, and a cotton mill in the center area of the city. In spring, autumn and winter, northern and northeastern winds are dominant; in summer, southern wind directions occur frequently in Guiyang). Therefore, the local sources pollute the center area of the city seriously.

The distribution of housing and industry over the city is not very functional to prevent pollution. In the densely populated mixed region, not only coal causes air pollution, but also many coal-burning domestic boilers contribute to the emissions. According to the data, SO_2 emission in the mixed region amount to 1850 ton/month per sq.km, while the $S0_2$ emission in the industrial region is only 1029.72 ton/month per sq.km. In the highest polluted area of the mixed region, $S0_2$ emission is up to 3780 ton/month/sq.km, exceeding the national standard seriously.

Natural environmental factor

The central area of Guiyang is in a basin, surround by mountains. This situation is unfavourable for the dispersion of pollution.

In wintertime atmospheric mixing is reduced because of frequently occurring inversions. The sun shines only during 6% of the days and strong vertical mixing is observed during 1% of the time.

Inversion can be stable for long periods. Around 6:30 P.M. in winter the ground air temperature begins to drop, and the lowest air temperature occurs in the next morning at 8:00 or 9:00. This phenomenon prolongs the inversion time, which just coincides with the peak hours of the area source emissions. In addition, the average wind speed is low and often downward winds converge in the center of the city. These meteorological conditions agravate the pollution in the center area of the city.

Abatement

To abate emissions of non-point sources the use of fuel can be changed to electricity, Liquefied Petroleum Gas, coal-gas and desulphurised briquettes. After the coal-gas project in Guiyang is put into effect this year, there will be 85 thousand households using coal-gas, which will reduce $S0_2$ by 0.013 million Ton/year. In addition, of production 1000 ton/year of low-sulfur containing briquets will be started by the end of this year. In 1995, there will be 42 000 households using low-sulfur briquets and 50 000 households will use liquefied petroleum gas. The three measures will reduce SO_2 by 3000 ton/year, 7000 ton/year and 14000 respectively. In 1995, SO_2 emission in area sources in Guiyang will be reduced with 90%. The environmental quality in the center area of the city will be improved greatly.

The use of low-sulfur briquets in small boilers with a capacity of less than 4 ton coal per hour for industrial application will reduce SO_2 with 40 000 ton/year. In addition, the National Science Committee and the National Environmental Agency are developing the demonstration of circulation fluidised bed boilers; of wet dust removal and desulphuration, and of desulphurised briquettes. These advanced techniques will be employed to improve the boiler efficiency and the emissions of SO_2 and dust.

Central heating will be developed step by step in some areas.
The area of forests in the city is expanded with 35%.

Abatement is based on suitable local standards of atmospheric environmental quality, according to the control scheme of the total of air pollution emissions. The maximal allowable emission amount of and the reduction for each pollution source is regulated. Control of air pollution is obtained by emission control. All emissions are licensed in terms of maximum allowable limits.

Conclusion

1. The main problem to control atmospheric pollution in Guiyang are emissions of area sources.
2. Changing the use of fuel and switching to electricity, natural gas, coal gas and desulfurised briquettes as enery sources is an efficient measure to reduce the emission of these area sources.
3. The applications of these techniques provide efficient countermeasures to improve the atmospheric environmental quality of Guiyang.
4. According to an optimised control scheme, the allowable emissions of each source is regulated, and emission control is implemented step by step.

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SOURCE APPORTIONMENT FOR AIR PARTICULATE MATTER IN DAGANG OIL FIELD

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Abstract - The chemical composition of particulate matter, sampled near Dagang oil field gas been measured and statistical analysis has been applied to these results in order to assess the contribution of different sources. This approach leads to coherent results and indicates that soil is the major source of particulate material, followed by emissions of coal combustion and, depending on the season, either emissions due to construction or oil combustion.

Introduction

Air particulate matter is a major atmospheric pollutant in north China (1). The sources of particulate matter are relatively complicated. Except for the major sources including dust and ash of coal combustion, industrial emissions, oil-combustion, motor vehicle exhaust, sea salt and soil, some secondary particulate matter such as sulphate and nitrate is also observed. The assessment of determinating the contributions of various sources in different seasons provides the basis for controlling air particulate matter, and it is also an important guide for environmental management and planning.

Sampling and analysis of total suspended particulate (TSP)

TSP samples representative for periods when heating is necessary and for periods when heating of houses is not required were collected from four sites during two sampling periods, from October 26 to October 31 and from December 17 to December 21, 1992 respectively. The sampling sites during the heating season were the same as those of the non-heating seasons. 0.8 μm organic micro-pore membrane filters (Beijing Chemical Engineering Professional School, China) and a Model-120A high volume sampler (KIMOTO Electronical Company, Japan) were used for sampling. The sampling period of every sample was 24 hrs, and 40 samples of TSP were collected during a five-day period.

Sixteen elements, including Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb, were analyzed for each sample (2-4). In addition, we also analyzed 5 soil GSD standard samples provided by the Ministry of Geology and Minerals as quality control.

Source profile determination and tracer element selection

In the investigation of the TSP sources in the area, soil dust, coal combustion fly-ash, constructional material dust, oil-combustion fly-ash, marine aerosol, motor vehicle exhaust, and iron and steel dust were selected as the major sources of TSP in this region.

The source profile of all sources could not be determined. Assuming that the conditions of other sources were similar to those of Tianjin, data were used as reported in the materials of research on sources of atmospheric particulate in Tianjin as reported (5). The source profile of coal-combustion fly-ash was adopted as the whole-particulate composition of medium and small boilers. By weighing the source compositions of cement and lime, we obtained the source profile of building material dust. The profiles of vehicle dust and oceanic aerosol were adopted from Kowalczyk's paper (6). In accordance with the relevant literature Si, Al, Ti were selected as tracer elements of soil dust, and coal combustion fly-ash, and K and As as subsidiary tracer elements for these sources. Ca, Ni, Pb, Na were selected as tracer elements of building material dust, oil-combustion fly-ash, motor vehicle exhaust, and oceanic aerosol respectively. The tracer elements of iron- and steel-dust selected were Fe and Mn. Building materials and soil-dust are sources of Mg, so this element was incorporated into the Model (see Table 1).

Table 1. Source profile (unit: μg/mg)

	Soil dust	Coal combus. flying dust	Construct. mater. dust	Oil combus. flying dust	Marine aerosol	Motor exhaust	Iron & Steel dust
Na	18.53±7.13	2.20±1.17	1.01±0.56	4.90±2.10	310.00±31.00	0	6.65±0.66
Mg	11.62±3.00	2.70±1.33	17.80±5.10	0.67±0.52	40.30±0.19	0	7.13±0.71
Al	69.70±16.45	156.00±41.50	30.70±4.12	1.36±0.44	0	0	25.30±2.53
Si	256.98±12.98	156.00±38.00	92.70±9.00	3.28±1.32	0.08±0.01	0	95.00±9.50
K	16.83±8.84	2.90±0.17	6.40±0.60	0.90±0.30	10.85±1.55	0	16.80±1.68
Ca	35.00±16.75	25.40±8.80	379.00±24.00	6.03±1.16	11.78±1.68	7.50±0.80	6.07±0.61
Ti	3.87±0.71	4.92±1.70	1.30±0.60	0.05±0.02	0	0	2.74±0.27
V	0.07±0.04	0.10±0.04	0.04±0.03	0.04±0.02	0	0	0.06±0.01
Cr	0.09±0.04	0.03±0.01	0.04±0.02	0	0	0	0.17±0.02
Mn	0.17±0.06	0.36±0.11	0.48±0.12	0.07±0.02	0	0	5.14±0.51
Fe	34.00±6.07	23.80±13.12	22.90±9.80	1.01±0.18	0	7.50±0.95	22.50±2.25
Ni	0.08±0.01	0.02±0.01	0.06±0.01	1.87±1.26	0	0	0.24±0.02
Cu	0.06±0.02	0.07±0.02	0.06±0.02	0.01±0.00	0	0	0
Zn	0.50±0.38	0.27±0.19	0.11±0.05	0.08±0.02	0	2.25±0.30	13.30±1.33
As	0.03±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0	0	0.02±0.01
Pb	0.04±0.01	0.03±0.01	0.07±0.03	0.02±0.02	0	40.00±5.10	0.39±0.04

Receptor model – chemical mass balance (CMB)

The Chemical Mass Balance (CMB) equations were solved by an effective variance weighted least squares estimation method in this study. The normalized Modified Pseudo Inverted Matrix was used to test the sensitivity of different fitting elements to various fitting sources and singular value decomposition (SVD) was used to determinate the collinearity among different profiles (7,8).

Results of the source apportionment

Results of TSP concentration analysis

Table 2 shows the average concentrations and standard errors of TSP samples in non-heating and heating seasons.

Results of source apportionment

By selecting and adjusting the sources and components put into the model, we obtained the source contributions, standard deviation, T statistics and the source apportionments, listed in Table 3.

According to the results, in the non-heating season, soil dust accounts for 42.6% of regional TSP, then comes coal combustion fly ash, which accounts for 15.3%. Accounting for 11.7% of total particulate matter, oceanic aerosol is also one of the largest sources, while oil-combustion fly ash contributes only 3.5% to the total amount of TSP. In a relatively windy and dusty area as well as one with a few green fields, it is no surprise that the contribution of soil dust is the largest. Because there is no other oil combustion source except for several oil combustion boilers in an oil refinery plant and, since the particulate matter produced by oil combustion is relatively low, the contribution of oil combustion fly ash is only 6.4 $\mu g/m^3$. According to the table, the standard error associated with the contribution of oil combustion fly ash, which is 9.6 $\mu g/m^3$, is larger than its source contribution, and its T statistic is 0.67, which is less than 2. Thus, it is clear that the contribution of oil combustion dust is not significant.

Table 2. The average concentration and standard errors of TSP samples in non-heating and heating seasons (unit: μg/m^3).

Species	average of 20 species in "non-heating seasons"	average of species in "heating seasons"	Species	average of 20 species in "non-hcating seasons"	average of species in "heating seasons"
TOT	196.0 ± 114.1	335.0 ± 109.0	Cr	0.075 ± 0.045	0.145 ± 0.035
Na	8.41 ± 4.62	8.84 ± 1.07	Mn	0.207 ± 0.095	0.356 ± 0.060
Mg	2.84 ± 1.54	5.82 ± 1.04	Fe	6.01 ± 2.16	13.10 ± 2.10
Al	10.5 ± 4.1	20.6 ± 3.0	Ni	0.024 ± 0.016	0.122 ± 0.048
Si	32.46 ± 12.14	56.7 ± 11.7	Cu	0.088 ± 0.040	0.102 ± 0.031
K	5.76 ± 2.49	6.81 ± 0.94	Zn	1.01 ± 0.52	1.67 ± 0.40
Ca	11.5 ± 4.2	14.5 ± 2.6	As	0.015 ± 0.007	0.033 ± 0.004
Ti	0.545 ± 0.228	1.29 ± 0.25	Pb	0.609 ± 0.262	0.617 ± 0.578
V	0.071 ± 0.054	0.025 ± 0.002			

Table 3. Results of source apportionment

	Non-heating Seasons				Heating Seasons			
Source type	SCE (μg/m^3)	SD	TSTAT	%	SCE (μg/m^3)	SD	TSTAT	%
Soil	79.3	67.2	1.18	42.6	134.3	66.3	2.0	37.5
Coal	28.5	46.9	0.61	15.3	75.9	49.3	1.5	21.2
Construct.	20.3	12.6	1.61	10.9	18.9	10.3	1.8	5.3
Oil	6.4	9.6	0.67	3.5	54.8	44.9	1.2	15.3
Motor	21.7	15.6	1.39	11.7	18.1	6.18	2.9	5.1
Marine	14.9	6.81	2.18	8.0	14.6	14.8	0.98	4.1
Iron	14.9	10.5	1.42	8.0	41.6	9.55	4.4	11.6
Total	186	---	----	100	358.2	---	---	100.1

In the heating season, the contribution of soil dust - 37.5% is still the highest, then comes coal combustion fly-ash, which accounts for 21.2% of the total amount. In winter, there are several coal-combustion boilers in Dagang oil field, and some coal combustion boilers in the Dagang oil refinery, so the contribution of coal combustion was only second to that of soil. Since oil combustion is the major fuel for heating, the source contribution of fly ash of oil combustion, which accounted for 15.3% of the total amount, is also high.

Diagnostic test on the results of source apportionment

The regression coefficients of the fitting equation is 0.97 (see Table 4), which is nearly equal to 1, reduced chi square is 0.74, and the ratio of the calculated and measured concentration is 95.0% with a range between 80% and 120%. This result is very satisfactory.

Table 4. Diagnostic coefficients of multi-linear equations

	R^2	reduced chi(X^2)	percent(%)
non heating seasons	0.97	0.74	95.0
heating seasons	0.98	2.05	106.9

From the matrix values of Table 5, in the "non-heating season", Na, Al, Si, Ca, Fe, Ni, Pb are most sensitive to sea-salt, coal combustion fly ash, soil, constructional materials dust, iron and steel dust and motor vehicle exhaust dust respectively, and their normalized modified pseudo-inverse matrix (MPIN) values are all equal to 1.0. The MPIN value of Mn to iron and steel dust, which is 0.78 (and larger than 0.5), shows that Mn has a great influence on this kind of dust. The MPIN values of Ti to soil and to coal combustion fly ash are 0.23 and 0.10 respectively, although less than 0.5, Ti also accounted for certain concentration in these two kinds of dust. So, it is reasonable to choose the elements of Na, Al, Si, Ca, Fe, Ni, Pb, Mn, Ti as tracer elements. In the heating seasons, Na, Al, Si, Ca, Mn, Ni, Pb were most sensitive to oceanic aerosol, coal combustion, dust on fly-ash from soil construction materials, iron and steel manufacture oil-combustion and emissions of motor vehicles respectively, their values of MPIN are all equal to

Table 5. Transpose of sensitivity matrix of fitting elements

	Non-heating Seasons							Heating Seasons						
Species	soil	coal	const.	oil	motor	marine	iron	soil	coal	const.	oil	motor	marine	iron
Na	0.00	0.00	-0.04	0.00	1.00	0.00	0.00	0.00	0.00	-0.02	0.00	1.00	0.00	0.00
Al	-0.48	1.00	0.00	0.09	0.09	-0.01	-0.05	-0.50	1.00	-0.02	0.02	0.27	-0.01	-0.15
Si	1.00	-0.73	-0.26	-0.16	-0.20	-0.01	-0.55	1.00	-0.65	-0.32	-0.03	-0.60	-0.02	-0.39
Ca	-0.06	-0.02	1.00	-0.02	0.01	-0.00	-0.10	-0.05	-0.02	1.00	-0.00	0.03	0.00	-0.09
Ti	0.23	0.10	-0.12	-0.04	-0.05	0.02	-0.19	0.18	0.14	-0.14	-0.01	-0.12	0.03	-0.15
Mn	-0.35	0.26	0.10	0.00	0.06	-0.01	0.78	-0.37	0.24	0.12	0.01	0.19	-0.02	1.00
Fe	0.12	-0.16	-0.03	-0.13	-0.03	-0.01	1.00	0.26	-0.24	-0.08	-0.04	-0.17	0.01	0.83
Ni	0.00	-0.00	-0.01	1.00	-0.01	0.00	1.00	0.01	-0.01	-0.07	1.00	-0.15	0.00	-0.05
Pb	-0.01	0.00	0.00	0.00	0.00	1.00	-0.02	-0.02	0.00	0.01	0.00	0.01	1.00	-0.03

Table 6. The measured values against their calculated values of the fitting and non-fitting elements (unit: $\mu g/m^3$)

	Non-heating seasons			Heating seasons		
Species	meas.	calc.	C/M	meas.	calc.	C/M
TOT	196.0	186.1	0.95	335.0	358.1	1.07
Na*	8.41	8.41	1.00	8.84	8.84	1.00
Mg	2.84	2.35	0.83	5.82	3.16	0.54
Al*	10.5	11.0	1.04	20.6	22.9	1.11
Si*	32.5	28.2	0.87	56.7	52.2	0.92
K	5.76	2.04	0.35	6.81	3.55	0.52
Ca*	11.5	11.6	1.01	14.5	14.6	1.00
Ti*	0.545	0.527	0.97	1.29	1.04	0.81
V	0.071	0.010	0.15	0.025	0.022	0.90
Cr	0.075	0.011	0.15	0.145	0.022	0.15
Mn*	0.207	0.111	0.54	0.356	0.277	0.78
Fe*	6.01	7.32	1.22	13.1	16.3	1.25
Ni*	0.024	0.024	1.00	0.122	0.126	1.03
Cu	0.088	0.008	0.09	0.102	0.015	0.15
Zn	1.01	0.283	0.28	1.67	0.680	0.41
As	0.015	0.003	0.22	0.033	0.006	0.19
Pb*	0.609	0.606	1.00	0.617	0.608	0.99

1. Different from non-heating seasons, it is not Fe but Mn whose MPIN value is equal to 1. There, the MPIN value of Fe to iron and steel dust is 0.83, only secondary to that of Mn. So, Fe was also selected as fitting elements along with Na, Al, Si, Ca, Mn, Ni, Pb.

In the fitting elements of the non-heating season, the average of the ratio of measured value and calculated value (M/C) of the elements being fitted is 1.04 (see Table 6). Caused by the corrosion of electrical brushes, the measured value of Cu concentration is 11 times larger than its calculated value. Cr was analyzed by AAS (air-ethene flame), so the error is relative larger. After removing the data of Cr, Cu, the average M/C of non-fitting elements, which should be 1 in an ideal situation, is 2.73. In the study of Kowalozyk et. al. on the sources of TSP in Washington D.C., the average of M/C of elements being fitted is 1.08 (6). After removing such erroneous data, the average of non-heating elements is 2.0. In the source apportionment of Inhaled Particulate of Tianjin in heating seasons, the M/C of fitting elements is 1.09, while the M/C of non-fitting elements is 2.34 (4). In the source apportionment of particulate matters in Tianjin coastal region, the M/C of fitting elements is 1.10 and that of non-fitting elements is 2.92. From these results, the average M/C of fitting and non-fitting elements in this paper are all near to 1, so the results are reasonable.

Conclusion

By using an effective variance weighted least squares estimation method to solve the chemical mass balance (CMB) equation and using the standard errors associated with source profiles and receptor concentrations, the source apportionment of TSP in the Dagang oil field has proven to be feasible. Soil dust is the major source of regional TSP, followed by combustion fly-ash.

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MEASUREMENT OF DIMETHYL SULFIDE IN THE BO SEA AND GULF OF JIAOZHOU

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Abstract – Measurements of the concentration of dimethyl sulfide (DMS) in surface waters have been carried out in the Bo Sea in March, 1993 and April, 1994. DMS concentrations in the Bo Sea in the end of winter were between 7 and 163 ng/l, 81 ng/l on average. A seasonal variation of DMS concentrations was observed in the Gulf of Jiaozhou by a factor of 4 between spring and winter with mean concentrations of 363 ng/l and 408 ng/1 in the spring seasons of 1993 and 1994 and 87 ng/l in the 1993 winter season. The flux of DMS from the sea to the air also showed a seasonal variation.

Key words: Dimethyl sulfide, Flux, seawater, atmosphere.

Introduction

The combustion of fossil fuels is generally considered to be the primary source of sulfur emissions in China. But measurements of acid precipitation in seaside cities, such as Qingdao, Shandong Province, Xiamen, Fujian Province and Shanghai, indicate that ocean emissions of dimethyl sulfide (DMS) may be another important source of sulfur to the atmosphere.

The ocean surface layer plays an important role in the global biogeochemical sulfur cycle. Dimethyl sulfide (CH_3SCH_3, DMS) constitutes about 90% of the reduced volatile sulfur in surface sea water (Wake ham et al., 1987; Leck and Bagander, 1988). The concentration in sea water is far in excess of the concentration at equilibrium with atmospheric concentration (Cline and Bates, 1983; Dacey and Wakeham, 1984). This over saturation causes a flux of DMS from the ocean to the boundary layer of marine atmosphere where DMS is photo chemically oxidized to non-sea-salt sulfate ($NSS-SO_4$) via intermediates such as sulfur dioxide (SO_2) and methane sulfonuic acid (CH_3SO_3H) (Andreae, 1986) or oxidized directly to SO_4. MSA and $NSS-SO_4$ in the marine troposphere are the major contributors to the acidity of natural precipitation and probably also constitute the largest fraction of cloud condensation nuclei CCN, especially in remote oceanic areas. CCN are critical to cloud formation, therefore, potentially important to the earth's radiation budget (Charlson et al., 1987).

In recent years a large number of DMS measurements have been made covering regions of the Atlantic Ocean, Pacific Ocean and Indian Ocean (Andreae, 1986; Bates et al., 1987; Turner and Liss, 1985; Turner et al., 1988; Leck et al., 1990). However, so far there has not been a report on DMS emission from the seas around China. The Chinese South Sea, the Chinese East Sea, the Yellow Sea and the Bo Sea are situated in the tropics, subtropics and temperate zone respectively.

Measurements of DMS concentrations along the eastern coastline of China and estimations of DMS fluxes are necessary for predicting DMS roles in acid precipitation and provide important information regarding climate change.

Described here are the first-reported of the concentrations of sea water DMS over the Bo Sea and Gulf of Jiaozhou.

Determination of DMS in sea water

A sea water sample of 50 ml was purged with pure nitrogen gas flow of 20 to 30 ml per minute for a period 35 minutes. Before entering the cryotrap the gas stream was dried by a Teflon tube immersed into an ice-salt bath (-10 °C) to prevent icing. This gas was then passed through a U-shaped concentration tube filled with chromosorb R packing and immersed in liquid nitrogen. After sampling DMS samples were analyzed by gas chromatography with flame photometric detection as soon as possible. The cryotrap (liquid N2) was connected to the gas chromatographic system via six-way-valve purged with dry nitrogen gas. The column used was 2m x 3mm Carbopack B/1.5%XE-60/1.0% H3PO4 60-80 mesh packed in teflon tubing. The liquid nitrogen was removed and the trap heated at around 90 °C by a glycerine bath, then DMS was released and injected into a packed column for separation and detection. This desorption temperature (90 °C) gave a maximal desorption efficiency of DMS and a minimal release of water vapor from the cold trap.

Calibration of the DMS chromatographic system is performed by injecting a few microliters in the range of 2.0-30.0 ng of DMS in ethylene glycol into a 50-ml volume of degassed sea water. The standard was purged with pure nitrogen gas onto a cryotrap and analyzed in the same manner as the sea water samples.

The accuracy and precision for DMS measurement method are 10% and 12% respectively, based on analysis of series of samples and comparison with standards.

Results and discussion

Sea water samples were obtained from sea surface water by using a bucket. The sea water was transferred, after measuring the temperature, into a polyvinyl chloride sampler.

The surface samples were analyzed by the method mentioned above as soon as possible to avoid possible storage artifacts.

Measurements of DMS in sea water were carried out in the Bo Sea in March, 1993, and the Gulf of Jiaozhou between January, 1993 and April, 1994. The cruise tracks are showed in figure 1 and figure 2. Samples were collected at the locations marked on the cruise track.

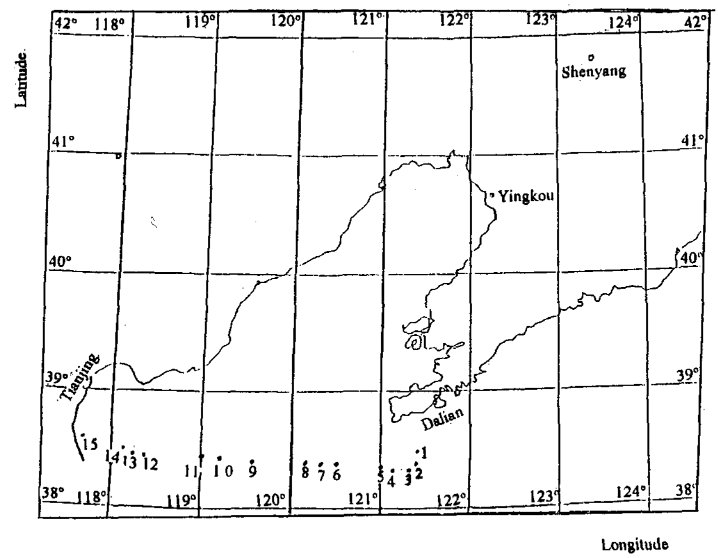

Fig. 1. Map of the Bo Sea; numbers refer to the Sampling Station Locations

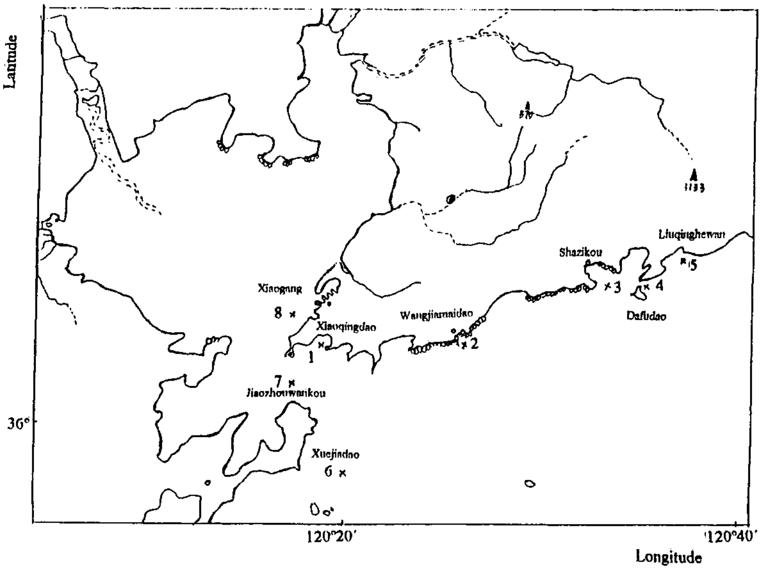

Fig. 2. Map of the Gulf of Jiaozhou; numbers refer to the Sampling Station Locations

Measurement results of DMS in the Bo Sea along the cruise track from Dalian to Tianjin in the end of winter, 1993 are shown in table 1. DMS concentrations in the sea water were between 7 and 163 ng/l with an average of 81 ng/l. These low DMS concentrations were connected with the decrease in phytoplankton production. DMS concentrations varied considerably along the cruise track. These variations are probably related to the distribution of phytoplankton in this area.

It was evident that a seasonal variation of the oceanic DMS was observed in the Gulf of Jiaozhou with a maximum in spring and a minimum in winter. In 1993 DMS concentrations vary by a factor of 4 between spring and winter, with mean concentrations of 363 and 87 ng/l, respectively. DMS concentrations in each sampling location also show obvious seasonal variation. The difference in DMS concentrations among the sampling stations during the same season reflects, as already mentioned, the variation in the phytoplanton production and species. Measured DMS concentrations in winter in the Bo Sea were very close to values found in the Gulf of Jiaozhou.

Table 1. Measurement Results of DMS(ng/l) in the Bo Sea

Station	1	2	3	4	5	6	7	8
DMS(ng/l)	21	139	63	32	45	44	7	163
Station	9	10	11	12	13	14	15	
DMS(ng/l)	102	98	32	146	156	91	78	

Table 2. Measurement Results of DMS(ngll) in the Gulf of Jiaozhou

Station	Winter (1993,1)	Spring (1993,5)	Summer (1993,7)	Autumn (1993,10)	Spring (1994,4)
1		419	253	204	543
2	56	243	382	208	483
3		397			418
4	229	392			556
5	61	286			337
6	53	430	203		435
7		364			223
8		376			269
Avg.	87	363	279	206	408

Flux of DMS from the Ocean of the Atmosphere

The model of Liss and Slater (1974) was used to predict the sea-to-air flux of DMS. In this model the flux between liquid and gas phase is determined by the rate of molecular diffusion across a stagnant film with the thickness z. The concentrations in the gas and liquid phase are Cg and C_1, respectively. The transfer rate is determined by the exchange constant K:

$$F=K(\frac{C_g}{H}-C_1) = \frac{D}{z}(\frac{C_g}{H}-C_1)$$

(H: Henry's law constant; D: coefficient of molecular diffusion of gas in stagnate layer). In the case of DMS, the atmosphere is highly under saturated with respect to the coexisting sea water (H = 0.3 (g per cm^3 air)/(g per cm^3 water) (Lisa and Slater, 1974), so that

$$\frac{C_g}{H} < C_1$$

and thus

$$F = K\, C_1$$

Different approaches have been used to obtain the exchange constant K. Here a method described by Kromer(1979) is applied. Based on field experiments with the radon method, a bilinear function for the dependence of K_{Rn} on V is derived:

$K_{Rn} = 0.075V$ $0<V<4$ m/s
$K_{Rn} = 0.72\,(V-4) + 0.3$ $V>4$ m/s

The exchange constants obtained by this method for radon were converted for DMS using the following relationship

$$K_{DMS} = K_{Rn}\frac{\sqrt{D_{DMS}}}{\sqrt{D_{Rn}}}$$

Assuming that the salinity of sea water in the Gulf of Jiaozhou and the Bo Sea is 30‰, and wind velocity ranges between level 3 to 5 m/s with an average of 5.4 m/s an estimate of DMS fluxes can be made. In table 3 the reflux estimates are given, based on the sea water temperatures (T), coefficient of molecular diffusion of DMS (D, 10^{-5}, cm^2/s), exchange constant (K, m/d), DMS concentration (C, ng/l), and sea-to-air flux of DMS ($\mu mol/m^2/d$). In winter the flux of DMS in the Gulf of Jiaozhou (1.24 ,$\mu mol/m^2/d$) is close to that in the Bo Sea (1.16 $\mu mol/m^2/d$). It was evident that a seasonal variation of the sea-toair flux of DMS was observed with a maximum in spring or summer and minimum in winter in the Gulf of Jiaozhou.

Table 3. Sea-to-air flux DMS in the Gulf of Jiaozhou and Bo Sea

Items	Spring	Summer	Autumn	Winter
T(Water)(°C)	10	24	20	4
D(x 10^{-5})	0.676	1.105	0.971	0.527
K(m/d)	0.993	1.270	1.190	0.887
C(ng/l)	363;408**	279	206	87;81*
F ($\mu mol/m^2/d$)	5.81;6.53**	5.72	3.95	1.24;1.16*

** the values of 1993 and 1994 in the Gulf of Jiaozhou, respectively;
* the values of the Gulf of Jiaozhou and Bo Sea in 1993, respectively.
The others are values measured in the Gulf of Jiaozhou in 1993.

Conclusions

In table 4 the estimated fluxes in Chinese waters are compared with the values reported in the literature.

Table 4. DMS fluxes (μmol/m^2/d)

	Winter(W)	Summer(S)	Ratio(S/W)	References
North Pacific				
Subarctic 50–65°N	1.40	6.75	4.7	Bates et al. (1987)
Temperate 35–50°N	2.21	4.96	2.2	Bates et al. (1987)
Subtropical 20–35°N	2.15	5.14	2.4	Bates et al. (1987)
Seawater around main land Britain	0.5	29.2	58.4	Turner et al. (1988)
Indian ocean Amsterdam Island	1.3	3.0	2.3	Nguyen et al. (1990)

The conclusion is that DMS fluxes from the Bo sea and the Gulf of Jiaozhou are close to values for the North Pacific in the zone 35–50°N. The fluxes in the Chinese waters are slightly higher than the North Pacific values, probably because the rate of primary production in the Bo sea and the Gulf of Jiaozhou is higher than in the other seas in this temperature zone. Furthermore the average values for the Chinese waters are clearly influenced by the strong maximum in the spring due to a strong development of phytoplankton in this period.

A model to evaluate the impact of the DMS fluxes in coastal waters on acid deposition in the coastal area will be developed in the near future. But a first order comparison with anthropogenic sources in the area indicates a contribution of the order of 10% by DMS to local acid deposition.

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Abrev.	Explanantion
AMS	Acelerator Mass Spectrometry
APCA	Absolute Principal Component Analysis
bext	Total light scattering coeficient for particles
BTX	Sum of Benzene, Toluene and Xylene in air, microgram per m-3
CFA	Corrspondence Factor Analysis
CMB	Chemical Mass Balance
DMS	Dimethyl Sulfide
GC	Gas-Chromatography
GC-FID	Gas Chromatography with Flame Ionisation detection
GC/MS	Gas Chromatography with mass Spectrometric detection
HC	Hydrocarbons (generally referring to volatile species)
IGBP	International Geosphere Biosphere Program
IP	Inhalable Particles
Ki	Contribution of one compound to tatal burden Pi/sum(Pi)
LNG	Liquefied Natural Gas
MPIN	Modified Pseudo Inverted Matrix (statistical technique)
MS	Mass Spectrometry
NHC	"natural" hydrocarbons (biogenically emitted hydrocarbons)
NMHC	non-methane hydrocarbons (all volatile hydrocarbons except methane)
NOx	Nitrogen oxides (NO and NO2)
NOy	Sum of all reactive oxidised nitrogen compounds
PAH	Polycyclic Aromatic Hydrocarbons
PAN	Peroxyacetyl nitrate
PCA	Principal Component Analysis
PCB	Pollution Concentration Burden, contribution of certain sources
PFA	Principal Factor Analysis
Pi	Isopollutant burden, ratio between emission and allowable concentrat
PM	Particulate Material
PM-3	Particulate Material sampled with a cut off at 3 micron diameter
ppb	parts per billion volume ratio (not recommended by IUPAC)
ppbv	parts per billion volume ratio (not recommended by IUPAC)
ppm	Parts per million volume ratio (not recommended by IUPAC)
RAINS	Regional Acidification Information and Simulation
RH	Relative Humidity
RMC	Respirable Mass Concentration (of particles in air)
RSPM	Respirable Suspended Particulate Material
SPM	Sea-salt Particulate Matter (amount of sea salt particles in air)
SPM	Suspended Particulate Material
SVD	Singular Value Decomposition (statistical technique)
TRFA	Target Transformation Factor Analysis
TSP	Total Suspended Material (total load of all particles in air)
USEPA	United States Environmental Protection Agency
VOC	Volatile organic Compounds