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EMEP-WMO Workshop on fine particles – emissions, modelling and measurements

Interlaken, Switzerland
22–25 November 1999

Edited by
Jan Erik Hanssen, Richard Ballaman and Robert Gehrig

World Meteorological Organization

Swiss Agency for the Environment, Forests and Landscape

Swiss Federal Laboratories for Materials Testing and Research

Norwegian Institute for Air Research

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EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe

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Preface

This Workshop was organized in co-operation between Swiss Agency for the Environment, Forests and Landscape (BUWAL) and Swiss Federal Laboratories for Materials Testing and Research (EMPA). The organizers wish to thank the participants for their contributions to the success of the Workshop and the chair persons and rapporteurs for valuable assistance.

The Chemical Co-ordinating Centre of EMEP (CCC) will express its gratitude to BUWAL and EMPA for their excellent organization of the Workshop.

This Workshop has given a valuable input to the planning of the coming work in EMEP on fine particles, with excellent presentations given by leading scientists within their field of environmental research.

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EMEP-WMO Workshop on fine particles – emissions, modelling and measurements

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1. Introduction

The EMEP-WMO Workshop on fine particles – emissions, modelling and measurements took place from 22–25 November 1999 in Interlaken, Switzerland. The Workshop was organized by the Swiss Agency for the Environment, Forest and Landscape (BUWAL) and Swiss Federal Laboratories for Materials Testing and Research (EMPA).

The Workshop was attended by 69 participants form Austria, Belgium, Canada, Croatia, Cyprus, Czech Republic, Estonia, Finland, France, Germany, Italy, Latvia, Lithuania, Netherlands, Norway, Russian Federation, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

The following international organizations and centres where present: European Commission, Joint Research Centre of the European Commission, UN-ECE, World Health Organization, World Meteorological Organization, Chemical Co-ordinating Centre of EMEP, Meteorological Synthesizing Centre East of EMEP and Meteorological Synthesizing Centre West of EMEP.

The Workshop was organized in three main parts: Oral presentations, poster sessions and discussions in Working Groups.

Twelve oral presentations were given as an introduction to the discussions in the Working Groups. 25 posters were presented during two poster sessions. Three Working Groups covering emission, modelling and measurements were discussing in parallel sessions before presenting their conclusions and recommendations in the plenary.

In Appendix C the papers available for the editors are printed. Some of the papers were not available in electronic form, consequently some of the figures are not of a good quality.

2. Scope of the Workshop

There is a growing concern relating to the health effects of fine particles. Recent studies have demonstrated consistent associations between concentrations of fine particles (PM_{10} and $PM_{2.5}$) and adverse effects on human health (respiratory symptoms, morbidity and mortality) at concentrations commonly encountered in Europe and North America.

A significant fraction of the ambient concentrations of fine particles in Europe is made up from the so-called secondary aerosol, i.e. particles formed by atmospheric reactions involving long-range transboundary pollutants, primarily oxides of sulphur and nitrogen as well as ammonia.

Consequently, this issue is now placed in the work programme of the Convention on Long Range Transboundary Air Pollution, which has established a joint Task Force with the World Health Organization to deal with the topic. The WMO Scientific Advisory Group on Aerosols is addressing the issue of aerosol measurements on the global scale. Moreover, EMEP will provide further information on the transboundary aspects of this problem. In this context, the EMEP Steering Body in co-sponsorship with the WMO has welcomed the arranging of an international scientific workshop, with the aim to carefully review emission inventories, modelling, and measurement of fine particles. A main objective of the workshop is to provide recommendations for future EMEP/WMO activities on this issue.

The workshop will include invited introductory **plenary presentations** of the main topics dealt with and **poster presentations**. Ample time will be devoted to **expert discussions both in working groups and in the plenary** in the following 3 areas :

- **Emissions**: For most countries there is a lack of quantitative data on emissions of primary particulate matter. More or less rough estimates of the emissions from the main sources, such as the combustion of solid fuels, road and off-road transport, and industrial processes have been carried out in some countries. Suitable approaches for improving emission inventories (and emission estimates) and the submittal and archiving of the emission data therefore need to be discussed and developed. This group will e.g. address the following questions:

  – Are regional emission inventories of primary particles available and required? If that is the case, for which components are they available?

  – An example of emission inventory for primary particles covering the whole of Europe is the one estimated by TNO. Can this inventory be used as a first estimate? Would it be useful to submit the TNO data to the Parties to be checked and authorized by the countries for their validity?

  – Is there an useful correlation between primary particle emissions with other already registered pollutants (e.g. NO_x)?

  - How to improve the EMEP/CORINAIR emission inventory guidebook for the inclusion of particulate matter?
  - What emission estimation procedures can be recommended?
  - Which particle sizes should be distinguished and reported?
  - What information relating to chemical composition of primary particles is plausible to report?
  - To what extent is it possible (and/or necessary) to provide emission data of fine particles with their chemical speciation?

- **Modelling**: A thorough review of the general state of the art of modelling the long range transport of fine particulates is needed in order to identify useful approaches for the purposes of EMEP and WMO. Present EMEP models for the acidifying pollutants have already been used to estimate the concentration of particles arising from gaseous emissions of SO_2, NO_x and NH_3. These secondary particles generally constitute a significant part of the fine aerosol ($PM_{2.5}$). This group will e.g. address the following questions:

  - Which models covering Europe are actually available and what is their usefulness for the EMEP purposes? Should EMEP develop a new model or is it enough to modify/improve existing models?
  - What are the main input data required for the modelling exercise?
  - Which measuring frequency (daily values or weekly means or other) are required for the model validation? Which type of data series are required (pilot measuring campaigns or rather daily values over a long time period or annual average)?
  - How can we validate or evaluate the performance of the models (concentrations of $PM_{2.5}$)? Does the modellers need information relating to the chemical composition of the measured PM?
  - Which level of detail relating to particle size distribution is needed for comparison with the model results?
  - Long-range transboundary transport is clearly identified for fine particles below 2.5 µm. Air quality guidelines are established on the basis of epidemiological studies for PM_{10}. How to fill the gap between the models results and the measuring data requirements?
  - What is the expected impact of existing protocols on the concentrations of secondary particles?
  - Is it conceivable to compare the performance of the available model results with the measured data in several sites in Europe (mainly in urban areas)?
  - What about the representativeness of the measuring stations (mainly located in urban areas) for the purpose of model validation ?

- **Measurements**: Measuring ambient air concentrations of suspended particles is a difficult task. The currently used methods (manual gravimetric procedures, automatic monitors etc.) all have their drawbacks and artefacts and, therefore, can give different results. Suitable approaches how to measure fine particulates for the EMEP needs have to be discussed. In most European countries monitoring activities of PM_{10} (but also $PM_{2.5}$) have already started or will start soon in order to comply with the requirements of the first EU daughter directive on air quality, which is expected to be adopted shortly. This group will e.g. address the following questions:

- Which particle size should be measured (PM_{10}, $PM_{2.5}$ or other)? Which measurement method(s) should we recommend (manual gravimetry or monitors)? Can we use CEN or US standard methods or are other methods more appropriate for EMEP needs?
- Should a small number of "super stations" provide in addition more sophisticated particle information, including chemical speciation and/or particle size distributions?
- Which time resolution (daily, weekly or other) is needed for the EMEP purpose and required from the health survey community?
- As a starting phase, should EMEP launch a pilot measuring campaign in a limited number of EMEP stations or in other sites (in urban areas for example)? Which measurements should be made (PM, chemical composition)?
- Can we use correlations with other available pollutant data like black smoke, nitrogen oxides or carbon monoxide to get useful information?
- What is the available experience from the various countries?
- Are information relating to the chemical composition of PM needed and available for the validation of the models?
- What about the representativeness of the EMEP measuring stations concerning PM exposure of the population ?

3. Conclusions and recommendations[1]

3.1 Conclusions and recommendations from Working group on emissions

1. The sessional working group on emissions was attended by about 17 participants, both users and providers of inventories, representing modelling, regulatory, government and industry interests. The working group explored and prioritized the issues associated with establishing fine particulate inventories before 2003. The following items were identified as needing special attention:

- The physical and chemical characteristics of particles;
- Source apportionment;
- Data quality and confidence;
- Speed of delivery.

2. To meet any future reporting requirements under the Convention and provide input for the CORINAIR/EMEP Atmospheric Emission Inventory Guidebook, Parties should prepare an interim emission inventory by the end of 2000. A formal system will be required by 2001 for reporting fine particle emissions. 1995 would be a suitable base year from a technical point of view.

3. The inventory of the Netherlands Organization for Applied Scientific Research (TNO) for 1990 could be used as a basis for the interim emission inventory. It should be revised and updated during 2000. The Executive Body should include this activity in its 2000 work-plan[2]. The revision should be undertaken by a contractor and funding should be earmarked for this purpose. The work should be supervised by Parties to the Convention. This inventory will be supplemented by national information where available.

4. From 2001 onwards the Executive Body should include establishing a fine particulate emission inventory in its annual work-plan. This will require strong involvement from the Task Force on Emission Inventories and Projections. PM_{10} and $PM_{2.5}$, heavy metal, elemental/organic carbon and mineral dust data should be reported at a minimum at SNAP level 2. Also, the reporting instructions should be revised to reflect this. In addition, the SNAP coding and any linking statistics should be extended and the Guidebook revised accordingly.

5. The experience of the European Environment Agency is highly relevant to the establishment of high-quality fine particulate inventories. The European Community expressed its strong interest in this work and it was agreed that it,

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[1] As adopted by the participants and finalized by the ECE secretariat in consultation with the representatives of the host country, Switzerland and the Chairman of the EMEP Steering Body. The conclusions and recommendations will be submitted to the EMEP Steering Body at its twenty-fourth session (4–6 September 2000).

[2] At its seventeenth session (29 November-3 December 1999), the Executive Body took the action proposed in paragraphs 2 and 3 into account when finalizing its work-plan for 2000. In this context, it also agreed that a decision on including a fine particulate emission inventory in the annual work-plans from 2001 onwards would be taken at its eighteenth session, following the final advice of the EMEP Steering Body.

possibly through the European Environment Agency, should be invited, to continue with its valuable contribution to the EMEP programme.

6. Inventory quality management should be introduced as a prerequisite for data validation and inventory verification. Guidance on the quality management of the inventories should be included in the Guidebook.

7. The working group recognized the value and relevance of work on fine particulate emissions by a number of other organizations. Wherever possible EMEP should cooperate with these groups to avoid duplication and to promote harmonisation. In particular, contact should be maintained with the fine particulate programme of the United States Environment Protection Agency (US/EPA) and the inventory best practice programme of the Intergovernmental Panel on Climate Change (IPCC).

8. Assistance should be provided to characterize temporal variations of emissions through a formal liaison with the European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe (EUROTRAC) via the GENEMIS programme.

3.2 Conclusions and recommendations from Working group on measurements

9. The sessional working group on measurements was attended by about 30 participants, mainly measurement experts involved in EMEP and in other national and international research programmes. They explored the possibilities for introducing measurements of fine particulates into the future EMEP measurement programme, bearing in mind:

- The needs of the data users, in particular the modellers;
- The current state of measurement techniques for sampling and analysis;
- The limitations of resources at most EMEP sites;
- The possible synergistic effects of cooperation with other scientific programmes.

10. EMEP should give first priority to PM_{10} measurements. For this purpose the gravimetric method is the preferred method, particularly because the filters allow subsequent chemical analysis for quantification of different compounds. Monitors are acceptable if they have been shown to deliver equivalent results for the specific site and for all seasons.

11. EMEP sites should also determine secondary inorganic particulate matter, i.e. ammonium sulphate and ammonium nitrate, as well as other water-soluble ions when these make up a significant part of PM_{10} mass.

12. Measurements of particles with an aerodynamic diameter less than 2.5 or 1 µm should be carried out in the near future when the definition of the European reference method is in place.

13. For chemical characterization, determination of elemental and organic carbon is highly desirable. The subsequent determination of organic and elemental carbon by thermodesorption and oxidation is subject to artefacts, and care has to be taken to avoid results that are not comparable. There are also sampling artefacts related to organic compounds. EMEP will need to consult with other bodies on these issues. If they can be resolved, centralized laboratories for the determination of elemental and organic carbon should be established for the analysis of samples from EMEP sites.

14. More detailed size fractionated chemical speciation would be desirable and should be done in the context of scientific projects.

15. “Superstations” should be set up together with other scientific organizations and programmes. These could be used for a number of chemical and physical measurements that go beyond the scope of the “normal” EMEP site, e.g. for determination of some of the organic compounds, size distribution, detailed size fractionated chemical speciation, optical properties, water uptake, cloud condensation nuclei, vertical distribution and better time resolution (1 hour) for certain parameters.

16. EMEP welcomes closer collaboration with other international initiatives, such as the Global Atmospheric Watch (GAW) of the World Meteorological Organization (WMO) and EUROTRAC, as well as national programmes. This collaboration would concern both measurements and modelling, in particular the EUROTRAC subproject AEROSOL. It would accelerate the exchange of scientific and technical information and improve understanding between EUROTRAC and EMEP.

17. EMEP and WMO see a large potential for collaboration in the fine particulate programme. Many measurement sites in Europe are already both EMEP and GAW sites. This could still be extended. In particular, global GAW stations could possibly be designated as “superstations” within EMEP (see para. 15 above). It is expected that the newly formed Task Force on Measurements and Modelling, which is co-chaired by Austria and WMO, will be best suited to address this task. These joint activities at common sites will help to produce more comprehensive results.

18. The EMEP/CCC website (http://www.emep.int) should be used to share information on ongoing and planned research and intercomparison of measurement techniques.

3.3 Conclusions and recommendations from Working group on modelling

19. The sessional working group on modelling was attended by about 15 participants, mainly modelling experts involved in EMEP and in other national and international research programmes. The working group discussed the main objectives for modelling particulate matter and set requirements for:

- The development of chemical and physical model parametrization;
- The necessary input emission data;

- The necessary measurement data for model validation and model development.

20. The working group appreciated the MSC-W proposal to couple the Eulerian photo-oxidant model with an aerosol model and encouraged the ongoing collaboration between the Meteorological Synthesizing Centre-West (MSC-W), the Chemical Coordinating Centre (CCC), the University of Helsinki, the University of Stockholm and the Finnish Meteorological Institute, in the framework of the Nordic Research Council (NMR). This modelling effort is likely to produce preliminary initial results on the long-range transport of particulate matter in the EMEP area by the beginning of 2001.

21. The working group requested MSC-W to investigate cloud effects, gas-aerosol interaction through evaporation and condensation processes, sea-salt chemistry and resuspension processes, already at the initial model development stages.

22. EMEP welcomes cooperation with national and international research programmes. In particular, areas for cooperation were identified, both in terms of process studies and suggestions for parametrization schemes, model inter-comparisons and testing of different model approaches with national experts from the United Kingdom and the research group at Ford Aachen.

23. As a first priority, the particulate matter model used by EMEP should provide daily values of PM_{10} and PM_x and be able to characterize the chemical speciation of the aerosol. Concerning the size distribution of the aerosol, the model approach should be flexible enough to allow for any changes in the ranges defined by legislation. Monitoring sites should include daily measurements of PM_{10} and $PM_{2.5}$ and chemical characterization of secondary inorganic aerosols and other water-soluble ions.

24. Chemical speciation of particulate matter is important for source allocation and it is recommended that secondary inorganic particulate matter should be separated from the other components of particulate mass. The quantification of elemental carbon and organic carbon is also desirable, as these represent the major part of the primary emissions of particulate matter. In view of the technical difficulties in the separate determination of elemental carbon and organic carbon, centralized laboratory facilities should be established to ensure compatible data.

25. A minimum of 5 to 10 sites should be selected to carry out detailed chemical speciation and chemical mass balance of measured PM_{10} and eventually also $PM_{2.5}$ or PM_1. These sites should be part of the basic EMEP measurement network, or other related monitoring activities, and should cover the following areas: southern Europe (Saharian dust, biomass burning), eastern Europe (biomass burning), central Europe (anthropogenic), marine and remote areas. CCC, in cooperation with WMO, should select them.

26. In addition, campaign sites and “superstations” (see para. 15 above) related to the specific research programmes would be specially useful for the testing of the model parametrization.

27. The working group also considered the requirements for emissions inventories which were further considered by the working group on emissions. Natural and biogenic emissions and resuspended material should be directly treated by models in collaboration with emission experts.

28. Work should be initiated within the Task Force on Integrated Assessment Modelling to investigate, in collaboration with the Working Group on Effects and the World Health Organization, the robustness of different statistics that can be used in atmospheric modelling as indicators of the effect of particulate matter on human health.

Appendix A

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Appendix B

Agenda

EMEP/WMO Workshop on fine particles – emissions, modelling and measurements

22–25 November 1999
Interlaken, Switzerland

Organized by
Swiss Agency for the Environment, Forests and Landscape
Swiss Federal Laboratories for Materials Testing and Research
in co-operation with
Chemical Co-ordination Centre (CCC)
Meteorological Synthesizing Centre West (MSC-W)
World Meteorological Organization (WMO)

Programme

Sunday, 21 November

18.00	Early registration
19.00	Dinner

Monday, 22 November

08.30	Registration	
Plenary session	Chair: U. Nyffeler	
09.00 – 09.20	Opening of the workshop Aim of the workshop	U. Nyffeler
09.20 – 09.30	Fine particles, a new pollutant under the UN/ECE Geneva convention?	E. Lumme/ M. Williams
09.30 – 09.40	Activities on fine particles within WMO/GAW	L. Jalkanen
09.40 – 10.00	Plans of the European Commission regarding particulate matter	L. Edwards
10.00 - 10.30	Break	
10.30 – 11.00	Health aspects of fine particles	M. Krzyzanowski
11.00 – 11.30	Emission inventories of primary fine particles	M. Woodfield
11.30 – 12.00	European PM_{10} and $PM_{2.5}$ emission inventory from anthropogenic sources	J. Berdowski

12.00 – 12.30	Long-range transport modelling of fine particles	L. Tarrason
12.30	Lunch	
14.00 – 14.30	Current measurement techniques for compliance monitoring of fine particles	R. Gehrig
14.30 – 15.00	Advanced measurement techniques	J. Heintzenberg
15.00 – 15.30	Aerosol measurements within WMO/GAW Providing data related to climate forcing and air quality	U. Baltensperger
15.30 – 16.00	Break	
16.00 – 16.30	Introduction to the activities on fine particles within EUROTRAC	H.M. ten Brink
16.30 – 18.00	Poster session (First part)	
19.0	Dinner	

Tuesday, 23 November

09.00 – 09.20	Introduction to the workshops (Plenary)	R. Gehrig
09.30 – 12.15	Discussions in the working groups (Individual break)	Chairpersons: A. Semb (Measurements) M. Woodfield (Emissions) L. Tarrason (Modelling)
12.30	Lunch	
14.00 – 15.00	Plenary presentation of the status of work	Chair: J. Schaug WG-Rapporteurs
15.00 – 16.00	Plenary discussion of the status of work	
16.00 – 16.30	Break	
16.30 – 18.00	Poster session (Second part)	
19.00	Dinner	

Wednesday, 24 November

09.00 – 10.30	Discussions in the working groups including preparation of the draft conclusions and recommendations
10.30 – 11.00	Break

		Chair: R. Ballaman
11.00 – 12.15	Plenary presentation and discussion of the draft conclusions and recommendations of the working groups	WG-Rapporteurs
12.30	Lunch	
14.00	Technical excursion	
19.30	Dinner	

Thursday, 25 November

Final plenary session		Chair: M. Williams
09.00 – 10.30	Final discussion and adoption of the conclusions and recommendations of the workshop	
	Closing of the workshop	

Appendix C

Papers and posters presented

Opening of the workshop / Aim of the workshop

by

Urs P. Nyffeler

Swiss Agency for the Environment, Forests and Landscape

Ladies and gentlemen

On behalf of the Swiss government I have the great pleasure to welcome you in Interlaken and to open this EMEP / WMO workshop on fine particles.

I am particularly glad to see that we have a broad participation: more than 60 experts from 22 countries are a clear sign that important items are on the agenda of this workshop. A great variety of problems will be discussed in depth and proposals for advanced solutions need to be elaborated. It is expected that the announced contributions will lead to many interesting conclusions which you may take with you at the end of this workshop.

In the last decade many studies, conducted in various parts of the world as well as in Switzerland, have shown a clear link between a wide range of health effects and exposure to particulate matter in ambient air. The small size fraction of the ambient aerosol, measured as PM_{10} and $PM_{2.5}$, is considered to be responsible for most of the health effects. In the report of the World Health Organisation entitled “Health Costs due to Road Traffic-related Air Pollution” (published in June 1999) there is shown that e.g. in Switzerland - with a population of 7 Million - there are 3'300 additional cases of mortality estimated from the PM_{10} exposure-response function. The related health costs of the mortality together with the morbidity costs are estimated over 4 Billion Euros per year. It is therefore important to increase the awareness of the problem of air pollution by particles and the willingness to implement adequate solutions.

I think that this workshop can contribute in this context. Let me say some words on the aims of the workshop.

Even though most countries have national networks for monitoring particulate matter there are still considerable gaps in the knowledge of PM_{10} and particularly $PM_{2.5}$ mass concentrations across Europe, especially in less populated areas. On the other hand the EMEP monitoring programme includes measurement of secondary inorganic compounds which are major contributors to PM_{10} mass in rural areas. One aim of the workshop is therefore to make good recommendations on the type of compounds to be measured, the location of monitoring sites to be selected and the frequency of measurement to be performed.

Fine particles have a relatively long residence time in the atmosphere. For that reason they may travel over long distances. This is especially true for the secondary particles which also are significant contributors to the total exposure of the European population to airborne particles. Even if there are good models for some precursors of the secondary particles it is important to develop further the assessment of the contribution of long-range transport to particle concentrations.

With respect to emission inventories of primary particles it is required to reduce the uncertainties on the size distribution of the particles emitted by the different sources and on the emission factors. An in-depth analysis of the available data and a certain harmonisation of the methods at the international level are also important aims.

To improve our knowledge on particulate matter and to implement tailored abatement strategies we need better models as well as more ample and precise input data for the models in terms of emission inventories and ambient air pollution measurements. For me there is no doubt that during this week your experience will greatly contribute to improve the level of knowledge and allow a breakthrough in the development of the relevant new activities under the EMEP work programme.

In Switzerland we developed an intensive monitoring programme to follow the implementation of the new air quality standards adopted in December 1997 for PM_{10}. An annual mean of 20 $\mu g/m^3$ and a daily mean of 50 $\mu g/m^3$ to be exceeded only once a year were set as standards in the Ordinance on Air Pollution Control. To document the evolution of the fine particulate matter concentrations over years, we have conducted several parallel monitoring campaigns of TSP, PM_{10} as well as $PM_{2.5}$. During this week you will have the opportunity to take note of different reports in relation to the experience acquired in Switzerland in this field.

In conclusion, we should always keep in mind that air quality measurements and modelling by themselves do not improve the quality of the environment. But they give information about the sources of particulate pollution, they help to evaluate the effect of emission changes and allow a comparison with the air quality goals. A better air quality can only be realized by implementing appropriate measures to reduce the emissions of air pollutants.

With this ultimate goal in mind – namely to improve air quality – I finish my opening remarks. The workshop on fine particles is opened.

Fine particles under the convention on LRTAP

Discussions/Decisions

by

the EMEP Steering Body 1998–1999
E. Lumme
Secretary of the EMEF Steering Body
UN/ECE

- 1997 the Executive Body: the need for a protocol on particles? Established a joint task force with the World Health Organization to investigate the scientific and health-related issues.

- 1998 discussion paper on the visions for the EMEP work by 2005/2010 EB.AIR/GE.1/1998/3/Rev. 1.

- 1998 MSC-W and CCC background notes for the Steering Body’s twenty-second session.

- 1999 workplan for EMEP.

- 1999 Steering Body twenty—third session

- Draft 2000 workplan for EMEP.

Fine particles under the convention on LRTAP Discussions/Decisions

by the EMEP Steering Body 1998-1999

E. Lumme
Secretary of the EMEP Steering Body
UN/ECE

The 1998 discussion **paper on the visions for the EMEP work by 2005/2010** (EB.AIR/GE.1/1998/3/Rev.1) addressed, for the first time, problems related to the long-range transport of fine particulates. It had been recognized that the health effects of fine particles are more important than previously thought. Epidemiological studies, initially in the United States, but more recently also in Europe, had derived associations between PM_{10} and $PM_{2.5}$ and mortality. Overall risk estimates had suggested that, of the pollutants covered by current legislation, those associated with particles tended to be among the highest. Moreover, a significant fraction of ambient concentrations of fine particles in Europe arised from the long-range transboundary transport of particles formed by atmospheric reactions chiefly involving sulphur and nitrogen oxides and ammonia.

The Executive Body had, at the end of 1997, duly discussed the need for a protocol on particles and decided to establish a joint task force with the World Health Organization to investigate the scientific and health-related issues. The work of EMEP was expected to provide this task force and the Executive Body with further information on the transboundary transport of particles.

Furthermore, in the 1998 considerations, it was assessed that the present EMEP models for the acidifying pollutants could be used to estimate the concentration of particles arising from gaseous emissions of SO_2, NO_x and NH_3. These particles generally constitute a large part of the small aerosol ($PM_{2.5}$) but a smaller part of the large aerosol (PM_{10}). The models for acidifying pollutants could, therefore, be used with some adjustment to estimate the regional concentrations of the small particles but not of the large ones. Developing models for the long-range transport of the large aerosol would be a major effort. It would be necessary, **inter alia**, to establish a finer geographical resolution than 50 km.

It was also noted that much of the needed research for sulphur, ozone and fine particulate matter overlapped. Atmospheric oxidation reactions were important also in particle formation, besides ozone. Modelling the transport and fate of sulphur, ozone and particles relied on similar meteorological processes, the same computational framework, similar emission inventories and model initializations. However, there were a number of necessary steps required for performing a realistic modelling of particulate matter. This would involve considerations of emission inventories for primary particles, the atmospheric chemistry of secondary particle formation including fog and cloud processes, the incorporation of aerosol dynamics and deposition, and the characterization of background aerosols. In

1998, in the EMEP long-term strategy paper it was estimated that, as a first step, the existing **EMEP models** could be modified as follows:

(a) The sulphate and nitrate concentrations are already determined by the acid deposition models. These contribute to the aerosol mass in the size range below 2.5 µm;

(b) The Lagrangian model, or one of the models which are being used to model HM transport, may both be easily modified to describe the concentration of primary aerosol particle components, provided that adequate emission data can be made available;

(c) Secondary organic aerosol concentrations will be estimated by the EMEP photo-oxidant model, adding a secondary organic aerosol formation module;

(d) Adding an aerosol dynamics module, which is necessary to determine the size distribution of the aerosol components, will require the combination of information from three models.

Further, it was noted that the **measurement of particles** is a complex task, and proposed that, as a first step, the following action could be taken:

(a) The existing EMEP monitoring sites should be used for $PM_{2.5}$ and PM_{10} monitoring. This will achieve multiple monitoring objectives for a moderate increase in costs. The $PM_{2.5}$ and PM_{10} measurements will need to be carried out with at least daily time resolution, in order to determine actual exposure of human receptors;

(b) A network of core monitoring sites could be established for determining the chemical composition of the aerosols, and relate the aerosol mass to different types of primary aerosol emissions and secondary aerosol formation under different conditions and in different parts of Europe. These core monitoring sites should also be able to carry out denuder measurements to separate nitrate in aerosols from HNO_3;

(c) The Working Group on Effects under the Convention has highlighted the need for measurements of the base cation content of aerosols, and for separation of the gaseous and particulate nitrogen species in air. These objectives should also be taken into account.

In 1998, MSC-W’s and CCC’s background notes facilitated the **Steering Body’s** discussion at its **twenty-second session** on needs and possibilities to start EMEP work on fine particles. It was agreed that there was enough scientific evidence of the adverse health effects of fine particles on health and that their long-range transport played an important role. The Steering Body supported starting EMEP work in this field. It agreed that EMEP will, by 2000, evaluate the basic long-range transboundary problems of small particles and, as needed, develop its monitoring and modelling activities in this field to be able to respond to the issues raised under the Convention. EMEP would also contribute to the work of the joint Task Force with the World Health Organization set up by the Executive Body.

Based on the above considerations, **the 1999 workplan for EMEP** set as objective of the first phase to provide the joint Task Force and the Executive Body with further information on the transboundary transport of fine particles. It was agreed that this year

(a) The EMEP centres will provide background information to the Task Force on health aspects on available long-range transported monitoring and modelling results of the atmospheric concentrations of primary and secondary particles;

(b) CCC will, in cooperation with the other EMEP centres, evaluate the quality of the available expert emission estimates of primary particles. Based on these analysis MSC-W will evaluate the possibility of including primary aerosols in the Eulerian acid deposition model;

(c) MSC-W will develop further the Eulerian acid deposition model in order to include secondary aerosols resulting from the atmospheric oxidation of volatile organic compounds;

(d) The Task Force on Emission Inventories will consider work needed for emission inventories;

(e) Switzerland, in cooperation with the EMEP centres, will organize a workshop to consider further the state of the art in particle measurements and modelling and to prepare recommendations on future work in autumn 1999.

The workplan defines the expected output of this year work be: Background information to the joint Task Force on health aspects of fine particles. Progress report on modelling activities. Recommendations by the workshop on directions and priorities of the future work.

At the **twenty-third session of the Steering Body** in September 1999, CCC reported on progress in producing and collecting background information on the long-range transport of primary and secondary particles. As requested in the work-plan, MSC-W and CCC had actively contributed to the work of the Task Force on the Health Aspects of Air Pollution of the Working Group on Effects. A document had been prepared for the Working Group’s 1999 session (EB.AIR/WG.l/ 1999/11). Steering Body welcomed the fact that fine particulates were incorporated in the Convention’s 1999 work-plan and that the situation would be further considered in detail at this workshop.

Unfortunately the outcome of this workshop was not yet available when the secretariat had to **draft a workplan for 2000**. The Executive Body will consider it at its seventeenth session starting 29 of November 1999. The draft work-plan gives the following description/objectives for the work in 2000: Develop transport and integrated assessment models to provide the Steering Body, the Task Force on the Health Aspects of Air Pollution and the Executive Body with further information on the transboundary transport of fine particulates. Draw up recommendations for emission reporting and monitoring of air concentrations of atmospheric particles relevant to the Convention.

Furthermore, it details the main activities and their time schedule as follows:

(a) The Task Force on Emission Inventories will consider work needed for emission inventories. The discussions at the EMEP workshop in Interlaken in November 1999 are expected to provide input for these considerations;

(b) The discussion of measurement at the EMEP workshop in Interlaken is also expected to form the basis for the drawing-up of detailed procedures and recommendations with respect to quality assurance. The measurements of fine particles within EMEP should be compatible with recent regulations concerning the measurements of PM_{10} and $PM_{2.5}$ in urban areas. On the basis of these discussions CCC will put forward a proposal with monitoring requirements for atmospheric particles useful to EMEP;

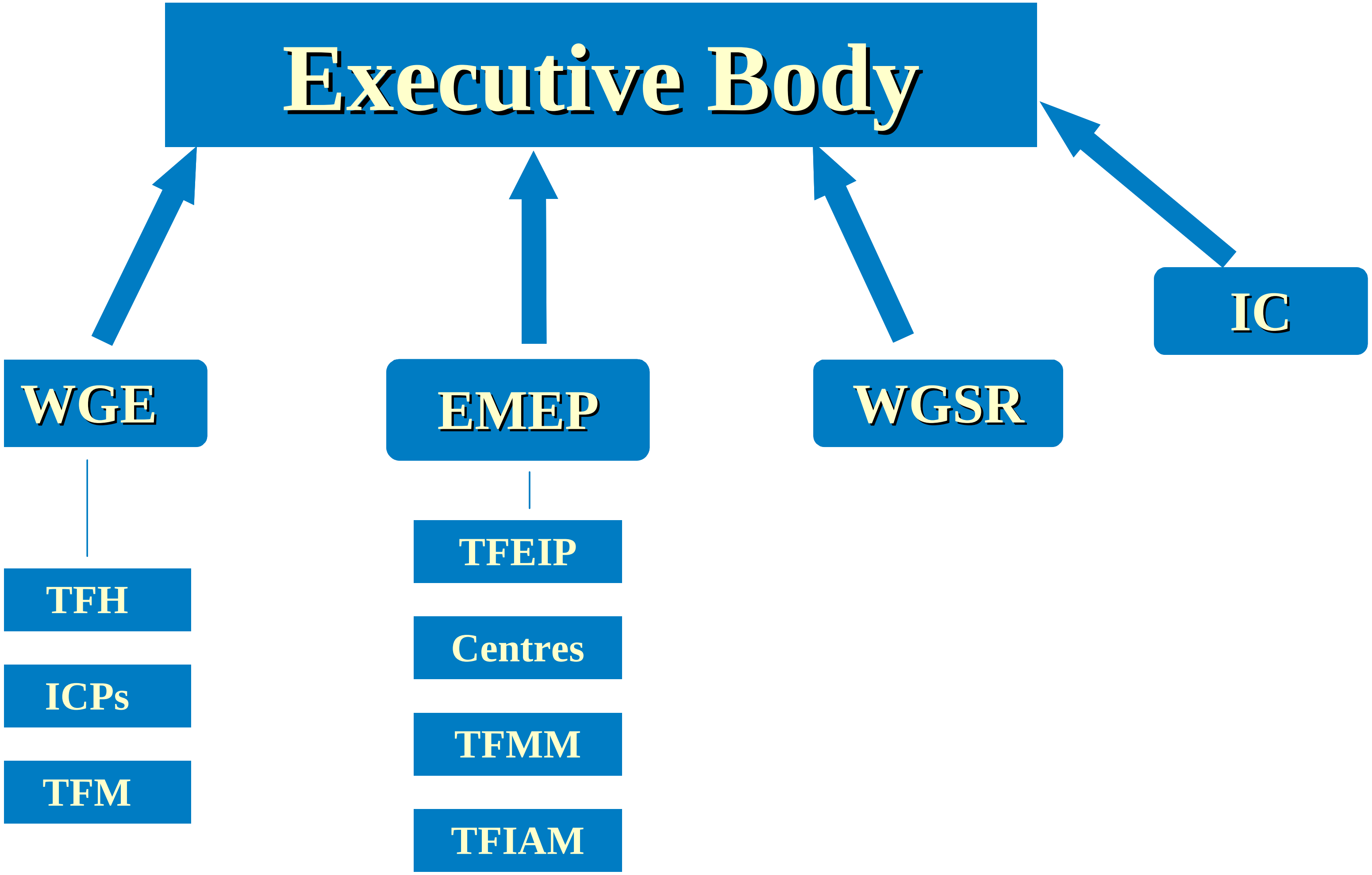
(c) MSC-W will evaluate the possibility of including primary aerosols in the Eulerian acid deposition model. It will develop the Eulerian model further in order to include secondary aerosols resulting from the atmospheric oxidation of volatile organic compounds. MSC-W, in cooperation with Nordic experts, will initiate the incorporation of an aerosol dynamic module in the Eulerian model. The discussions at the EMEP workshop in Interlaken are expected to help direct the modelling work as well;

(d) MSC-E, in cooperation with MSC-W, will study further the physico-chemical properties of primary particles which are relevant for the modelling of heavy metals;

(e) The Task Force on Integrated Assessment Modelling will also include fine particulates in its work. To support this, IIASA/CIAM will initiate work to integrate particulate matter into the model and present a progress report. It will also report on the work conducted for the German Federal Environmental Agency (UBA) and the United Kingdom’s Department for the Environment, Transport and the Regions;

(f) The centres will present a joint progress report to the Steering Body and inform the Task Force on the Health Aspects of Air Pollution about their work.

1979	Convention on LRTAP
1984	EMEP
1985	Sulphur
1988	Nitrogen oxides
1991	Volatile organic compounds
1994	Sulphur
1998	Heavy metals
1998	Persistent organic pollutants
1999	Multi-pollutant multi-effect


Executive Body
WGE
EMEP
WGSR
IC
TFH
ICPs
TFM
TFEIP
Centres
TFMM
TFIAM

New under EMEP

Seventh-phase programme 1999-2001 five thematic areas:

- 1. Acidification and eutrophication
  2. Photo-oxidants
  3. Heavy metals
  4. Persistent organic pollutants
  5. Fine particulates

- Problem-oriented workplan

- Problem-oriented analysis of results and reporting **together** by the EMEP centres

- Closer cooperation between centres and Parties and with other organizations

- Closer links to scientific research including effect-related research

- Change of focus from supporting negotiations to following the outcome of agreements

Plans of the European Commission regarding particulate matter

by

Lynne Edwards

European Commission, DG XI

There is a large body of European legislation that is directly or indirectly concerned with particulate matter. Most notably, Directive 1999/30/EC sets ambient air quality limit values for PM_{10}, to be met in 2005. From 2001 EU Member States will be required to measure PM_{10} and $PM_{2.5,}$ to identify areas where limit values may not be met without additional measures, and to draw up action programmes to ensure that they are met on time. These action programmes will have to identify sources, identify the contribution of transboundary pollution, and set out the measures that will be used to reduce concentrations. Countries which have applied to join the European Union will also be implementing this legislation over the next few years.

In addition, the Directive sets more stringent indicative limit values for PM_{10}, with a deadline of 2010. These indicative limit values will not, however, come into force unless the Commission brings forward a proposal to confirm them, and the European Parliament and the Council adopt the proposal.

The Commission will report to Parliament and Council by the end of 2003 on implementation of the Directive and on the latest evidence on health effects, technical matters and abatement possibilities. It will bring forward any necessary specific proposals at this time. The Commission intends also to report by the end of 2004 on an integrated air quality strategy, which may also be accompanied by proposals.

No decision has yet been made on whether the Commission will propose confirming the indicative limit values for PM_{10} or propose a change, for example to some other metric. It is however clear that the Commission will need to take into account both local sources and transboundary pollution. Any action on transboundary aerosols will need to be integrated with action against tropospheric ozone, acidification and eutrophication.

The scientific and technical base for EU decisions on both local and long-range particle pollution contains many gaps. It urgently needs improvement. There are important unsolved questions concerning the mechanism by which particles affect health, which particles are most important, what the most important sources are and concerning air chemistry and transport. It would be unrealistic to expect all these uncertainties to be resolved by 2003/2004. Decisions will nevertheless have to be made even if the scientific and technical base still contains important gaps. There is no “no-decision” option. Doing no more than is already being done is a decision with risks and consequences. It will be important to be clear about uncertainties, about the risks of potential decisions and to try to make recommendations as far as possible for “no regrets strategies”.

Legislators will wish to take a snapshot of the scientific evidence on health effects at the latest possible moment before 2003/2004 and develop a comprehensive strategy covering the types of particle to be tackled as a priority and the technical measures needed to succeed. Some decisions must however be taken before 2003/2004 even though they will only have their effect after that date. Manufacturers need to gear up some years in advance in order to produce equipment or reorganise processes. Measurement standards also take some years to develop.

Current legislation sets timetables for making decisions on fuel quality from 2005, on technical aspects of motor vehicles, and on emission standards for stationary sources under IPPC and other legislation, all of which may affect particle concentrations. These decisions cannot be postponed but it is important that they should not unnecessarily constrain scope for future decision making. Researchers, regulators and officials working in different areas need to be aware of developments and to try to minimise potential constraints.

The Commission is now considering how best to develop an integrated air quality strategy, making sure that all interests are properly involved. Co-ordination with EMEP will be important. In particular the technical base for developing strategies to deal with transboundary aerosols must be consistent with the technical base of any future UN-ECE protocol. DG Environment hopes to hold a workshop during the autumn of 2000 to launch the development phase of the programme. EMEP will be invited to participate.

Health aspects of fine particles

by

Michal Krzyzanowski

WHO European Centre for Environment and Health, Bilthoven Division

The evidence on adverse impact of suspended particulate matter on health has been growing rapidly over the last decade. Most of the evidence comes from the epidemiological studies. While only two-three studies per year on that subject were published in the 1980s, ten to thirty research reports from relevant epidemiological studies appeared each year in the 1990s. Vast majority of the available studies analyze the relationship of health with a mass concentration of particulates with aerodynamic diameter less than 10 µm (PM_{10}); fewer consider specifically the fine fraction of the particulates, measured as $PM_{2.5}$. Chemical composition of the particles is quite complex, but its characteristics have rarely been included into the assessment of health impacts. This is a result of the use of existing, routinely collected, air quality monitoring data for estimation of population exposure in most of the completed studies.

In spite of the relatively crude description of the exposure, the range and magnitude of health effects of PM_{10}, and $PM_{2.5}$, is quite consistent across a large variety of environments, climatic conditions and predominant pollution sources. The impacts range from decrements in lung function, through increased incidence of acute respiratory or cardiovascular symptoms, to increased mortality. The increased incidence of symptoms is reflected by the frequency of the use of health services, such as health care visits or hospital admissions on, or directly following, the days with the elevated air pollution levels. Several studies show also the effects of the prolonged exposure, expressed by an increased mortality, increased incidence of chronic pulmonary diseases and chronically decreased lung function. The latter effects create the most significant burden to population health.

In the process of the update of WHO Air Quality Guidelines, the information gathered until 1996 has been assessed. The Guidelines do not specify a concentration of PM_{10} or $PM_{2.5}$ below which no effects would be expected and provide risk estimates for standard setting. The Guidelines assume a linear relationship between the considered health effects and ambient concentration of PM_{10} and $PM_{2.5}$. The more recent epidemiological studies confirm the validity of the approach proposed by the updated guidelines.

Mechanisms of the observed health effects are still not certain and are a subject of intensive research. Better understanding of the mechanisms through laboratory experiments and a more precise description of exposures in epidemiological studies are necessary to identify which of the many components of particulate matter, or which physical or chemical characteristics, are responsible for the observed health effects. The few epidemiological studies where $PM_{2.5}$ was measured directly or as a concentration of sulphates (also present as fine aerosol in the atmosphere) are suggestive of the predominant health significance of the fine fraction of the particulates. It is consistent with the exposure assessment studies, which show that the ambient concentrations of fine fraction of the particulates ($PM_{2.5}$) tend to be better correlated with personal exposures than the PM_{10} concentrations.

Some toxicological experiments have suggested that it is the number concentration of fine particles, and not their mass concentration, which is the health-relevant parameter for the exposure. Few epidemiological studies, where the number concentration of particles was assessed, tend to confirm the possible relevance of that parameter. However, this does not explain the relation of health to PM_{10} mass concentration, which is largely uncorrelated with the particle number.

Other existing hypotheses consider particle surface area, particle surface chemistry (e.g. metals contents or acidity) and the ability to create oxidative stress in the target tissue as the parameters responsible for, or contributing to, the observed health effects. However, more toxicological and epidemiological research is needed to verify if, and which, hypothesis may be correct.

The joint Task Force of WHO and UNECE, has been created in 1998 to assess Health Aspects of Long Range Transboundary Air Pollution. The Task Force considered particulate matter as its first topic for evaluation. The Task Force report[1], presented to the Workshop participants, states that the particles transported over long distances or created in the atmosphere from gaseous emissions contribute a significant part of the ambient concentration of PM_{10} and $PM_{2.5}$. In many populated areas, particularly where there are no heavily polluting local sources of particulate matter, as much as 40-60% of PM_{10} levels may be attributable to long-range transport.

The Task Force made an attempt to estimate the possible health burden of the particulate matter from the LRTAP in Europe. The exposure estimates, derived by the experts from EMEP and from the Imperial College, London, combined with the information on exposure – response associations derived from epidemiological studies on the effects of long-term exposure to particles, indicate that as many as between 95 thousand and 382 thousand premature deaths per year may be associated with the exposure to particulate matter from LRTAP in Europe. Some 75% of this number is attributable to the exposure to secondary particles, calculated by the models using the emission data from 1996. Validity of these calculations depends on the applicability of the results of epidemiological studies, which were conducted mostly in respect to urban air pollution. It is not certain to what extent the different composition and low concentration of the particles from long-range transport have the same effects.

The estimated impacts vary considerably across Europe, with the largest effects expected to occur in the densely populated parts of central and Western Europe. The changes of emission of (gaseous) pollutants in the 1990s should have resulted in overall reduction of the impacts and in the shift of the most affected areas to the south of Europe.

The present exposure estimates, and their changes in time, are rather uncertain. While the emission inventories of gaseous precursors of secondary particles are relatively well established, calculations of primary PM_{10} and $PM_{2.5}$ emissions are much more uncertain. This hampers the modelling of the spatial distribution of PM levels. Also the models used to estimate air pollution with particulates are in the early stages of development and the pollution levels predicted by the existing models are associated with substantial uncertainties.

The report of the Task Force illustrates the potential significance of the health risk of the particulate air pollution from the pollution transported over long distances and identifies areas where new information is necessary for reduction of uncertainties in the present assessment. The improvement of the air pollution characteristics, together with the better understanding of health effects of the pollution, are urgently needed to provide a more precise advice to the policy makers and to devise pollution abatement strategies protecting health more effectively.

Reference:

1. Task Force of Health Aspects of Long Range Transboundary Air Pollution. *Health Risk of Particulate Matter from Long Range Transboundary Air Pollution. Preliminary Assessment.* WHO European Centre for Environment and Health, Bilthoven Division, 1999 (56 pages).

Emission inventories of primary fine particles

by

M. Woodfield, P. Van Der Most, J. Goodwin, J. McAughey

The aim of this paper is to review the current status of fine particulate inventories and to comment on the problems facing their further development. It will also describe the activities in the Task Force on Emission Inventories and suggest improvement opportunities for discussion at the Workshop.

Background:

There are a number of activities setting or driving the ‘operational requirements’ of fine particulate inventories, these include:

- state of the environment reporting at national and regional level (for air quality improvement, health and amenity purposes etc.),
- transboundary pollution modelling (LRTAP Convention and the POPs and Heavy Metals Protocols),
- the development of national and international regulatory controls (which need to take into account the effectiveness of alternative remedies and their interaction with other regulations or instruments - such as the impact of POPs and HM on particulate emission levels),
- regulatory compliance testing (for UN ECE, OSPAR, and EU Air Quality Directive for instance).

However ‘fine particulate matter’ is not a single entity but a short hand term used to encompass a range of particle related characteristics including: particle mass, size and number. The inventory compiler is faced with the dilemma of knowing exactly where to apply his limited resources and which of these to inventorise first.

There is a considerable amount of inventory development work ongoing at both international and national level but too often the focus of this work is split between toxicological, epidemiological and methodology issues and is not co-ordinated. There are a number of different groups involved, each with their own special interests - be it academic, commercial or regulatory.

Current Status of Fine Particulate Inventories From Primary Sources:

<u>International level:</u>

There are very few truly international inventories. That of TNO was compiled to assist international policy development and is the only inventory presently available which has self consistently, estimated, size differentiated particulate emissions for the whole of Europe. It broke down emissions from five major emission categories (Stationary combustion, process industries, transport, waste incineration, and agriculture) and suggested default emissions for three size fractions ($PM_{10,2.5,0.1}$) for about 25 countries. It used literature values and expert judgement to develop emission factor defaults, it did not include natural sources.

CORINAIR, the initiative of the European Environment Agency, is stimulating the collection and reporting of a range of emissions from European countries. The programme collects emissions for a range of pollutants, including PM_{10}, on a regular basis. The CORINAIR system encourages quality control and consistency of approach between contributing countries and is becoming increasingly important. Guidance for the estimation of emissions for reporting is provided by the EMEP/CORINAIR Guidebook. This document (available via the EEA website http://eionet.eea.eu.int/aegb/default.htm) sets out in considerable detail how to estimate emissions from most known sources of emission. It provides guidance at a basic level for inexperienced compilers or less important sources and at more detailed levels for more comprehensive reporting.

Work is proceeding in the UN ECE regional area under the long range transboundary air pollution convention (LRTAP) to control the emission and transport of acidifying, eutrophying, photochemical and toxic and persistent pollutants, all these in various forms require the estimation of particulate emissions and the modelling of their capacity to be carried long distances. As a result the EMEP centres MSC-W and MSC-E (Moscow) are developing particulate models and examining the likely distribution of POPs and heavy metals in Europe. Much of the predictive work on POPs and heavy metals is being done with the TNO inventory. The task force on integrated assessment modelling (TFIA) also uses the TNO inventory when integrating particulates into the IIASA Rains and other models, the data being disaggregated as a function of NO_x emission data.

Other international organisations/groups carrying out activities requiring fine particulate inventories include the GAEI project, GENEMIS (part of the EUROTRAC programme), the OECD/Eurostat - which collects TSP and PM_{10} information in its joint questionnaire process, and the Auto-oil II consortium.

National Programmes

Much inventory activity is ongoing in the US/N America where interest is progressing from PM_{10} to $PM_{2.5}$. A $PM_{2.5}$ committee has been set up to discuss the inventory issues and to develop the emission estimation tools needed to enable individual states to report their emissions (see Airchief site http://www.epa.gov/ttn/chief/eiip/eiip_p25.htm). The major output will be a report which will describe current $PM_{2.5}$ emission estimation techniques and evaluate emission factors, specify the precursor emission data requirements, and prioritise issues requiring further work.

Work is also progressing within a number of Europe and the EU members states – examples include the Dutch (to be described by Berdowski) and UK work (described in NAEI http://www.environment.detr.gov.uk/airq/aqinfo.htm and http://www.etsu.com/en env).

Inventory Development Issues:

In developing particulate inventories the following factors need to be taken into account:

i) The size distribution of particles of the particle mixture making up total suspended particulate (TSP). In the light of current knowledge especial attention is being paid to $PM_{10/2.5/1/0.1}$.

ii) The chemical composition, health concerns relating to both toxicity and carcinogenicity are drawing attention to particulate bound heavy metals (Cd, Ni, Hg and As) and organic carcinogens (polycyclic aromatic compounds PAH).

iii) The development of consistent and comprehensive source lists, especially for poorly defined particulates (tyre wear, road re-suspension and 'natural' emissions such as sea salt from oceans, wind blown dust/soil and volcanic ash).

iv) The nature of the emission and whether it is a contained or fugitive emission.

v) Whether the source is stationary or mobile (i.e. transport related).

vi) Whether emission factors are based on measurement or are estimation. Of relevance here is weather reported data has been validated and consequently whether inventories as a whole are of sufficient quality that they can be verified by an independent source.

vii) In allocating valuable and limited resources is there a minimum acceptable coverage (i.e. is it sufficient or possible to characterise the to 80% of emissions relatively quickly?)

EMEP Task Force on Emission Inventories:

The EMEP/CORINAIR Guidebook, referred to above, is a source of information and a vehicle for co-ordinating information exchange. The Task Force, via a number of Expert Panels, compiles and manages the Guidebook, updating it as and when necessary. In view of the importance of fine particulate emissions an increasing amount of effort is being directed to including PM estimation when updating.

Some groundbreaking work has been carried out by Van Der Most, the IFARE team (University of Karlsruhe) and AEA Technology to develop 'model chapters' to guide the work of the Expert Panels in the production of their chapters of the guide book. This has entailed extending process descriptions to include all the stages which can give rise to PM emissions; in the past, for example, the handling of process raw material and the handling of waste products would not have been included. The chapter revisions will also need to feature extended descriptions of process emission abatement and default emission factors.

A number of other new features will need to be added to the Guidebook. Additional emission categories will also be needed. A means of estimating and reporting size fractions must be developed; an approach similar to that used for estimating PAH speciation is being considered. This entails identifying a small number of reference processes and tabling a default size fractionation which is to be used until measured data becomes available.

Way Forward:

1. Inventory developers need clear and unambiguous priorities to function, particular regarding what is important for health: is it numbers of particles, as it is for miners; particulate shape as for asbestosis; or is it chemical composition as for toxicity.
2. Resources are extremely limited and should be pooled wherever possible; so establishing effective communication between groups will be critical factor in the future. This will require the linking of expert networks where they have been established (as for, example, that used by the TFEI).
3. An undue reliance is currently placed on estimation technique. As a result of a number of recent regulatory initiatives an increasing amount of measurement work is being undertaken which can be used to supplement, extend and verify inventories. The ECE Protocols and EU emission reduction directives will require substantial source measurement programmes. Similarly EMEP activity and EU air quality management initiatives will result in the generation of an increasing amount of size resolved, good quality, ambient data. Effective communication and access to monitoring data developed for regulatory purposes will become increasingly important. This in turn will require that procedures for making, compiling and reporting data will be important.

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European PM_{10} and $PM_{2.5}$ Emission Inventory of anthropogenic Sources

by

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Introduction

For the outlining of policy on the ambient air concentration of fine particulates in the Netherlands by the Ministry of Environment additional knowledge on particulate emissions was required on a European scale. This information had to be suitable as input for atmospheric dispersion modelling, for scenario calculation and for presentation purposes. A sector-split European emission inventory has been prepared for PM_{10} and $PM_{2.5}$ for the years 1990 and 1993 on a 0.5° x 1° latitude – longitude grid scale [1]. The inventory has been restricted to primary aerosols from a number of sectors, which are expected to cover the bulk of the anthropogenic sources: stationary combustion, industrial process emissions, transport (including maintenance, tyre wear, road abrasion and re-suspension for road transport), agricultural practise (pig and chicken factory farming) and waste incineration.

General and country specific information was collected on emission control for a range of combustion and production processes [1,2]. Subsequently, the emissions were calculated by applying emission factors for each process to a certain activity rate. The emission factors for PM_{10} were derived from open literature and specific measurement reports. Activity rates for combustion and production processes for each country were used from official statistics or when absent from other international emission databases. The $PM_{2.5}$ emissions were calculated by characterizing the PM_{10} emissions with respect to the $PM_{2.5}$ fractions. Firstly, total emission estimates were set for the individual source groups for each individual European country. Next, the country totals were spatially distributed in a 0.5° x 1° latitude – longitude grid by using specific point source information (location, capacity) for a large number of combustion and production plants, population density distribution data and land use information.

Emission inventory results

The total European (excluding the former SU) anthropogenic PM_{10} and $PM_{2.5}$ emissions were about 5100 and 2900 ktonnes for 1990 respectively (figure 1). Including the European part of the former SU would roughly double these emission figures. For PM_{10} and $PM_{2.5}$, stationary combustion processes contributed about 55% of total emissions, while industrial processes and transport contributed between 14-19% of total emissions.

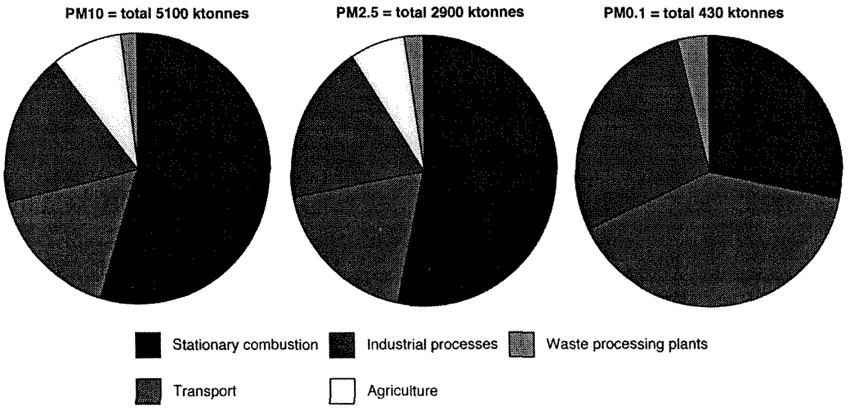

Figure 1: *PM emissions in Europe (excluding the former SU) in 1990 by main source category.*

Power generation accounted for about 55% of total stationary combustion emissions. The contribution of residential combustion to total stationary combustion equals more or less the contribution of industrial combustion processes, but tends to be increase in importance for the most fine PM fractions.

The industrial process emissions of PM_{10} were dominated by activities from the iron and steel industry and refineries. The contribution of refineries emissions increase in importance for the finer PM fractions.

For the transport sector, the PM emissions were dominated by the contribution of heavy duty vehicles (60-70%). It is important to realize that in 1990, non-tail pipe emissions (tyre wear, re-suspension processes on roads etc.) accounted for 30-40% of the total PM emissions of transportation.

Between 1990 and 1993 the PM emissions decreased because of economic developments and change in especially the type of fuel used for residential combustion in a number of countries.

Scenario results for 2010

For the year 2010, three types of emission predictions have been prepared [2]: a 'Business as usual' scenario, assuming no emission reduction activity in Europe and applying the RAINS 7.2 Official Energy Pathway Scenario (OEP); a 'Baseline' scenario, applying OEP and assuming a range of agreed emission reduction activities (e.g. 2nd Sulphur Protocol); a 'Best Available Technology' scenario, applying OEP and BAT. The scenario results for 2010 presented in Figure 2, together with the 1990 PM_{10} emission data.

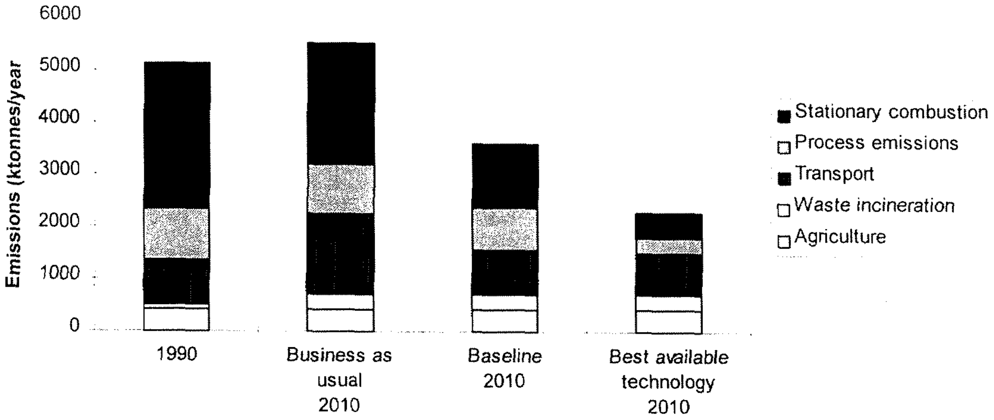

Figure 2: *PM_{10} emissions in 1990 and predictions for Europe (excluding the former SU) in 2010.*

When no emission reduction activities are applied the 2010 PM_{10} emission would increase slightly compared to the 1990 emission values (Business as usual). Especially, transport emissions would increase strongly. When a series of reduction measures will be applied (Baseline scenario), the 2010 emissions would probably be about 30% less than in 1990. When all Best Available Technology would be applied as well, an emission reduction of about 55% could be achieved, especially by the decrease of the emissions from stationary combustion and industrial production processes. The contribution of transportation emissions would hardly be reduced further compared to the Baseline scenario. The reason for this is that non-tailpipe emissions will hardly be reduced and are expected to become relatively more important (about 50% of total forecast transport emissions). Also, the strict EU regulations (EURO 4) have already been accounted for in the baseline scenario and will not lead to further decrease in the BAT scenario.

Uncertainties

A very first approach to calculate the uncertainties in the inventory data, has been based on the statistical analysis of the information on emission factors. For the sources considered, the uncertainty in emissions for total Europe (without the former Soviet Union) range between 10 - 20% for the different PM fractions.

In the Netherlands a qualitative approach to determine emission inventory data is being explored [4]. The emission factors and activity data are characterized by five quality classes, ranging from *A* to *E*. *A* - the highest quality - stands for a figure based on a large number of measurements of representative installations, while *E* - the class of lowest quality - represents a figure resulting from a technical calculation, which is based on a number of assumptions. The relative contribution of the five quality classes in the PM_{10} emission inventory of known sources for 1997 is strongly dominated by the classes *A* (34%) and *E* (53%). It can be seen that especially the emissions of transportation and residential activities are highly uncertain in the Netherlands (figure 3, below). Within the sector transportation, inland shipping and harbour activities are important contributors to overall uncertainty. Wood combustion accounts for a large part of the uncertainty of residential activities.

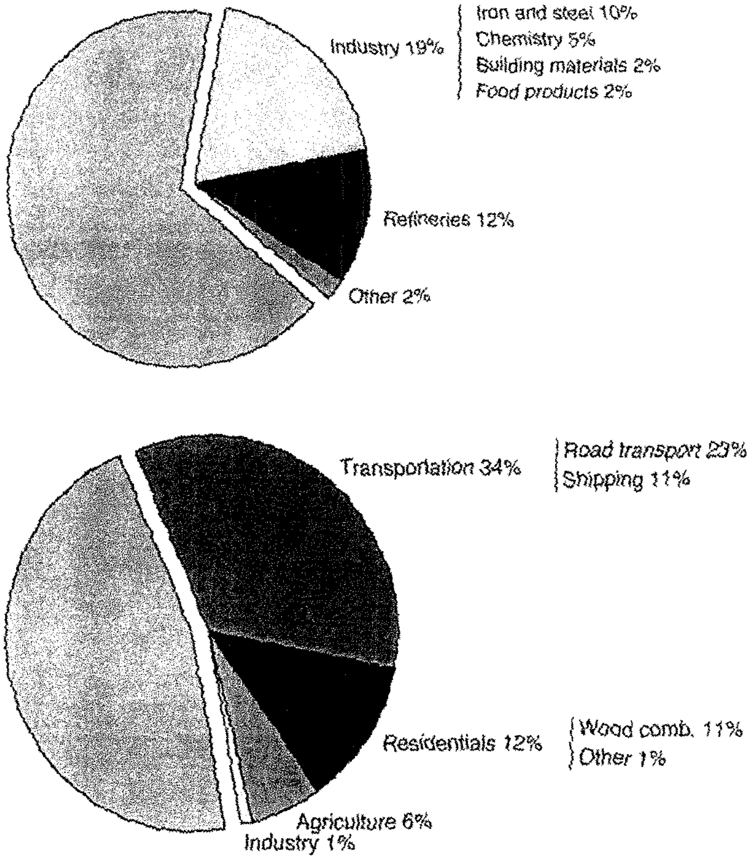

Figure 3: *Relative contribution of sectors to quality classes A (above - 34% of total) and E (below - 53% of total) of the PM_{10} emission inventory in the Netherlands in 1997.*

Verification

Modelled annual average PM_{10} concentrations of ambient air in the Netherlands (among others based on these inventory results) are about 50, 60 and 75% of the measured concentrations for respectively rural, urban and industrial areas [3]. This could indicate an underestimate of the emissions in this European scale inventory. This can be expected as a number of sources was not covered by this inventory (e.g. non-anthropogenic sources, incomplete re-suspension). On the other hand, it should be realized that both the measurement data and the model applied and the emission estimates contribute to the overall uncertainty observed as well, so that the discrepancy between measured and modelled concentrations cannot be attributed to only the inaccuracy of emission data.

Concluding remarks

It is clear that the emission inventory results as presented here can be improved further and become more complete by applying more up-to-date information, by evaluating the results with national experts and by adding non-anthropogenic sources and more complete re-suspension information. Also, the results could be improved by using verification methods, e.g. by applying the combination of measurements of concentration, size distribution and chemical speciation of PM in the ambient air, atmospheric models and chemical characterization of the emissions of different sources.

Large uncertainties with respect to source contribution can be attributed to:

- Non-combustion emissions from Transportation
- Several Industrial Processes
- Diffuse sources, e g.
    - Crops, Agricultural Soils, Tillage
    - Re-suspension processes
- European background concentrations (Ocean, other continents)
- Volcanoes, Wild fires etc.
- Residential activities

Several countries have prepared PM_{10} emission inventories by now. Comparing these data gives the impression that no uniform sets of emission factors are applied and that not in all cases the same set of emission sources is considered. This implies that using these national inventory data on a European scale will cause uncertainties with respect to especially:

- Differences in emission factors
- Incompleteness of sources
    - Non-combustion emissions road traffic;
    - Agriculture;
    - Construction/demolition activities;
    - Several industrial processes;
    - e.g. foundries, storage and handling;
    - Biomass burning, wild fires;
    - Shipping;
    - Smoking;
    - etc.

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Current measurement techniques for compliance monitoring of fine particles

by

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Introduction

Particles may occur in the atmosphere in the solid or in the liquid state. The particle size is a feature which cannot be discribed by a single parameter due to the often irregular shape of the particles. Therefore, so called equivalent diameters are used to describe the particle size. In the context of compliance monitoring the aerodynamic diameter is used. PM_{10} ($PM_{2.5}$) therefore means the particle fraction with less than 10 (2.5) µm aerodynamic diameter. Fig. 1 shows a practical example of how the aerodymanic diameter is derived from the normally irregular shape of a realistic particle.

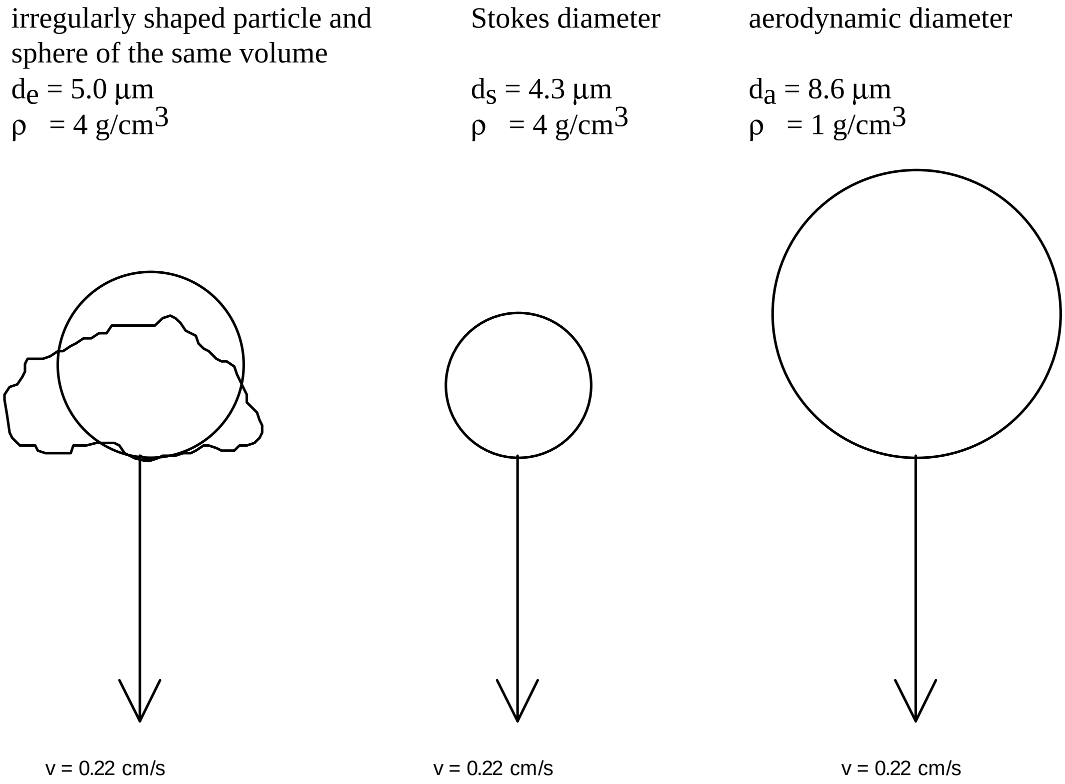

Fig. 1: Irregularly shaped particle and its equivalent diameters.

Harmonisation of PM_{10}- and $PM_{2.5}$ measurements in Europe

According to Community Directive 96/62/EC on ambient air quality assessment and management and Directive 1999/30/EC relating to the establishment of limit values, inter alia also for particulate matter, all member states of the EU are obliged to report PM_{10} and $PM_{2.5}$ data. In order to assess air quality across Europe on a consistent basis the measurements need to be performed with standarized measurement techniques. Therefore the European Commission has mandated the European Normalization Centre CEN to establish reference methods for measurement of PM_{10} and $PM_{2.5}$ and to define requirements for alternative methods to be considered as equivalent methods.

The work for PM_{10} is now completed and has led to the standard EN12341 while the work on $PM_{2.5}$ is still in its beginning phase. As it is already the case for PM_{10}, also for $PM_{2.5}$ a manual gravimetric reference method will be most probably defined as reference. With this procedure Europe is in line with the corresponding US-American methods as defined by the EPA.

Elements of the manual gravimetric methods

Basically a manual gravimetric method consists of an inlet system providing the desired particle fraction, a filter on which the particles are deposited, a regulated sampling pump and a detailled procedure for the gravimetric analysis of the filters.

Inlet systems:
The main task of an inlet system is to prevent particles which are larger than the desired fraction (e.g. $PM_{2.5}$) to enter the sampling line. Most of the currently used inlets work on the principle of impaction. Fig. 2 shows as an example the WINS impactor for $PM_{2.5}$ which is part of the American reference method for $PM_{2.5}$. This is an example of an inline impactor i.e. it is used after a PM_{10} preseparator which protects the fine nozzles from being clogged by coarse particles. These devices need to be cleaned and greased or oiled frequently. Fig. 3 shows a newly developed inlet system on the cyclone principle, the so-called sharp cut cyclone SCC with similar performance characteristics as the WINS but longer maintenance intervals.

Filters:
Generally filters are used to separate the particles from the carrier gas. They shall have a collection efficiency of >99.5% for particles around 0.3 µm aerodynamic diameter. Smaller and larger particles are usually collected with even better efficiency due to the involved deposition mechanisms (see Fig. 4). The filter materials used are, inter alia, glass and quartz fibre filters and membrane filters made of teflon, cellulose nitrate, cellulose acetate and polycarbonate.

Weighing procedure:
The mass of the particles collected on the filter is determined by weighing the filter before and after sampling after conditioning at defined climatic conditions.

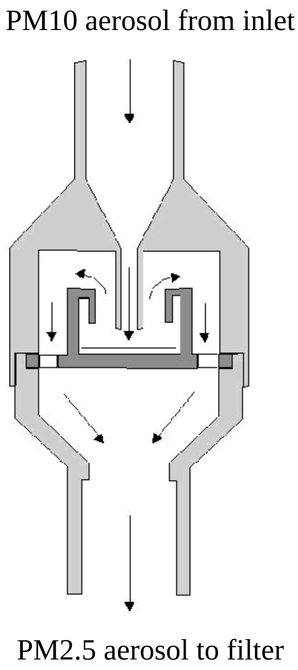

Fig. 2: WINS-impactor (EPA)

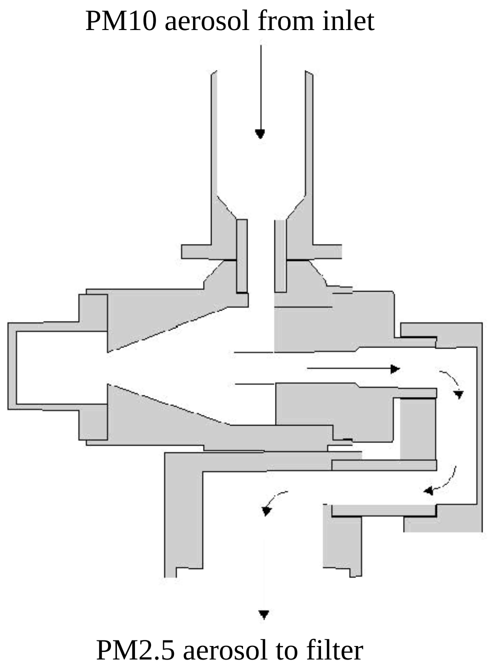

Fig. 3: Sharp cut cyclone (SCC)

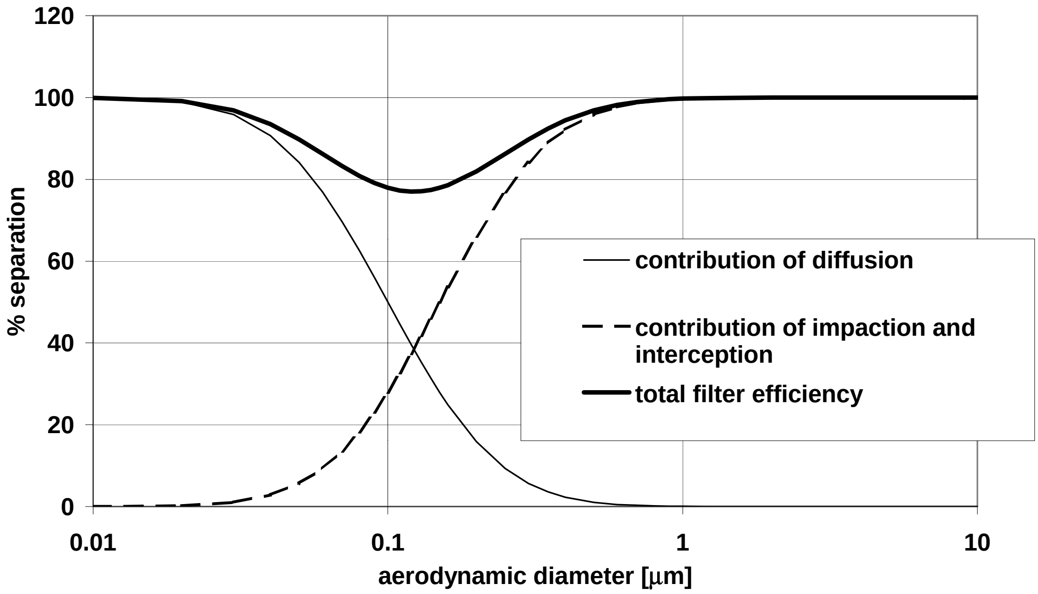

Fig. 4: Efficiency of a (bad) filter as a function of particle diameter

Automatic monitors

The manual gravimetric method is rather time consuming and normally gives only daily mean values. In order to obtain on-line data with higher time resolution, monitors are used in many air pollution networks. Most of them work either on the principle of the oscillating microbalance (TEOM) or the absorbtion of beta radiation.

To avoid water droplets (fog or condensation) being measured as particle mass, the inlets and filters of these monitors are generally heated to 35 – 50 °C. At this temperatures volatile particles (e.g. ammonium nitrate) are at least partly lost. Therefore the monitor data are not directly comparable to manual gravimetric data.

Compliance monitoring methods and EMEP needs

The main purpose of compliance monitoring of fine particles is not necessarily a scientifically sound measurement of the "true" concentrations but rather to check wether health related limit values are respected or exceeded. These limit values are based on epidemiologic studies of adverse health effects and/or mortality caused by ambient exposure to fine particle concentrations. These latter were mostly measured with manual gravimetric methods.

However, for EMEP purposes measurement methods would be desirable which give data which are directly comparable to modelled aerosol concentrations from emission of primary particles and aerosol formation in the atmosphere. Methods which are biased by sampling artefacts and losses (as the described manual gravimetric procedure and the monitors) are certainly not ideal.

It is therefore an open question in which way EMEP can make use of the compliance monitoring data which have the advantage to be available over large parts of Europe but with the disadvantage of not necessarily reflecting "true" ambient aerosol concentrations.

Aerosol Measurements Within the WMO Global Atmosphere Watch Programme: Providing Data Related to Climate Forcing and Air Quality

by

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The World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) Programme has been established to provide measurements, scientific assessments, and other information on changes in the global chemical composition and related physical characteristics of the atmosphere (WMO, 1997). Atmospheric aerosols influence our environment in various ways (IPCC, 1995; Baltensperger and Nyeki, 1998), and characterization of their properties has therefore been included in the GAW programme. Since the atmospheric residence time of aerosol particles is relatively short, a large number of measuring stations are needed. In addition, information on seasonal variations is required, which is mostly unavailable at present. Furthermore it is the goal of GAW to ensure long-term measurements in order to detect trends. In summary, the objective of the GAW aerosol programme is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality up to multi-decadal time scales.

For this purpose, the harmonization of aerosol measurements on the global scale is important in order to make results comparable. WMO therefore established Scientific Advisory Groups (SAGs) for various components of the measuring programme, including the SAG on Aerosols and Aerosol Optical Depth. The Aerosol SAG had its first meeting in December 1997, and two more in the following years. The SAG is currently formulating guidelines for measurement and quality assurance procedures in the extensive global programme. It is planned to publish these guidelines in the year 2000. In addition, an overview of all GAW parameters will be published as a combined effort of all SAGs. (For more information: The official GAW Web site can be accessed from the WMO site (www.wmo.ch) - go to AREP, then GAW. The front page of the WMO site will be revised in the near future so that GAW will appear immediately rather than through AREP).

Presently, GAW consists of 20 Global stations, which cover different types of aerosols: Clean and polluted continental, marine, arctic, dust, biomass burning, and free troposphere. These stations include Mauna Loa in Hawaii, Ny-Ålesund in Spitsbergen, Cape Point in South Africa, South Pole, and the Jungfraujoch in the Alps (WMO, 1997). Most of these sites are located in pristine areas and therefore, the SAG recently made additional recommendations that would provide better coverage of the polluted continental aerosol type. In addition, there are about

300 Regional stations where measurements are made closer to the source areas. In this way, Global stations may then serve as standards for Regional stations.

Priorities were set for measurements at the Global and Regional stations. According to the recommendations of the SAG, Regional stations will be expected to measure optical depth, mass concentration in two size fractions, major chemical components in two size fractions, and the scattering coefficient. At Global stations, a larger number of measurements are envisaged, with optical depth, mass concentration in two size fractions, major chemical components in two size fractions, the scattering and hemispheric backscattering coefficient at various wavelengths, the absorption coefficient, aerosol number concentration, cloud condensation nuclei (CCN) at 0.5% supersaturation, as well as diffuse, Global and direct solar radiation. Additional parameters such as aerosol size distribution, detailed size fractionated chemical composition, dependence on relative humidity, and vertical distribution of aerosol properties should be measured intermittently at the Global stations. Further research is needed, as for some parameters there is no suitable commercial instrumentation available (e.g., CCN), or calibration procedures are presently unclear (e.g., absorption coefficient).

The establishment of a World calibration centre for aerosols within GAW is an essential part of this process, however, due to funding problems no solution has been found so far.

A further essential part of the concept is a dedicated data centre, which makes the data available for their users in a most efficient way. The World Data Centre for Aerosols in Ispra (Italy) is currently undertaking all actions needed to fulfil this task.

While much of the recent international focus has been directed at assessing the impact of human activities on regional and global scales, there is growing recognition that the management of urban environments requires special attention. The poor air quality in many cities is the result of both high emissions and local meteorological conditions. It is clear that more effective management of urban/ regional problems must be science-based, and will require a marked enhancement in monitoring and modelling capabilities and infrastructure. GAW plans to continue its focus on high quality measurements, with added emphasis on data analysis and interpretation, and will continue to work with national and international organizations (such as WHO) on improving measurements in and around urban environments.

Furthermore, collaboration with other international programmes such as IGAC, WCRP is envisaged in order to obtain the optimum benefits from a combination of long-term measurement programmes and dedicated field campaigns.

While it is premature to give all operating procedure details, a few points may already be mentioned. No particular PM10 design is recommended in preference to others, but the apparatus should be characterized. The optimum size cut for differentiation between coarse and fine mode was decided by the SAG to be either of the two following: 10 μm ambient and 1 μm dry, or 10 μm ambient and 2.5 μm ambient, where 1 µm dry refers to 1 µm at low RH. A cut-off diameter at 1 µm for low RH and 2.5 µm ambient RH (wet) are expected to give roughly the same results. The dry value should be obtained by lowering the RH to 30-50% (aim for 40%) using a heater with absolute maximum heating temperature set at 40°C. Heating will introduce problems, e.g. due to nitrate and organic carbon losses. If drying by heating is problematic, then a diffusion drier (such as silica gel) or dilution with dry air is recommended. It was agreed that drying would pose difficulties at tropical sites. Another problem is very cold arctic conditions, where RH values are very low. However, humidifying of the samples is not recommended as being necessary.

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EUROTRAC-2 subproject AEROSOL
Composition/size evolution of the secondary aerosol
An introduction

by

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EUROTRAC

AEROSOL is one of twelve subprojects in EUROTRAC. The subproject has the aim of filling in gaps in knowledge on aerosol formation in Europe. EUROTRAC in total comprises some three hundred researchers. Every individual participation (via Principle Investigators) has been approved of and is documented in a two-page document. Every year an annual report of the subprojects is produced, which contains the contributions of the individual PI's. The work in EUROTRAC is of a generic nature and is basically performed on a voluntary basis. However several countries only support national projects on atmospheric chemistry when they are performed within the EUROTRAC framework.

The subproject(s) in EUROTRAC are divided into task-groups with co-ordinators who form the steering group. The EUROTRAC framework provides, via the responsible International Executive Committee and the Environmental Assessment (Advisory) Group of experts, a direct link with European and national policy. The Scientific Steering Committee watches over the scientific level of the research and co-ordinates the overall program. Via the secretariat exchange of information is provided, for instance by printing the annual reports, editing the newsletter and organisation of the biannual EUROTRAC symposium. This symposium is the central point of gathering of the atmospheric scientists in Europe.

AEROSOL

The subproject AEROSOL was officially approved at the end of 1997 and is therefore new in the EUROTRAC program, which has now been in existence for over 10 years. At present AEROSOL has 33 PI's from all over Europe.

In AEROSOL attention is not only on PM-related scientific questions, but the work is also aimed to provide relevant information on the reflection of light by aerosol. This reflection leads on the one hand to a reduction in solar irradiation and is thereby a key climate issue in Europe. On the other hand reflection of light leads to visibility impairment. Aerosol particles are also the sites on which heterogeneous reactions of gaseous trace constituents occur. Information should therefore become available on the composition of the aerosol surface. This surface, in turn, is mostly composed of the secondary compounds which either have condensed onto it or formed there. The focus of AEROSOL is on $PM_{2.5}$

because all of the phenomena mentioned are associated with particles of that size. AEROSOL serves also as the “mother” for information on aerosols in other subprojects.

AEROSOL has the following 6 year work planning:

First the problems of measurement and modelling of the semi-volatile secondary aerosol constituents are addressed, *in particular that of the organic fraction*. There is a lack of instrumentation for measurement of these aerosol components. Therefore, one of the subproject’s objectives is to **develop necessary instrumentation** for the representative measurement of semi-volatile aerosol components in the fine aerosol fraction and in well-defined size classes.

The instrumentation will then be applied to determine the aerosol components which constitute the total aerosol mass. The sum of the analytically determined masses of the individual components will systematically be compared to the total weighted mass, and the degree of ‘closure’ will serve as a consistency test. These **chemical mass closure experiments** will be performed during intensive campaigns at seleeted (“super”) sites, which include well-defined background sites to more complex polluted urban sites.

The **sources** of the major aerosol constituents will be identified according to general categories, e.g. local versus regional sources, anthropogenic versus natural sources, using compositional data (chemical mass balance), in combination with tracers, isotope measurements and back-trajectory analysis.

Where very large aerosol and precursors sources are to be expected, two AEROSOL sites will be simultaneously operated, one inside the source area and one outside, in a prevailing downwind location. Differences in composition/size at these **twin-sites** will provide insight in the relative importance of primary emissions inside the source region and secondary aerosol (formation) downwind. These data will be used to test models of aerosol evolution.

The data and models will finally guide the planning for one or two **Lagrangian process-studies** in which the evolution of aerosol properties will be followed as a function of travel time from a major source area. These process studies will necessitate fast physical aerosol characterisation to complement the relatively slow chemical measurements.

Models and field studies will be used in an iterative way to **evaluate and improve model descriptions** of secondary aerosol formation and evolution. These descriptions will be incorporated in 3-D regional transport models.

Structure of AEROSOL and relation with other subprojects

At the workshop the structure of the subproject will be presented. It can also be found in the workplan of AEROSOL. Information necessary for our research, like emissions of gaseous precursors and particles and chemical transformation of gases, to name a few items, come from other subprojects in EUROTRAC. The subproject AEROSOL has a close co-operation with the group of atmospheric scientists working on the mechanism of he transformations of VOC's. The reason is that important end products of these reactions are aerosol components.

Activities

1998 Annual report

The 1998 annual report, which is at the moment in print and will be available via the secretariat of EUROTRAC, provides information on the activities. The highlight in 1998 was the PIPAPO campaign in early summer, see below.

AEROSOL-3-day workshop March 1999

In March 1999 a 3-day symposium was held at which the PI's presented their individual annual reports and where the task-groups discussed the status of research and plans. Also the concept of the twin-sites was extensively discussed, using experience in the PIPAPO campaign, see below. The need of modellers for aerosol data and the availability of data was discussed, first within the task-groups and thereafter in a plenary discussion. Results of the workshop were documented in the minutes of the meeting in which also the main conclusions of the subtask-groups on measurements were reported in detail.

Major conclusions coming from the workshop are:

- Black carbon: several presentations showed that the instrumental absorption efficiency of 19 m^2/g as used in the aethalometer is too high, and values of 9.3 to 10 m^2/g were suggested instead.
- Within the problem of elemental and organic carbon one should also discuss how sampling artefacts (mainly of the organics) are avoided. Examples: O_3 denuder during sampling

Twin-site approach
The "Twin"-site concept of AEOSOL was extensively discussed on the basis of experience gained in the PIPAPO campaign, see below, and at the twin-site of Leipzig-Melpitz. It was concluded that a simple source receptor relation is not easy to establish and furthermore it appears that the two stations of a twin-site should be situated at larger distances than projected in the design-phase of AEROSOL. The larger distance should allow sufficient time for formation of the secondary products to be detectable. This will be further discussed at the coming workshop of AEROSOL in March 2000 to come to optimum design of such "simple" Lagrangian studies.

Analysis of carbon in aerosol
In conjunction with the mentioned "carbon shoot-out" there was a lively discussion on the collection of aerosol for assessment of the amount of organic aerosol material. At present, none of the participants is handling possible "positive" (adsorption of gases) or negative (evaporation of collected material) sampling artefacts. Some had experimented with the use of double (sequential) filters to assess the extent of such artefacts. Differentiation could be done in broad classes according to solubility, such as water-soluble and organic solvent extractable, with the latter separated in subclasses according to polarity.

PIPAPO

This was a EUROTRAC-LOOP initiative near the city of Milan, in which 3 institutes of AEROSOL participated to search for a possible correlation between oxidant and aerosol formation. Automated devices to measure the major ionic species in aerosol were successfully operated there for the first time side by side. Whatman 41 paper filters had much better agreement with the continuous aerosol collector systems for nitrate and ammonium than quartz filters. Other, preliminary, results of the campaign can be found in the 1998 annual report of AEROSOL. The campaign showed the real-life complexity of the simple source-receptor concept of "Twin"-sites.

Carbon shoot-out

In the course of 1998 a major initiative of H. Puxbaum, which fitted extremely well with our plans, was put under the umbrella of AEROSOL: This is the "carbon-shoot-out" which aims in first making an intercomparison of techniques used for determination of the amount of total carbon and "organic" carbon, using prepared filter samples and filters with collected material from at various sites. Those were/are: A) Urban high exposure B) Urban high exposure preextracted C) Urban low exposure. The first results are currently under evaluation.

Ammonium nitrate sampling workshop

In June 1999 a workshop was held at which an automated device for measurement of ammonium nitrate and other artefact-free tools for proper collection and analysis were compared. (The Swiss group suffered a severe accident on the way to the workshop and was not present with their automated instrument). Also simple filter techniques were involved. The tests were performed with pure ammonium nitrate in the reproducible setting of a wind-tunnel. The incomplete sampling of ammonium nitrate on quartz filters, as found in the PIIPAPO campaign, could be substantiated. It was further found that paper-filter collects nitric acid gas. This first evaluation of the results and other findings, recently evaluated by the participants, will be used as input in the discussion at the present workshop. The detailed results will be presented on the EUROTRAC symposium of March 2000.

Activities 2000

A field intercomparison in Melpitz near Leipzig is in preparation in which all participants are involved, either having either measuring tools there or analysing collected material.

Twin-site studies were proposed within the 5th framework program of the EU. Unfortunately these efforts were not approved of. The new approach is based on (bi)national initiatives. It would be very welcomed when these efforts could and would be combined with EMEP initiatives for supersites.

The regional aerosol transport and dynamics model MADE – applications to Europe

by

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The Aerosol Model MADE

In order to fulfill their scientific tasks state-of-the-art air quality models have to be capable of predicting particulate matter in addition to the gas-phase concentrations. A suitable model aerosol model has for the application in complex regional transport models has to provide sufficient information on the chemical composition as well as on the size distribution of the particles. Furthermore it has to be integrated into a photochemical model in order to be able to represent the numerous interactions between the phases. On the other such a model has to be computationally efficient to enable its use for numerous sensitivity studies. Such a model has been developed with MADE which is based on the Regional Particulate Model (RPM) and has been implemented into the regional model system EURAD. The model system has been applied in a one-way nesting scheme from the regional to the urban scale.

Figure 1 shows the current model structure of the aerosol model. The size distribution is approximated by three different modes spanning the size range of atmospheric particles. Each mode is described by a log-normal size distribution that is specified by the number concentration, the surface concentration and the mass concentration in each mode. The mass concentration is further sub-divided into the chemical compounds of tropospheric particles that are currently given by inorganic ions (sulfate, nitrate and ammonium), secondary organic compounds (in 4 different biogenic and anthropogenic species each), water and secondary particles. The model can treat different kinds of secondary particles depending on the availability of appropriate emission inventories. New particle formation by nucleation, growth by condensation, coagulation, sedimentation, aerosol-cloud interaction and transport processes are taken into account.

Although this model describes a rather complex aerosol system, it still can be used on large grids without causing an extensive computational burden.

Secondary Organic Particles

The aerosol model has recently been extended to include secondary organic particles, i.e. the particles that result from the low-vapor pressure products that are formed in gas-phase oxidation processes in the atmosphere. First applications of this model system to an episode in July 1994 show that these compounds cannot be neglected in assessing the tropospheric PM load.

Figure 2 shows an example of the daily average secondary organic PM mass resulting from biogenic and anthropogenic precursors. It can be clearly seen that the biogenic contribution to the total mass is significant. However these results are strongly sensitive to the biogenic VOC emission parameterization used. Due to the formation process of these particles, where the new mass formation is dependent on the mass that is already available, strong and non-linear interactions between the phases might occur.

Secondary Inorganic PM

Inorganic ions comprise a major fraction of tropospheric $PM_{2.5}$. Figure 3 shows the response of the model to a reduction in SO_2 emissions, i.e. one of the most important precursor species of these aerosol particles. Whereas the sulphate aerosol concentration shows the expected reduction due to the precursor reduction, it can be seen that the atmospheric bad of nitrate particles is increasing in some regions. This replacement of sulphate with nitrate aerosol might offset the benefit of emission reduction measures significantly, in some instances even leading to an increased $PM_{2.5}$ load.

An additional effect is a possible change in particle size distribution. Due to the strong impact of sulphuric acid vapour on nucleation processes, a reduction of SO_2 emissions might enhance nucleation, thus reducing the aerosol mass bad but increasing the number concentration.

Standard Stringency

Since two new EU-wide PM air-quality standards are planned for 2010 it seems worthwhile to investigate the relative stringency of these standards. Given the values for the annual and daily standard the ratio as defined in figure 4 can be used for this investigations. For values of this ratio larger 2.5 the daily standard can be considered more stringent and vice versa.

An analysis of PM_{10} measurements for different European countries in 1997 as taken from the EEA database shows strong geographical differences, with e.g. the annual standard being more stringent in the UK in contrast to the Czech Republic. Both standards where commonly exceeded in 1997.

Acknowledgments

The continued support from Dr. Francis S. Binkowski from the US-EPA and from the EURAD group (University o. Cologne), in particular E. Friese and Dr. M. Memmesheimer is gratefully acknowledged.

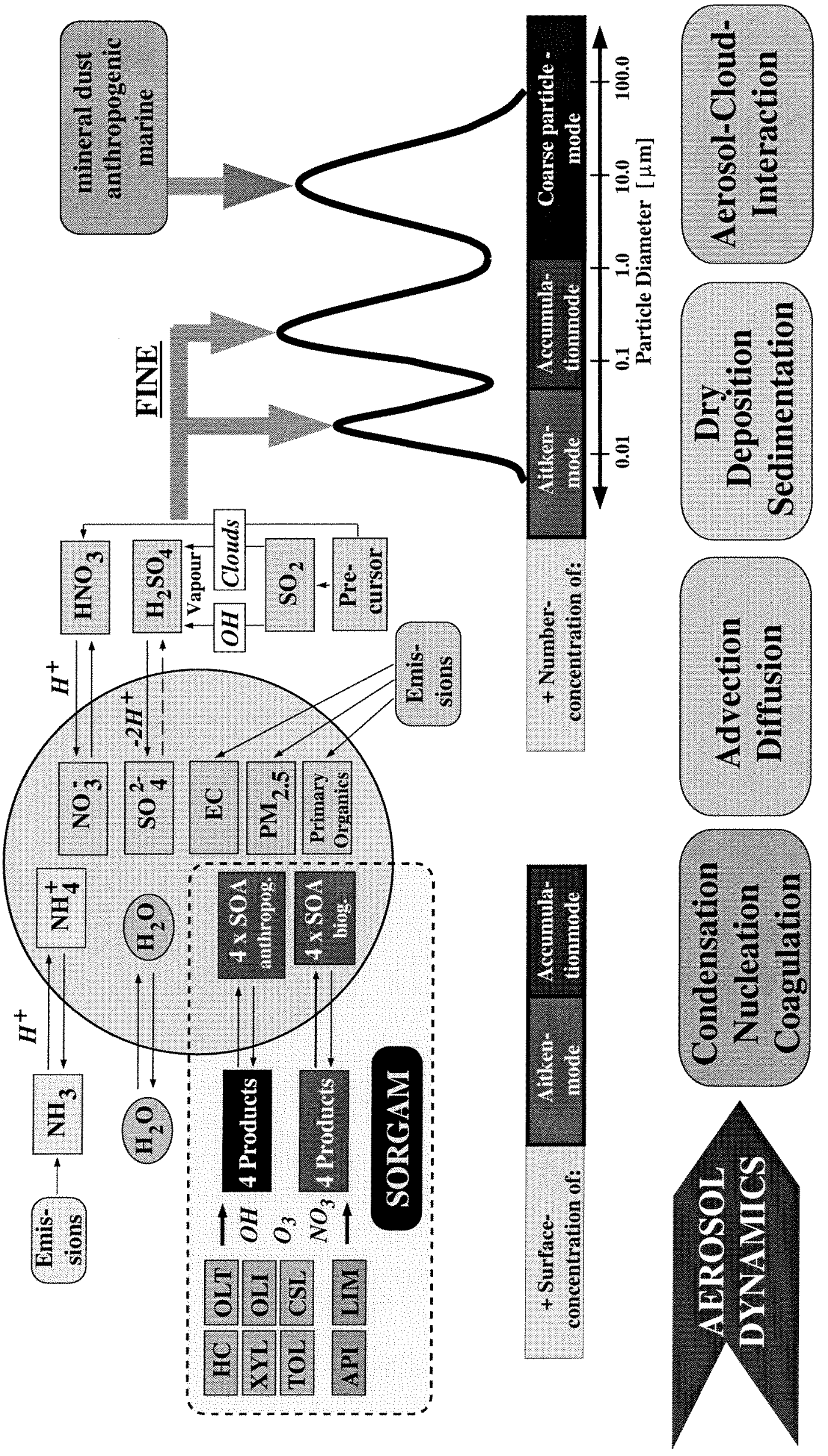


Figure 1: Structure of the Aerosol Dynamics Module MADE.

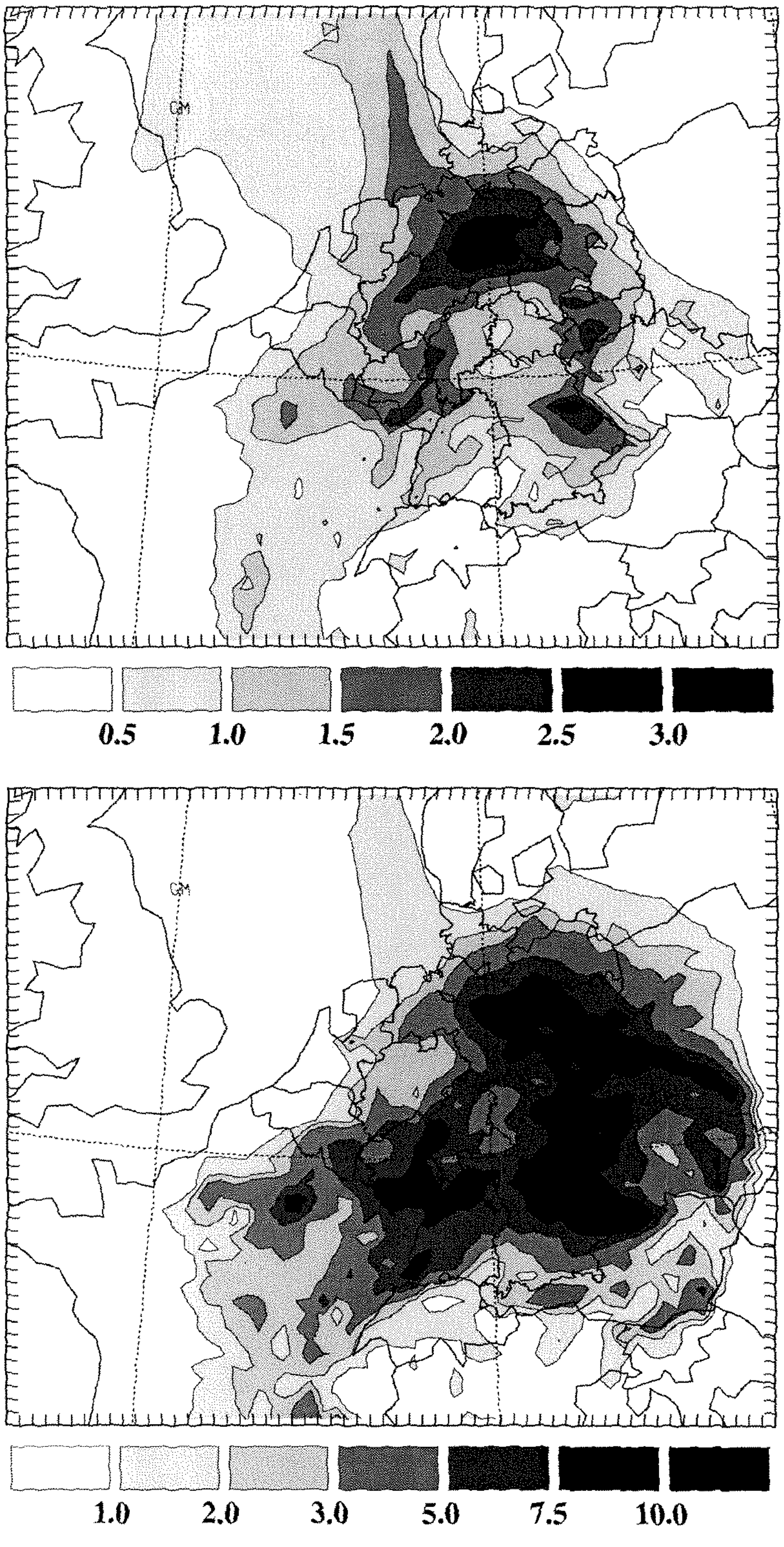


Figure 2: Simulated secondary organic aerosol concentration on July 26th 1994, 24-hour-averages in μg/m3. Shown are results for the anthropogenic (top) and biogenic (bottom) secondary aerosol component in the model surface layer.

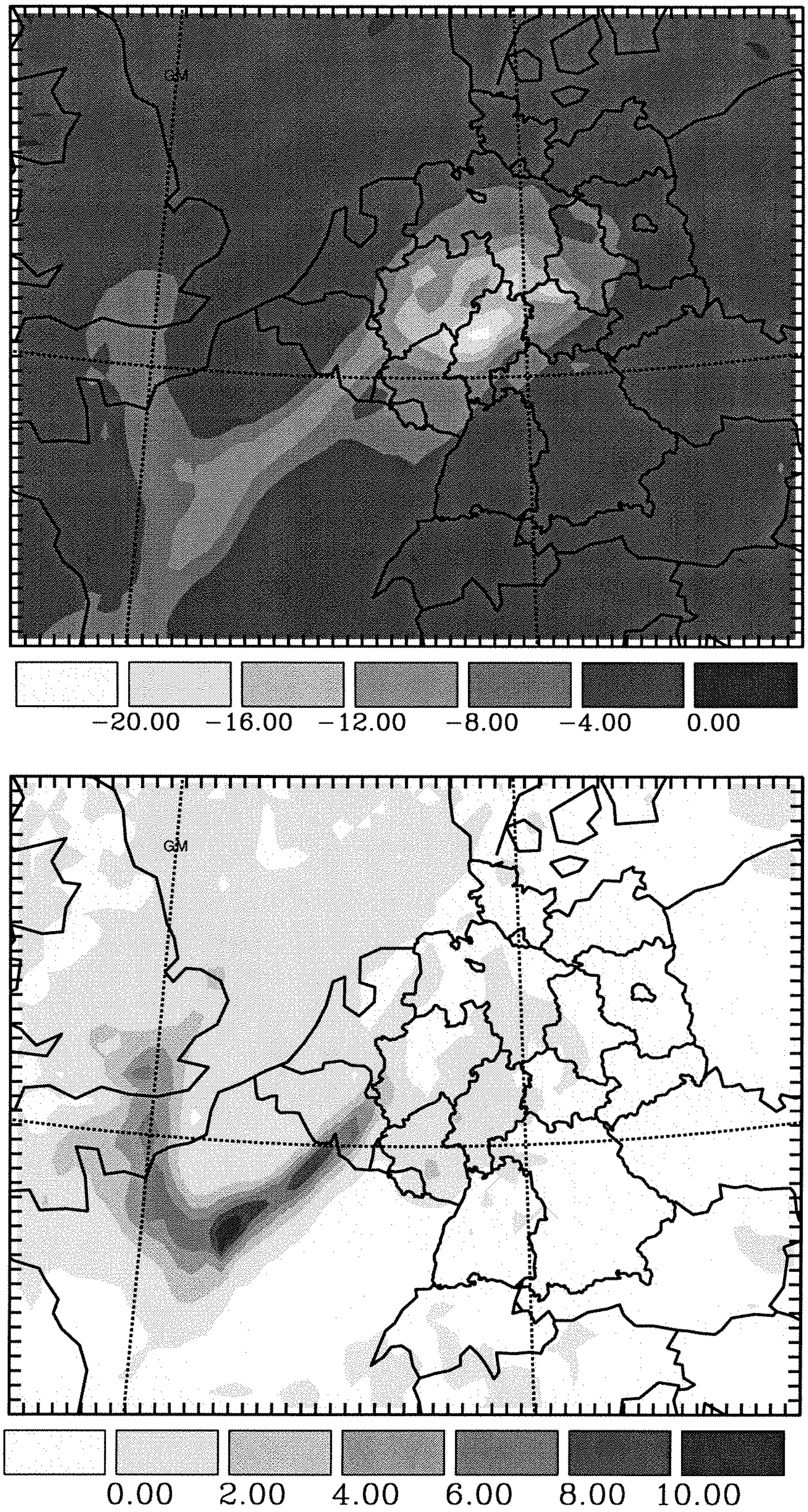
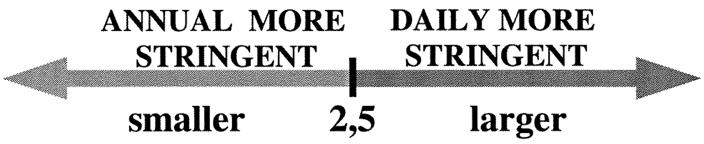


Figure 3: *Response of accumulation mode sulphate aerosol (top) and accumulation mode nitrate aerosol (bottom) to a 50% reduction in SO_2 emissions. Values are given in $\mu g/m^3$ in the model surface layer as difference between reduction and base case simulation.*

$$\text{RATIO} := \frac{\text{DAILY (98\%centile)}}{\text{ANNUAL AVERAGE}}$$



Country	# of Stations	Annual Average	# with Ratio>2.5	Aver. Ratio	More stringent
UK	40	22.95	5	2.3	Ann.
Poland	8	56.08	7	2.8	Daily
Belgium	11	31,40	2	2.3	Ann.
Czeck Rep.	56	30,98	42	2.7	Daily
Netherlands	19	40,72	7	2.5	? ?

PM10 measurements from Airbase (EEA) for 1997, only stations with more than 200 daily measurements considered.

Figure 4: *Analysis of relative stringency of daily and annual PM standard. See Text for further details.*

Concentrations of Primary Particulate Matter over Europe

by

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Introduction

As a result of epidemiological evidence linking adverse effects on human health to particulate exposure, there is currently much concern about concentrations of fine particulate matter (PM_{10} and $PM_{2.5}$). The European Commission has introduced new limits on particulate matter under an Air Quality Daughter Directive, reflecting control of episodic exposure (24-hour concentrations in excess of 50 µg m^{-3}), and annual mean concentrations. In this context local pollution in populated areas has to be superimposed on pollution imported from long-range transport, which can be substantial. We have previously indicated that a new multi-pollutant multi-effect protocol will bring a significant improvement in reducing the concentrations of secondary particulate material resulting from oxidation of gaseous SO_2, NOx and NH_3 emissions across Europe. This note is concerned with the complementary contribution from long-range transport of primary particulate emissions.

European emissions of primary particulate material

The only consistent pan-European inventory currently available is from a study by TNO (TNO, 1997), which provided estimates for emissions of the years 1990 and 1993. Recognising that it may be the finer particulate fraction below 2.5 microns in size which is most important for human health, in addition to PM_{10} emissions, TNO have also estimated emissions of $PM_{2.5}$; and also of the ultra fine particles, $PM_{0.1}$. The total European emission of PM_{10} (excluding the former Soviet Union) in 1990 is estimated at 5.1 million tonnes. Corresponding totals for $PM_{2.5}$ and $PM_{0.1}$ are 2.9 million tonnes and 3.8 thousand tonnes, respectively. This size differentiation is also important for modelling the atmospheric transport of the particles. According to the TNO inventory over half the 5.1 million tonnes of PM_{10} arose from stationary combustion (2.8 million tonnes). In addition there is 0,84 million tonnes from transport, another 0.94 from process emissions and 0.44 from agriculture.

For the modelling results presented below the TNO emissions have been mapped onto the EMEP grid by assigning national emissions to grid squares in proportion to the NOx emissions. This is an approximation to the real distribution, but is sufficient for preliminary modelling studies and commensurate with the level of detail in the inventories.

Annual average concentrations of primary PM_{10} and $PM_{2.5}$ for 1990 emissions

A simple model has been applied to simulate the atmospheric transport of primary particulate material across Europe, coupled with the emissions inventory described above. The model is derived from a model originally used for radioactive material. It is a statistical model, based on trajectory roses, and includes gravitational settling and dry deposition, which are dependent on the particle size; wet deposition is treated probabilistically by transitions from dry to wet and wet to dry periods along trajectories. The calculated concentrations represent average values over EMEP grid cells, but without allowing for the restricted local scale dispersion close to major sources or within urban areas.

The first and second figures appended give maps for the 1990 emissions described above, of the modelled concentrations of PM_{10} and $PM_{2.5}$, respectively, without taking into account the contributions from the local sources, i.e. only considering long-range transport. The highest concentrations of PM_{10} indicated are around 8 to 9 µg m^{-3} over central Europe, falling to 1–2 µg m^{-3} in the peripheral areas of Europe. For $PM_{2.5}$ the highest concentrations are lower at about 6 µg m^{-3}, but there is less difference from the total PM_{10} in more remote areas. This is consistent with longer-range transport of the finer $PM_{2.5}$ part of the overall PM_{10} emissions.

Although the concentrations in outer areas of Europe are small, the model implies that long-range transport can still give rise to substantial contributions to episodes of high concentration. For example with trajectories from central Europe to the UK corresponding to winter anti-cyclonic conditions with limited mixing, the imported contributions over London can be up to 15 to 30 µg m^{-3} (AEPG report, 1999).

The third and fourth figures show the modelled concentrations of PM_{10} and $PM_{2.5}$ respectively, taking into account the contribution from the local sources. In this case, the highest concentrations of PM_{10} can reach a maximum of 18 µg m^{-3}, with a number of areas over central Europe reaching 10 to 12 µg m^{-3}. Again in this case, the peripheral areas of Europe have concentrations of 1–2 µg m^{-3}. For $PM_{2.5}$ the highest concentrations are lower at about 10 to 11 µg m^{-3}, with, again, less difference from the total PM_{10} in more remote areas.

For development of integrated assessment modelling to address primary PM_{10}, preliminary source-receptor matrices have already been derived on a country to grid basis for the whole of Europe. These can be improved as more detailed modelling is undertaken. We are now concerned with the emissions data and associated cost curves. It is also recognised that steps taken to reduce SO_2 and NOx will also reduce primary particulate emissions; for example fitting FGD will also scrub particulate material efficiently. Thus primary PM_{10} emissions and concentrations will be reduced over central Europe since 1990 with the measures already taken there. It would therefore be useful to assess the side benefit of the measures indicated in the G5/2 scenario with respect to primary PM_{10} as well as secondary particulates.

References:

TNO (1997) particulate matter emissions (PM_{10}, $PM_{2.5}$, and $PM_{0.1}$) in Europe in 1990 and 1993. TNO report TNO-MEP-R96/472. Netherlands, February 1997.

APEG (1999) Source apportionment of airborne particulate matter in the United Kingdom.

N.B. A more detailed paper on the modelling of primary particulates over Europe is in preparation.

Fig.1 Primary PM10 annual mean conc. (1990 emissions) (out-of-square) (ug m-3)

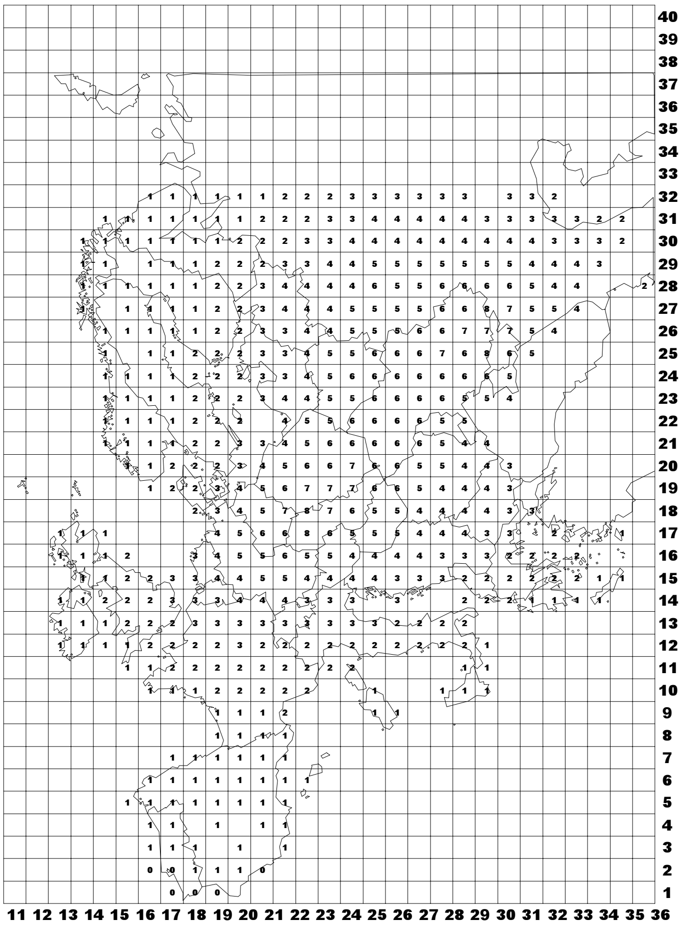
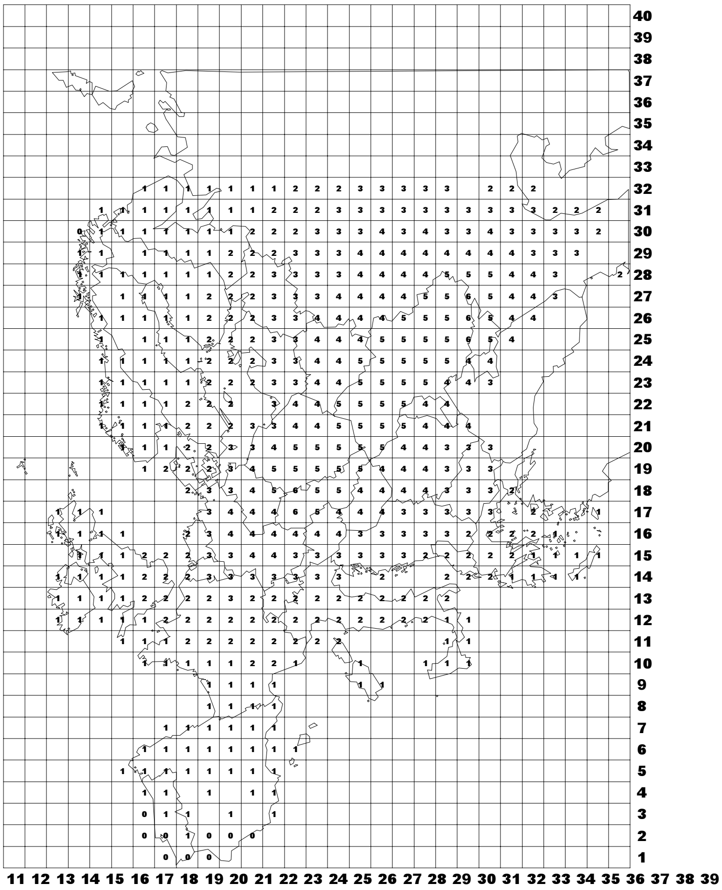


Fig.2 Primary PM2.5 annual mean conc. (1990 emissions) (out-of-square) (ug m-3)



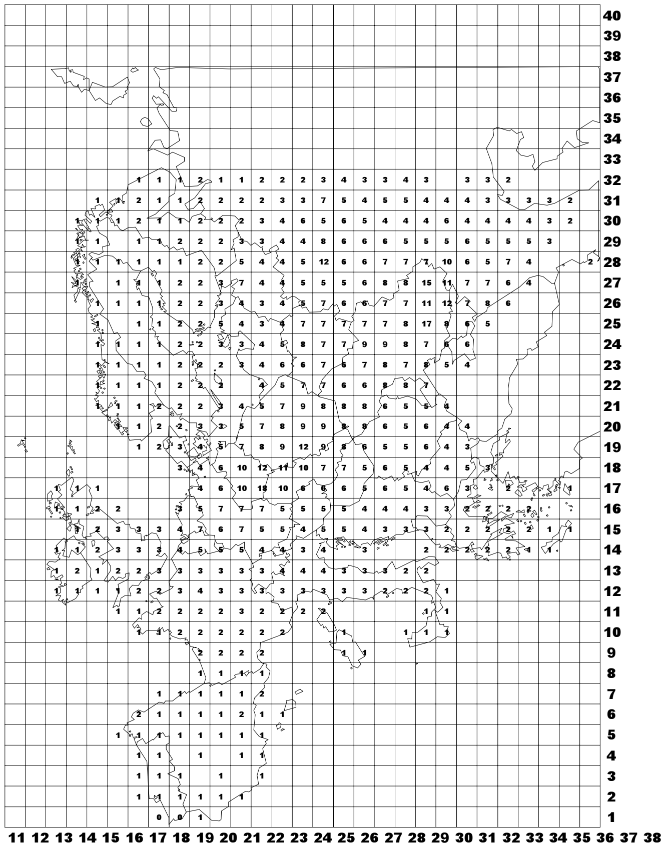


Fig 3. Primary PM10 annual

mean conc. (1990 emissions)

(incl. in-square)

(ug m-3)

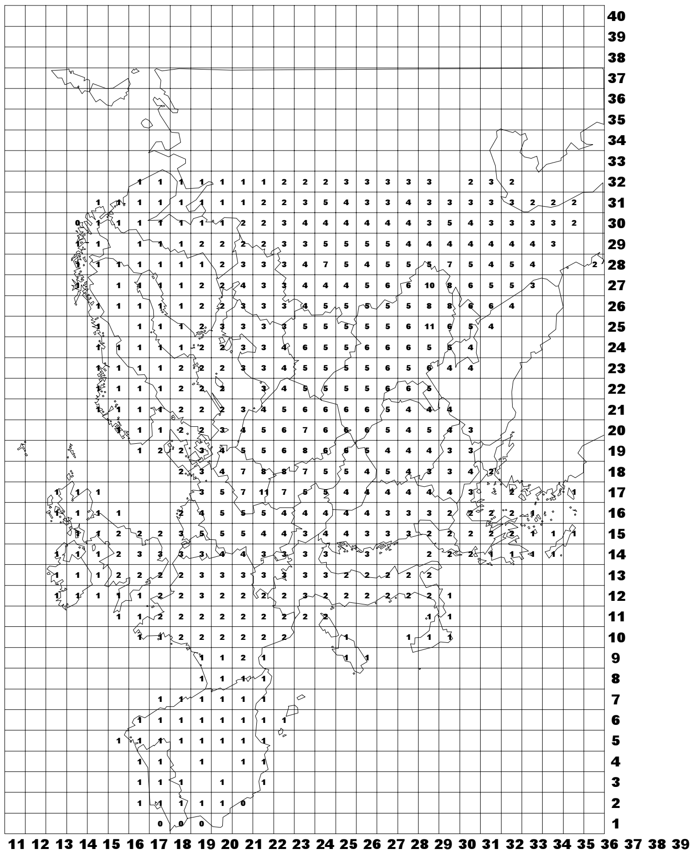


Fig 4. Primary PM2.5 annual

mean conc. (1990 emissions)

(incl. in-square)

(ug m-3)

Results of the heavy metal measurements at the EMEP Stations in Latvia

by

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I. Introduction

The Latvian Hydrometeorological Agency started the heavy metal measurements in 1972, first in river waters than in the air and precipitation. In the areas of the Latvian integrated monitoring stations, Zn, Pb, Cu and Cd measurements have been included in the programme activities of the EMEP stations Rucava and Zoseni since 1993-1994 (Table 1).

The present material provides the characterization of heavy metals in air and precipitation at the EMEP stations in the period 1994-1998.

Table 1: Heavy metal measurement programme.

Subprogramme	Parameters	Started	Periodicity
Precipitation (DC)	Cu, Cd, Pb, Zn	1993	Monthly exposure
Ambient air (AC)	Cu, Cd, Pb, Zn	1994	Weekly exposure

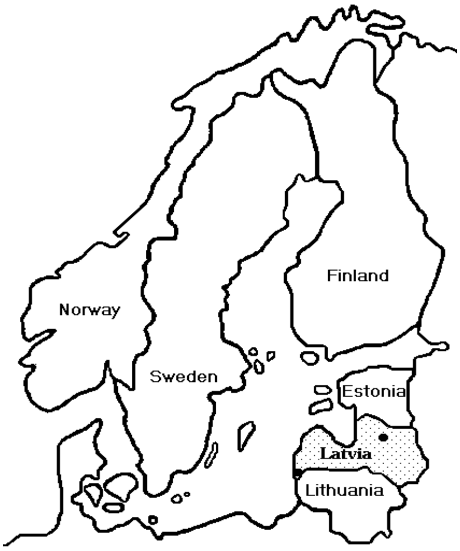

Figure 1: Scheme of Rucava and Zoseni stations.

The regional GAW/EMEP station Rucava is situated between 56°10'N 21°11'E, in the south-west of Latvia, some 10 km east from Baltic Sea and 50 km south from the city of Liepaja. The altitude is 18 above the Baltic Sea level.

The regional GAW/EMEP station Zoseni is situated between 57°08'N 25°55'E, in the east of the country, some 10 km south-east from the city of Cesis. The altitude of the station is 183 m.

II. Methodology

The analyses techniques for metals determination are acidification, filtration and metal concentration by liquid extraction (for precipitation samples) and ashing, evaporation to wet salts, dissolution (for aerosol samples). The Cu and Zn were analyzed by Flame Atomic Absorption Spectrometry and Cd, Pb by Graphite Furnace Atomic Absorption Spectrometry.

The analyses of heavy metals from the various environments rested on the monthly mean, annual mean and mean for 1994-1998 concentrations (Table 2).

The present results help us to compare the heavy metal concentrations between two stations, and follow up the intraannual dynamics of heavy metals in air and precipitation.

Table 2: Heavy metals, mean annual concentrations.

Rucava	**1994**	**1995**	**1996**	**1997**	**1998**	**1994-98**
Air, ng/m^3						
Cd	0.32	0.28	0.27	0.38	0.14	0.28
Cu	2.41	4.48	1.77	1.88	0.79	2.27
Pb	9.78	7.34	6.72	10.49	1.65	7.20
Zn	24.10	26.35	28.59	36.13	14.46	25.9
Precipitation, µg/l						
Cd	0.28	0.22	0.29	0.16	0.21	0.23
Cu	3.56	1.35	5.48	1.67	0.88	2.59
Pb	5.91	5.61	7.02	5.08	3.11	5.33
Zn	19.69	19.98	16.78	18.50	15.70	18.1
Zoseni	**1994**	**1995**	**1996**	**1997**	**1998**	**1994-98**
Air, ng/m^3						
Cd	0.46	0.27	0.18	0.16	0.21	0.26
Cu	6.06	2.94	1.38	1.77	1.02	2.63
Pb	4.19	5.85	3.34	3.47	2.75	3.92
Zn	34.14	37.50	26.19	***	9.49	26.8
Precipitation, µg/l						
Cd	0.34	0.16	0.23	0.38	0.09	0.24
Cu	5.30	4.39	4.33	5.19	2.12	4.27
Pb	3.63	6.38	4.72	4.57	2.32	4.32
Zn	15.11	19.88	18.34	14.88	19.08	17.46

III. Results

The **Zn** concentrations in the air and precipitation at the EMEP stations were at the same level (Figure 2).

Somewhat higher concentrations of Zn in the air of the EMEP stations were recorded in the cold period of the year. The increase is more marked at Zoseni.

The concentration of Zn decreased as a rule with the increase in the precipitation amount, especially at the EMEP station Zoseni (Figure 3).

The concentrations measured in the air and precipitation at the EMEP stations were normally 3 to 10 times lower than those observed in towns close to the stations.

The lowest mean annual wet Zn depositions measured 10.7 mg/m^2 at Rucava (EMEP) and 10.2 mg/m^2 at Zoseni (EMEP). The observational stations located in small and large towns reported concentration from 12.4 mg/m^2 and 42.7 mg/m^2.

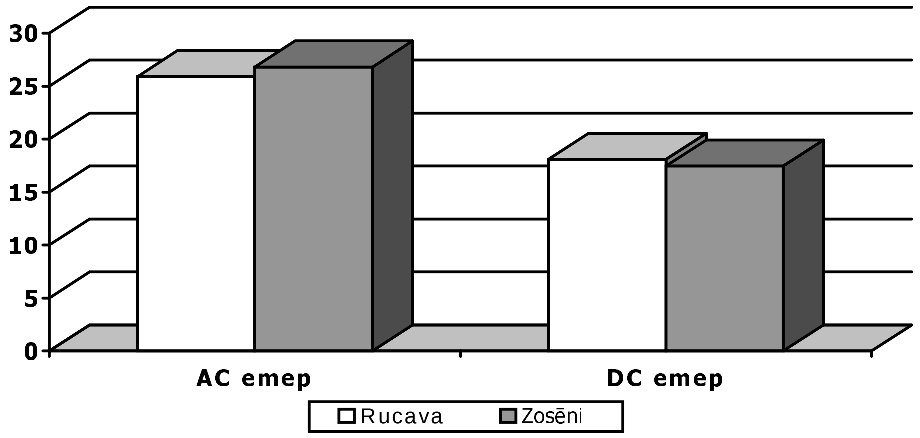

Figure 2: Zinc annual average concentrations in air (ng/m^3) and precipitation (µg/l), 1994-1998.

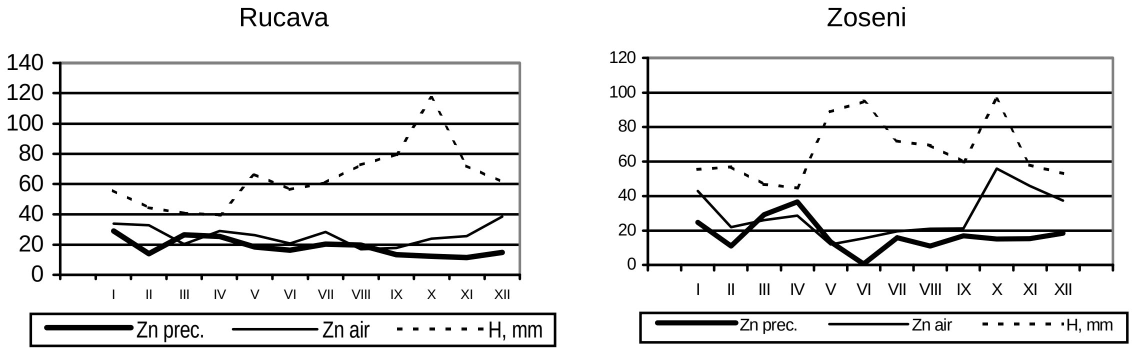

Figure 3: Intraannual dynamics of Zn in precipitation (µg/l) and air (ng/m^3), 1994-1998.

Higher concentrations of **Pb** were measured at Rucava that at Zoseni (Figure 4).

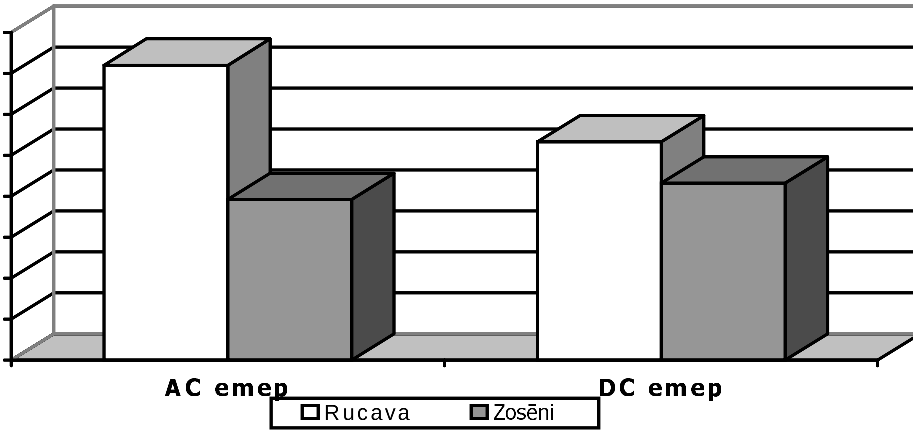

Figure 4: Pb annual average concentrations in air (ng/m^3) and precipitation (µg/l), 1994-1998.

The intraannual dynamics of Pb in the air and precipitation showed the maximum values in the cold period of the year in poor precipitation (Figure 5).

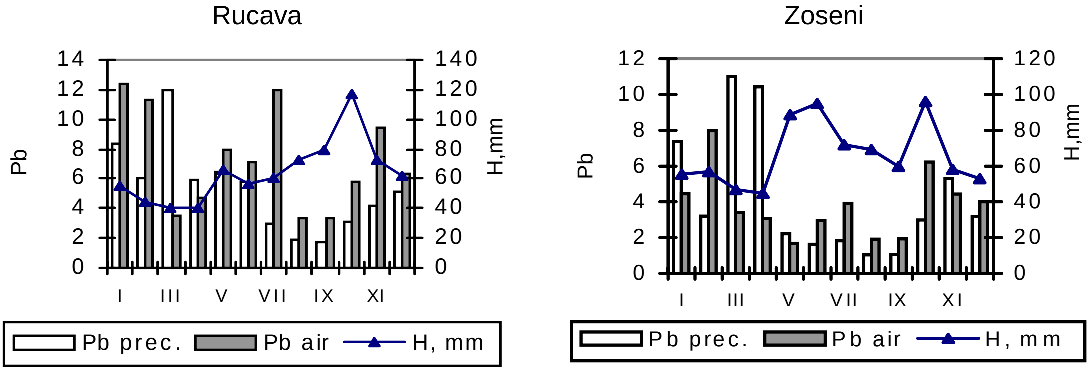

Figure 5: Intraannual dynamics of Pb in precipitation (µg/l) and air (ng/m^3), 1994-1998.

The air and precipitation concentrations of Pb were 2-7 times and 1.5 times lower at the EMEP stations Rucava and Zoseni, respectively as compared to those observed in the neighbouring towns.

The **Cu** concentrations are alike in the atmospheres of both EMEP stations (Figure 6).

In the intraannual dynamics, copper peaked in the air and precipitation in the cold period of the year, in low water discharge and poor precipitation (Figure 7).

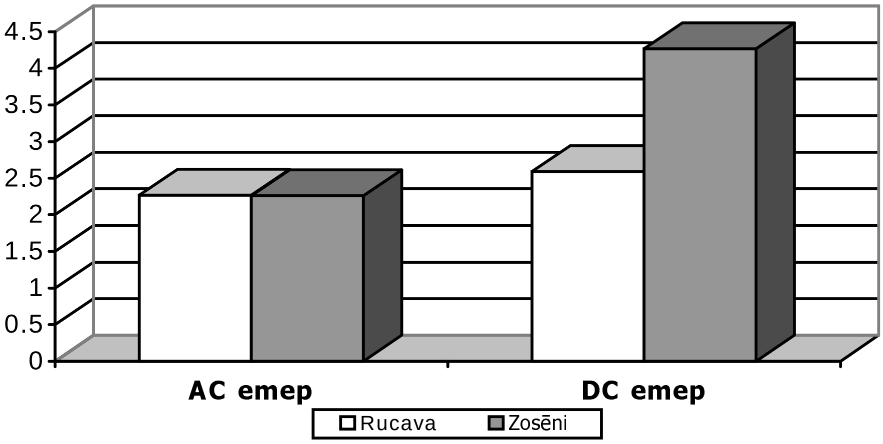

Figure 6: *Cu annual average concentrations in air (ng/m^3) and precipitation (µg/l), 1994-1998.*

In the intraannual dynamics, copper peaked in the air and precipitation in the cold period of the year, in low water discharge and poor precipitation (Figure 7).

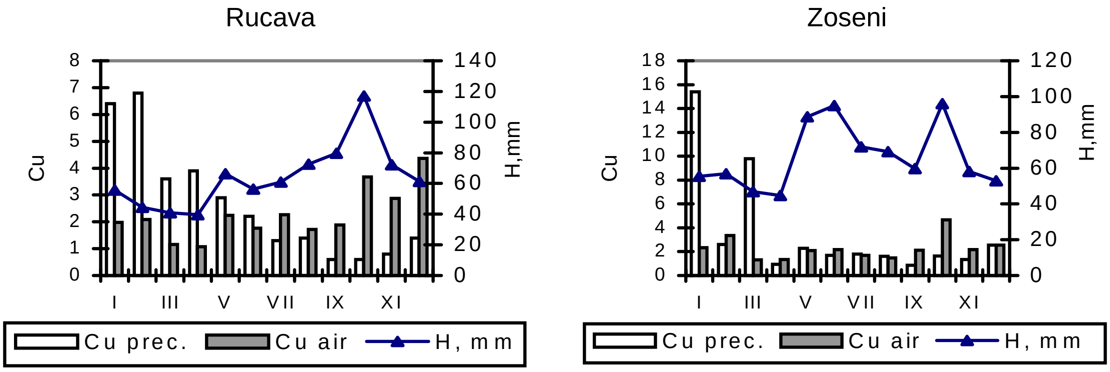

Figure 7: *Intraannual dynamics of Cu in precipitation (µg/l) and air (ng/m^3), 1994-1998.*

The EMEP stations reported the same levels of **Cd** in the air and precipitation (Figure 8).

The cold period of the year was characterized by increased Cd concentrations in the air and precipitation (Figure 9).

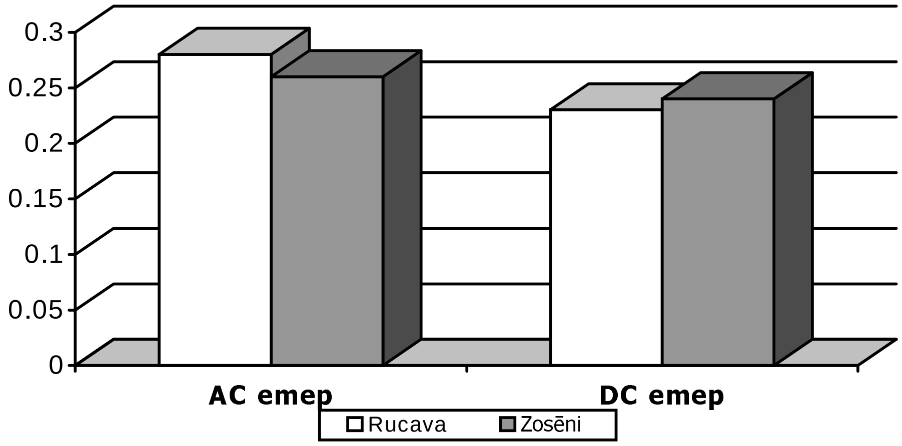

Figure 8: Cd annual average concentrations in air (ng/m3) and precipitation (µg/l), 1994-1998.

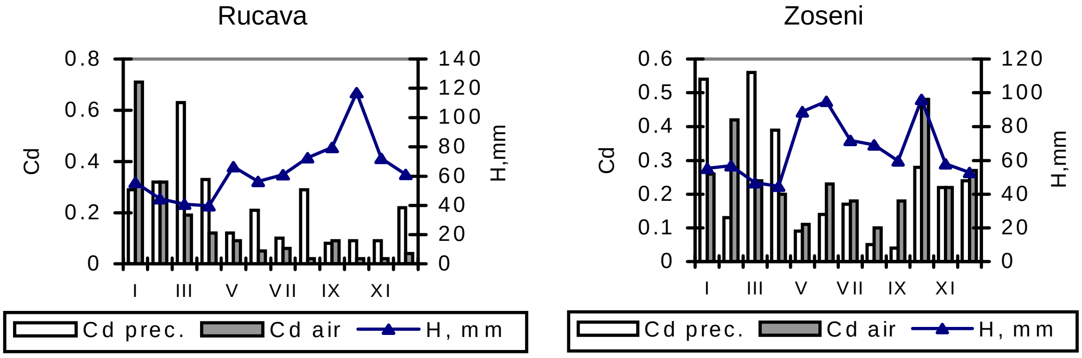

Figure 9: Intraannual dynamics of Cd in precipitation (µg/l) and air (ng/m^3), 1994-1998.

The values of Cd at background stations correlate with those in the areas under high anthropogenic impact.

Conclusions

The observation results for the period 1994-1998 allow to establish that:

- the heavy metal concentrations in air and precipitation are higher during the cold period of the year, in poor precipitation;
- the Zn and Cd concentrations are alike of both EMEP stations; the higher lead concentrations are present in air at the Rucava station ; the station Zoseni reported higher Cu concentration in precipitation;
- the Zn, Pb and Cu concentrations measured in the air and precipitation at the EMEP stations were lower than those observed in towns close to the stations, the values of Cd at the background stations correlate with those in the areas under high anthropogenic impact;

- for the provision of the adequate assessment of the heavy metal concentration it is necessary to unify the sampling equipment and enhance the analytical and sampling facilities, including reagents, standards, spare parts.

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Aerosol Measurements: Providing the Data for the Quantification of Aerosol Impact on Climate

by

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Aerosols may influence the atmosphere in two important ways, through direct and indirect effects (see Schwartz, 1998). Direct effects refer to the scattering and absorption of radiation and their subsequent influence on planetary albedo and the climate system. Indirect effects refer to the increase in available cloud condensation nuclei (CCN) due to an increase in anthropogenic aerosol concentration. This is suspected to increase the cloud droplet number concentration for a constant cloud liquid water content (LWC). As a result, the increase in cloud albedo is predicted to influence the Earth's radiation budget. Cloud lifetimes and precipitation frequencies are also thought to be affected. Despite the uncertainty, it is believed that in regions with high anthropogenic aerosol concentrations, aerosol forcing may be of the same magnitude, but opposite in sign to the combined effect of all greenhouse gases (Schwartz and Andreae, 1996). More information may for instance be found in IPCC (1995) or Baltensperger and Nyeki (1998).

It is the goal of GAW to ensure long-term measurements in order to detect secular trends (WMO, 1997). With respect to aerosols, the objective of GAW is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality up to multi-decadal time scales. Here it is interesting to note that while much of the recent international focus has been directed at assessing the impact of human activities on regional and global scales, there is growing recognition that the management of urban environments requires special attention, and has resulted in an increasing interest in regional air quality within WMO.

Since the atmospheric residence time of aerosol particles is relatively short, a large number of measuring stations are needed. GAW consists of 20 Global stations which cover different types of aerosols: Clean and polluted continental, marine, arctic, dust, biomass burning, and free troposphere. Recently, the scientific advisory group (SAG) for aerosols and optical depth within GAW made additional recommendations, mainly concerning better coverage of the polluted continental aerosol type. In addition, there are about 300 Regional stations. While Global stations are expected to measure as many of the key variables as possible, Regional stations generally carry out a smaller set of observations.

In order to quantify the aerosol impact on climate, a range of aerosol parameters need to be measured, as shown in equation 1 (Haywood and Shine, 1995):

$$\Delta F = -\frac{1}{2} F_0 T^2 \left(1 - A_c\right) \tau \overline{\beta} \omega \left\{ \left(1 - R\right)^2 - 2R\left(1 - \omega\right) / \overline{\beta} \omega \right\}. \tag{1}$$

Here, ΔF is the change in outgoing shortwave flux at the top of the atmosphere, F_0 is the incoming solar flux at the top of the atmosphere, T is the transmittance of the atmosphere above the aerosol layer, A_c is the fractional cloudiness, τ is the mean aerosol optical depth, β is the mean upscatter fraction (fraction of radiation scattered into the upward hemisphere), R is the surface reflectance, and ω is the single scattering albedo, which describes the ratio of the scattering coefficient σ_{SP} to the extinction coefficient σ_{EXT} (σ_{AP} = absorption coefficient):

$$\omega = \sigma_{SP}/\sigma_{EXT} = \sigma_{SP} / (\sigma_{SP} + \sigma_{AP}) \qquad (2)$$

The minus sign in equation (1) denotes convention that a negative forcing is a cooling influence. The factor ½ arises from the fact that only half of the planet is illuminated at any time. The factor $(1-R)^2$ accounts for multiple reflection between the aerosol layer and the surface.

At the last SAG meeting, a revised list of aerosol parameters was presented with recommendations that Regional stations should measure the optical depth, mass concentration and major chemical components in two size fractions, and the scattering coefficient. At Global stations, a larger number of measurements are envisaged and are to include the Regional parameters list as well as, the scattering and hemispheric backscattering coefficients at various wavelengths, the absorption coefficient, aerosol number concentration, cloud condensation nuclei (CCN) concentration at 0.5% supersaturation, and diffuse, global and direct solar radiation. Additional parameters such as the aerosol size distribution, detailed size fractionated chemical composition, dependence on relative humidity, CCN concentration at various supersaturations, and the vertical distribution of aerosol properties should be measured intermittently at Global stations. However, suitable instrumentation is not presently available for some of these parameters, and some calibration procedures require further international research efforts.

Data measured at the Jungfraujoch since July 1995 show a seasonal variation of σ_{SP}, the backscattering coefficient σ_{BSP} (which is related to β), σ_{AP}, the number concentration, and the surface area concentration S of aerosol particles at the Jungfraujoch (Nyeki *et al.*, 1998a), with a maximum in summer and a minimum in winter. This seasonal variation is about one order of magnitude except for the CN concentration where the variation is much smaller. A similar variation is found in long-term aerosol measurements at the same site (Baltensperger *et al.*, 1997) and is mainly due to the seasonal variation of thermal convection induced by solar radiation (Lugauer *et al.*, 1998).

One of the largest uncertainties in calculating direct aerosol forcing is as a result of uncertainty in the single scattering albedo ω. All parameters in equation (2) are essentially known. However, at present there is no internationally accepted calibration procedure for the determination of σ_{AP}, which calls for urgent research on this topic. A further point of uncertainty is that σ_{SP} is usually measured under dry aerosol conditions, even though relative humidity (RH) has a strong effect on σ_{SP}. Therefore, measurements which investigate the response of aerosol parameters to a change in RH will soon be started at the Jungfraujoch, using a so-called Hygroscopicity Tandem Differential Mobility Analyzer (Weingartner *et al.,* 1997, 1999a).

The indirect effects are far more complex and more difficult to assess than the direct effects, because they depend on a chain of phenomena that connect aerosol chemical and physical properties to concentrations of CCN, CCN concentrations to cloud droplet concentrations (and size) and these, in turn, to cloud albedo. Global coverage of aerosol volume concentrations will increasingly become available by satellite measurements, however, accurate descriptions of size distributions are needed to transform these data into number concentrations of aerosol particles which are sufficiently large to act as CCN. Initial measurements of the aerosol size distribution at the Jungfraujoch (Nyeki *et al.,* 1998b) illustrate an accumulation mode (i.e., particles with a diameter *d* between 0.1 and 1 µm) that seasonally varies in concentration but retains a stable distribution shape. However, more worldwide data are needed in order to establish a relationship between the aerosol volume and number concentrations.

Size determination is also important for source assessment. Atmospheric aerosols generally consist of an accumulation mode and a coarse mode (with $d > 1$ µm), which may be differentiated by their chemical composition as well as by their sources. In an ongoing field campaign, the cutoff diameter to distinguish between both modes at the Jungfraujoch is being investigated. Preliminary results indicate that a cutoff at $d \sim 1$ µm is optimal (Streit *et al.,* 1999).

Chemical information is required both for a better understanding of the direct and indirect effects. At the Jungfraujoch, such measurements have so far only been performed for certain components such as elemental/organic carbon (Lavanchy *et al.,* 1999) and in various field campaigns. These measurements begun at the JFJ in spring 1999.

Recent efforts have focused on understanding formation processes of new particles in the free troposphere **(**Weingartner *et al.,* 1999b). The number size distribution in the submicron $d = 10 - 750$ nm range was monitored at the Jungfraujoch over a 14-month period. Again, a high seasonality was found for particles in the accumulation mode. In contrast, ultrafine particles with $d < 18$ nm exhibited different behavior and exhibited a number concentration maximum in wintertime. An analysis of diurnal variations shows that these particles are mainly formed by photochemical reactions. The formation of new particles and the maintenance of a certain number concentration have also been observed in the free troposphere. Such mechanisms are of global importance and would therefore need to be further investigated.

Measurements conducted at the Jungfraujoch and elsewhere, only gain their full value in the international scientific community when made available from a managed database. Steps are presently being undertaken to centralize this task at the Joint Research Centre, Ispra, Italy. For the same reason, collaboration with other international programmes such as IGAC, WCRP is judged to be of high importance.

Another prerequisite for achieving the goals of GAW is an appropriate quality assurance programme. The WMO, through the Aerosol SAG, is striving for this by setting guidelines for the extensive global programme. The establishment of a World calibration centre for aerosols within GAW is an essential part of this process, however, this aspect remains to be urgently addressed.

Acknowledgment

We would like to thank the international foundation of the high-alpine research stations Jungfraujoch and Gornergrat (HFSJG) for their support.

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Modelling the formation and long range transport of secondary particulate matter

by

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1. Introduction

Whilst the formation of secondary particulate matter arising from the emissions of SO_2, NO_x and NH_3 has been widely studied in Europe, little attention had hitherto been given to the formation of secondary organic particulate matter. Laboratory studies have identified two major pathways that may potentially lead to the formation of atmospheric secondary organic particulate matter. The first pathway involves the photo-oxidation of aromatic organic compounds largely emitted by human activities. The second pathway involves the photo-oxidation of terpenes emitted by natural biogenic sources. A photochemical trajectory model has been used to investigate the formation of semi-volatile organic degradation products from the atmospheric photo-oxidation of terpenes during a summertime, regional-scale photochemical pollution episode.

2. The UK photochemical trajectory model

The formation of secondary organic particulate matter during a summertime regional scale pollution episode has been described using the UK Photochemical Trajectory Model. This model treats the detailed chemical development in an air parcel as it moves across the European emissions grid following a six-day trajectory from Austria through to its arrival point in Wales. The chemistry is described for a single air parcel whose base is at the surface and whose upper boundary is at the top of the atmospheric boundary layer. Temperatures, humidities, boundary layer depths, wind speeds and wind directions were all diurnally-varying and given values appropriate to the conditions of regional scale pollution episodes.

The UK PTM employs the Master Chemical Mechanism to describe the photochemical ozone production from 123 emitted organic compounds that generate 3482 reaction and degradation products and take part in over 10500 chemical reaction processes. The MCM also includes the reactions of the simple atoms and radicals containing oxygen, hydrogen and nitrogen and those of CO, SO_2 and H_2O_2 that together describe the fast photochemistry of the polluted atmospheric boundary layer. The MCM version 2.0 may be downloaded via the world wide web at:

http://chem.leeds.ac.uk:80/Atmospheric/MCM/mcmproj.html

The fast photochemistry and regional photochemical ozone production occurring in the UK PTM are driven by the emissions picked up by the air parcel as it traverses Europe. The emissions of NO_x, CO, SO_2, isoprene and VOCs were employed at 150 km x 150 km scale across Europe based on EMEP emissions, at 50 km x 50 km where available from either EMEP or EC CORINAIR and at 10 km x 10 km within the United Kingdom from the NAEI. The emissions of total VOCs were split into the emissions of individual organic compounds using the detailed speciated emission inventory available for the United Kingdom from the NAEI and this same speciation was assumed to hold across Europe.

The model also treated the dry deposition and surface removal of ozone, nitric acid, hydrogen peroxide and the peroxyacylnitrates.

3. Model treatment of secondary organic particulate matter

The formation of secondary organic particulate matter in the UK PTM was driven by the emissions of terpenes from natural biogenic emissions as the air parcel traversed Europe. Emissions of terpenes at a spatial resolution of 1° x 1° and for the month of July for Europe were taken from the GEIA emissions database :

http://blueskies.sprl.umich.edu/geia/

It was assumed that all the terpene emissions occurred into the UK PTM as • -pinene. No explicit temperature- or time-dependence was assumed for these emissions and the emissions from a particular grid square were held constant at the monthly average emission rate.

The Master Chemical Mechanism version 2.0 was used to describe the reactions of • -pinene with OH radicals and ozone during the daylight and with NO_3 radicals and ozone during night-time. Altogether the • -pinene degradation scheme contained over XY reactions and formed a number of low volatility degradation products which are classed as semi-volatile organic compounds, including:

- pinonaldehyde,
- peroxypinonic acid
- pinonic acid
- norpinonaldehyde
- hydroperoxypinonaldehyde.

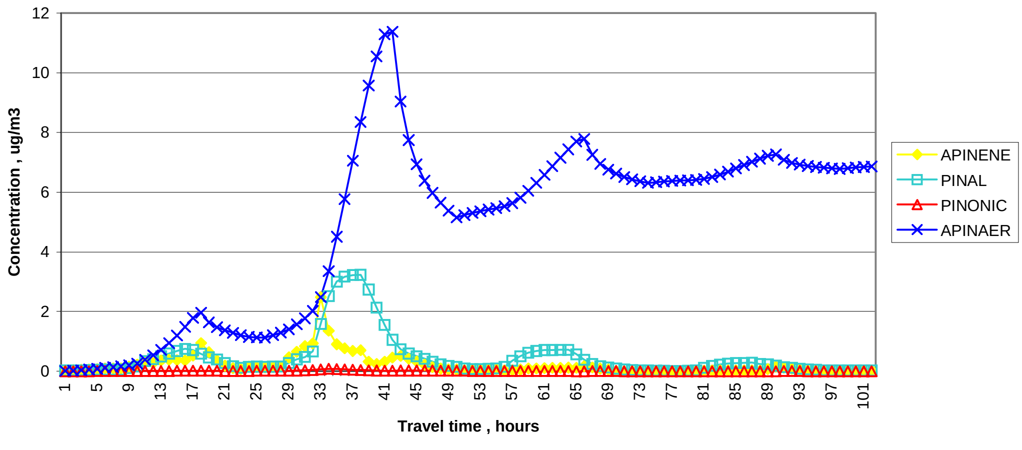
These semi-volatile organic compounds have been scavenged in the UK PTM by pre-existing aerosol species in competition with their subsequent atmospheric degradation. No loss of semi-volatile organic matter from the aerosol back into the gas-phase was allowed in order to simulate the upper limit concentrations of secondary organic particulate matter.

4. Results

Figure 1 presents the calculated concentrations of • -pinene, its degradation products and secondary organic particulate matter in the UK PTM as the air parcel traverses Europe from Austria across to Wales. Because no loss of semi-volatile organic matter from the aerosol once scavenged has been allowed, the concentrations of secondary organic particulate matter represent an upper limit to those anticipated in the real atmospheric boundary layer.

The modelled concentrations of 5–10 µg m^{-3} for secondary organic particulate matter suggest that natural biogenic • -pinene may potentially make a significant contribution to the concentration of secondary particulate matter and hence total fine particulate matter during summertime regional pollution episodes. However, significant uncertainties remain concerning the scavenging of the semi-volatile terpene degradation products by the ambient aerosol and the subsequent fate of this aerosol.

FIGURE 1. Alpha-pinene and its degradation products calculated during a summertime regional pollution episode.



5. Acknowledgements

This work was supported as part of the Air Quality Research Programme of the United Kingdom Department of the Environment, Transport and the Regions under contract EPG 1/3/128. Thanks are due to Michael Jenkin of NETCEN, Culham Laboratory and Sandra Saunders, Nicola Carslaw and Michael Pilling of the University of Leeds with the development of the Master Chemical Mechanism v2.0.

Cost-efficient measurements of PM_{10} using simple sampling equipment

by

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Introduction

In Sweden there is a need for low-cost equipment for automatic diurnal sampling of PM_{10} and $PM_{2.5}$. Except for gravimetric analysis there is sometimes also a need for chemical characterization. The European Union Daughter Directive states limit values for PM_{10} in ambient air as 24-hour averages and yearly means. EU further recommends the member countries to measure $PM_{2.5}$. A Daughter Directive with limit values for PAHs in ambient air is foreseen. PM_{10} measurements are also of interest in other contexts, for example in rural air at the EMEP stations.

To be used for compliance measurements the sampler must fulfil certain requirements specified in the test procedure CEN (1998). A low volume sampler, Kleinfiltergerät, fulfils the requirements and is now a proposed reference method. An automated version for weekly sampling (8 samples) of this instrument is available, but for surveillance of a country, with almost no earlier PM_{10} measurements, less costly sampling equipment is needed.

Measurements of soot in Sweden started in Gothenburg in 1959 (Brosset and Åkerström, 1972). In 1966 measurements in background air started at a number of lighthouses along the Swedish coast. The results from these measurements gave one of the first implications of long range transport of particle pollution. The soot method is simple. Air is sampled on a cellulose filter and the black carbon (graphite) amount is measured as reflection of visible light. The reflectance is then converted to a particle concentration expressed in $\mu g\ m^{-3}$ using a standardised correlation. The method has been standardised (OECD 1964). Soot measurements are today performed in Swedish background air at the EMEP sites and in a number of small to medium-size Swedish towns (Svanberg et al., 1998).

Particle measurements within the EMEP project is carried out using the so called "filter pack" method. Chemical analysis of the particle fraction is made for sulphate and the total (gas + particle) concentrations of ammonium and nitrate. The sampling efficiency of the filter pack as a function of size varies with wind speed, but there is mainly a problem for the larger particles (such as sodium nitrate).

To fill the need of a simple and robust sampler, based on daily sampling and with the possibility of chemical analysis of the particles, IVL started to develop low cost samplers for PM_{10} and $PM_{2.5}$. Some test results for the PM_{10} sampler is presented here. The $PM_{2.5}$ sampler has also done well compared to Kleinfiltergerät, but the results will be published elsewhere.

Principle of PM_{10} sampling

PM_{10} is a target specification for sampling thoracic particles (particles which penetrate beyond the larynx). The mass fraction as a function of aerodynamic size is specified in a table. A particle having an aerodynamic diameter of 10 µm has the same fall speed (3 mm/s) as a spherical particle of density 1000 kg m^{-3}. According to the table for an ideal PM_{10} sampler, the sampling efficiency of for instance a 10 µm particle should be 55.1 %. The sampling efficiency should further be independent of wind velocity. This implies that larger particles must enter the inlet of the sampler and later be partitioned according to the PM_{10} curve. The mass fraction is weighted at 20 °C and 50% r.h. Particles can be separated in many ways (cyclone, filter, foam plug, virtual impactor). PM_{10} particles are usually separated by a conventional impactor. The cut-off depends on the sampled air flow, which has to be constant.

Experimental

PM_{10} measurements using different methods have been made in several monitoring series during 1999. We have used Kleinfiltergerät as a reference method and made parallel measurement with the IVL method and with a TEOM instrument. The measurements have been carried out at different sites on roof level in central Gothenburg, partly influenced by traffic. For the Kleinfiltergerät quarts fibre filters were conditioned in a room with constant temperature and humidity before weighting. Soot measurements were also performed simultaneously.

The IVL method

A prototype of a new PM_{10} sampling head that could easily be manufactured in large quantities to a low cost has been produced. It is made of a plastic material that in the future can be casted in a mould. The inlet was designed in connection with wind tunnel tests to minimise losses of particles at high wind speeds. The head is 12 cm high and 7 cm in diameter, see Figure 1. An impactor was designed and tested with artificial particles using an aerodynamic particle counter.

The sampler has also been compared to the reference sampler in a field test. The flow was kept constant by utilising a vacuum pump with a capillary and using a low-pressure drop filter in the sampler. The comparison was made in Gothenburg ca 10 m above the ground.

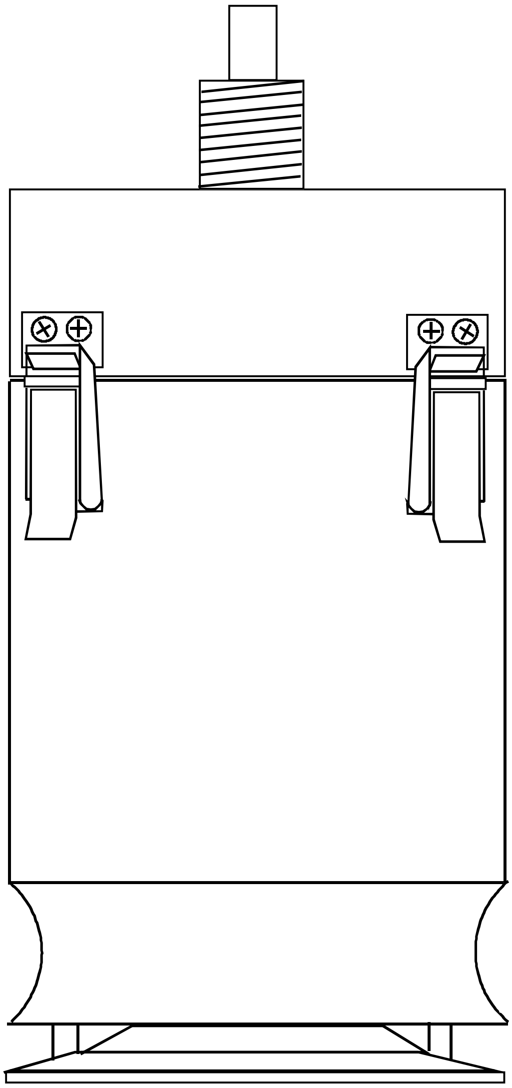

Figure 1: Outline of IVL's PM_{10} *sampler.*

Results

Scatter plots for the PM_{10} values obtained by IVL's sampler versus the reference method and for the TEOM results versus the reference sampler are given in Figure 2 and Figure 3.

A comparison of soot measurements and PM_{10} are shown for the same place and time period in Figure 4.

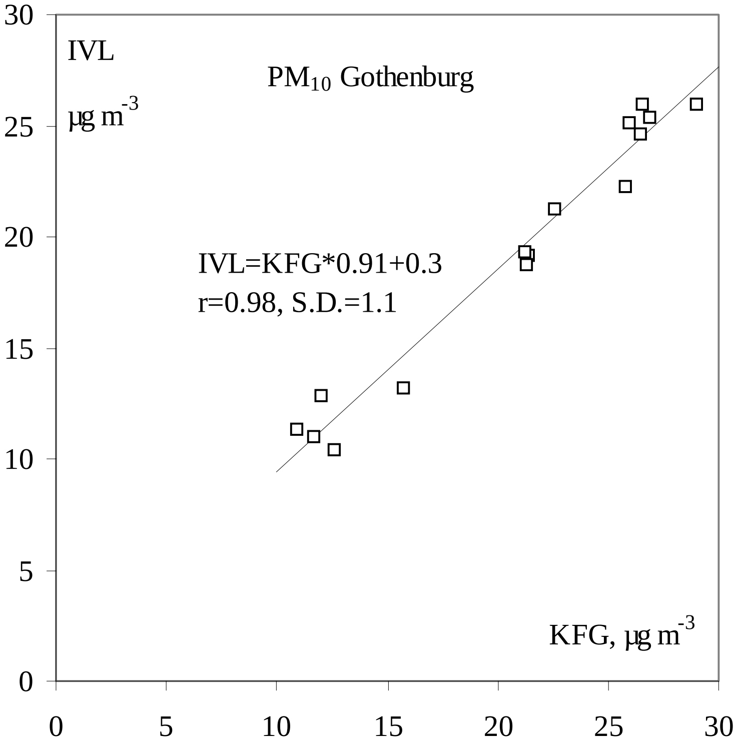

Figure 2: *Comparison between PM$_{10}$ sampled by IVL's prototype and Kleinfiltergerät in Gothenburg.*

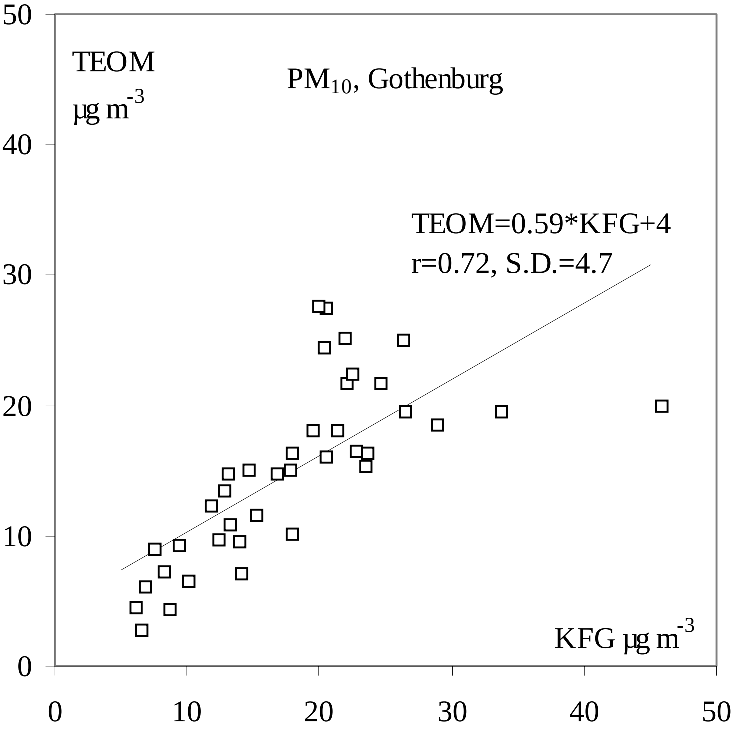

Figure 3: *Comparison between PM$_{10}$ sampled by Kleinfiltergerät and a TEOM instrument in central Gothenburg.*

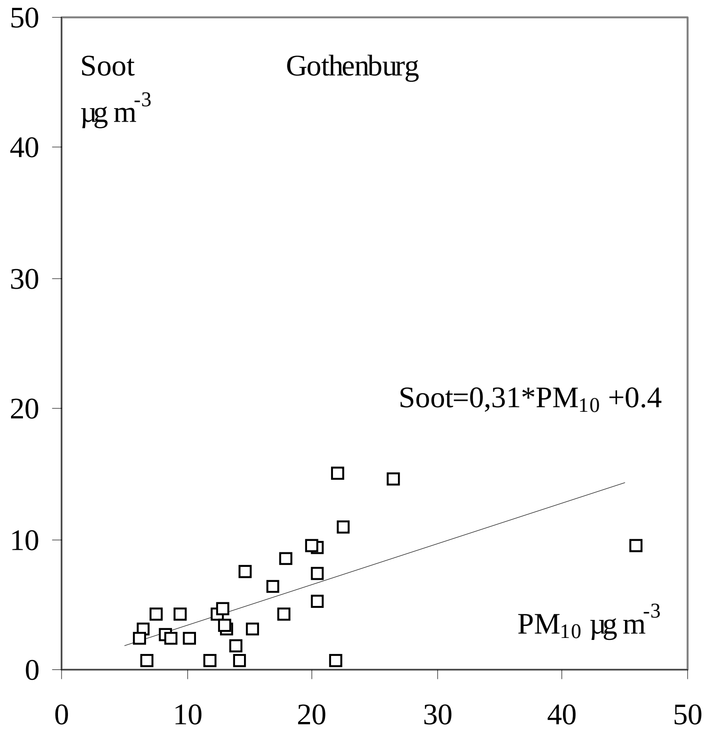

Figure 4: Comparison between soot measurements and PM_{10} sampled by Kleinfiltergerät, in central Gothenburg.

Discussion

The soot measurements represent mainly the blackness of accumulation mode particles since no special design of the inlet is used. It is therefore not surprising that the soot value is not well correlated with the PM_{10} value (r=0.63). The TEOM instrument gave on the average 17 % lower values with a standard deviation from the liner regression line of 4.7 µg m^{-3}. In the TEOM instrument the particles are heated to 50 °C on the oscillating balance. Water and other volatile substances are thereby lost. The correlation is very poor (r=0.72). The measurements with IVL’s low-cost intake show about 9% systematic lower PM_{10} values than Kleinfiltergerät, but the correlation is good (r=0.98). Further tests will be made this winter in Sweden.

Acknowledgement

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Chemical composition of $PM_{2.5}$ and PM_{10} at Birkenes

by

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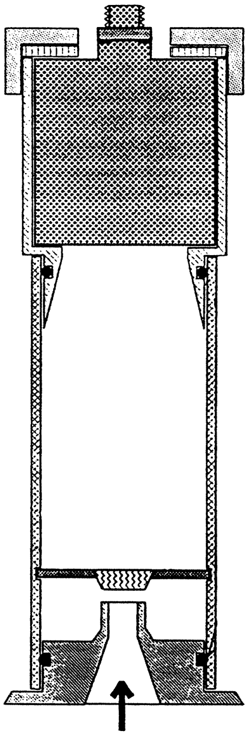
1. Sampling and chemical analyses

Before 1991: Campaigns with high-volume samplers, neutron activation, atomic absorption and other chemical analyses.

1991–1995: Sampling with ”Gent” stacked filter unit, PM_{10} impactor inlet, followed by two Nucleopore filters in a NILU filter holder. The air intake and the filter holder arrangement is shown diagrammatically in Figure 1.



The first Nucleopore filter (”coarse”) has a 8 µm nominal pore size, and is coated with Apiezon silicon grease to prevent blow-off. At a flow rate of 15-16 lpm, this gives a 50% efficiency cut-off at 2 µm EAD. The second filter is also a Nucleopore filter with a nominal pore size of 0.4.

The filters have been weighed at NILU, and analysed with PIXE at the University of Gent (W. Maenhaut, F. Francois). Black carbon is determined with a light reflection technique by J. Cafmeyer, University of Gent.

2. Annual averages and trends

Annual averages for Birkenes are indicated in Table 1. In order to determine the contributions from different sources to the particle mass, the following components have been defined:

Inorganic minerals:
Based on Al, Si, Fe, nss Ca and nss K – and the average contribution of Al to the composition of the earth's crust (except the oxides of the quantified elements).
Sea-salt. Sodium and chloride, with associated dissolved elements, estimated from Na. Chloride is depleted relative to Na in most filter samples.

Secondary inorganic aerosol:
Only sulphur has been determined by PIXE. Other measurements have shown that sulphate is mainly present as ammonium sulphate, and that nitrate at Birkenes occurs in the coarse particle fraction, in association with sea-salt particles. The contribution of ammonium sulphate to the $PM_{2.5}$ mass is very substantial.

Elementary and organic carbon:
Only elementary carbon has been determined with an optical method, which is not an absolute method. Nevertheless, the measured average concentrations (0.5-0.6 $\mu g/m^3$) are close to expected values.

Undefined components:
The difference between the calculated contributions from the components which have been quantified on the basis of chemical analyses, and the particulate mass determined by weighing of the sample filters, have been labelled "undefined".

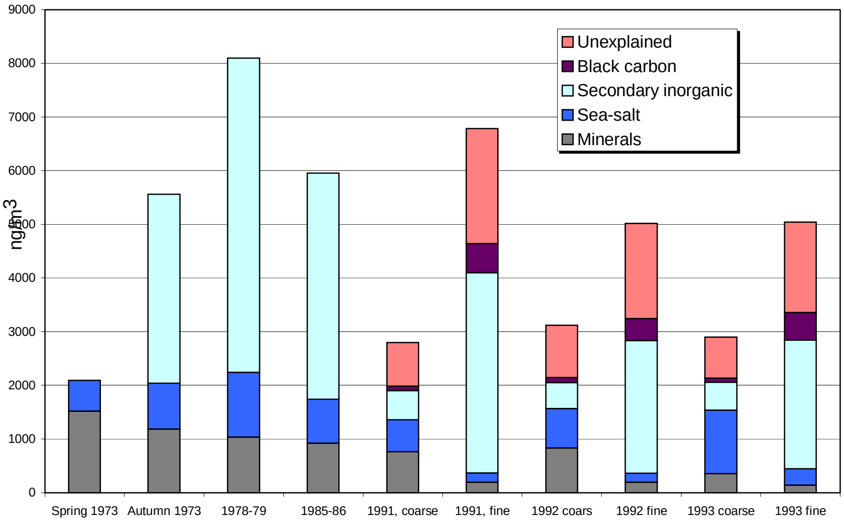


Figure 2: Summary of aerosol composition at Birkenes, 1973-1993.

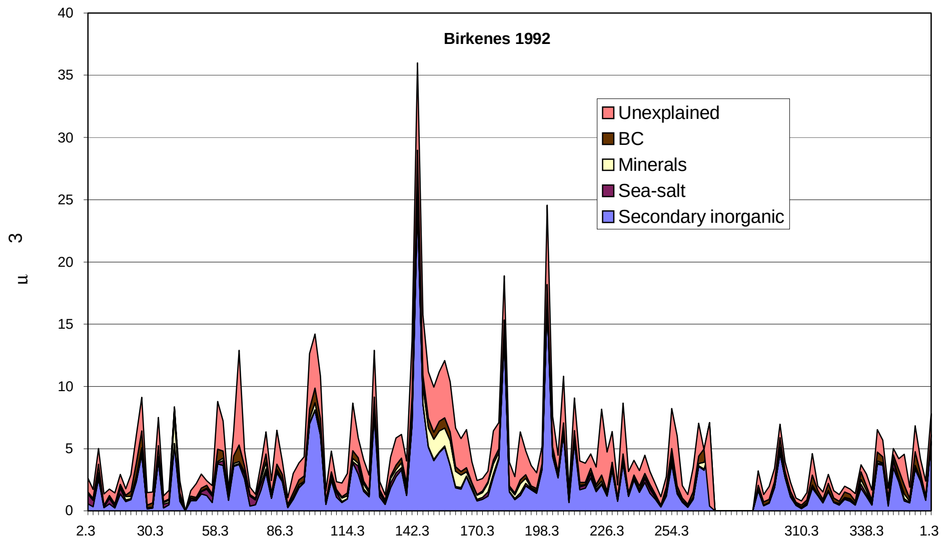
Table 1: Overview of aerosol concentrations at Birkenes, 1973-1993. All concentrations are given in nanogrammes/m^3*. Inferred values in italics. Spring 1973 and Autumn 1973 are neutron activation data by Rahn, compiled by Semb (1978); 1978-1979 data are from Pacyna et al. (1984); 1985-1986 data are from Amundsen et al. (1992), data from 1991 onwards are from Maenhaut et al. (1996).*

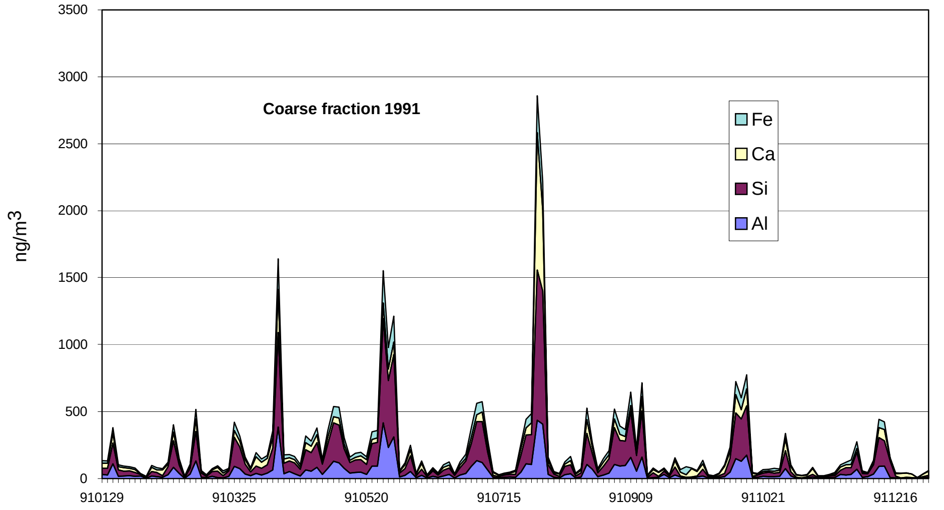
	Spring 1973	Autumn 1973	1978-79	1985-86	1991, coarse	1991, fine	1992, coarse	1992, fine	1993, coarse	1993, fine
Si	433	323	304	277	115	68	131	46	66	33
Al	114	85	80	73	58	14	64	14	26	10
Fe	96	95	84	61	35	14	41	13	17	10
Ca	80	74			47	11	47	12	31	11
nss Ca	*65*				*37*	*7*	*35*	*8*	*13*	*4*
K	138	-			37	36	39	24	29	28
nss K	*123*				*27*	*32*	*27*	*20*	*12*	*22*
Zn	29	35		15	2	6	1.5	4.2	1.7	6.4
Pb		23	18	11	1	4	1.10	3.20	0.70	3.50
Minerals	*1658*	*1090*	*1019*	*908*	*561*	*257*	*620*	*195*	*280*	*148*
Na	403	478	508	350	273	116	329	118	464	179
Cl	60	256	566	380	258	33	316	17	600	84
Br			4.7	5.3			1.03	2.55	1.29	2.68
I							0.2	0.8		0.72
Sea-salt	*568*	*858*	*1206*	*821*	*602*	*179*	*730*	*165*	*1185*	*310*
SO_4		2560	4260	3060	393	2712	354	1797	378	1740
nss SO_4		2520	4217	3031	370	2702	326	1787	339	1725
NO_3		n.a.	n.a.	n.a.		n.a.	n.a.			
NH_4		*960*	*1598*	*1148*	*147*	*1017*	*133*	*674*	*142*	*653*
Secondary inorganic		*3480*	*5815*	*4178*	*518*	*3719*	*459*	*2461*	*481*	*2378*
Black carbon					80	544	90	410	80	514
Sum quantified components		*5429*	*8040*	*5907*	*1760*	*4699*	*1899*	*3231*	*2026*	*3349*
Measured					2800	6780	3120	5018	2898	5037
Unexplained					*1040*	*2081*	*1221*	*1787*	*872*	*1688*

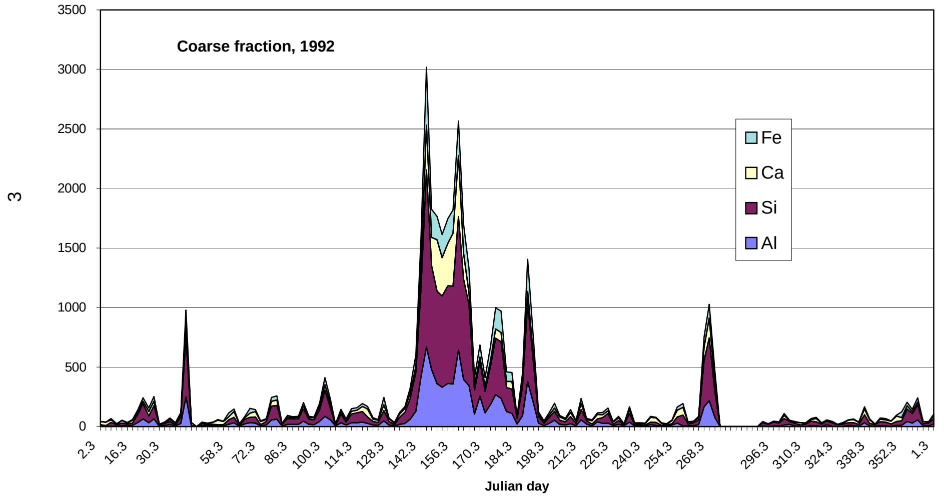
3. Some observations

The contribution from minerals, determined on the basis of Si, Al, Fe and Ca, is highly episodic. The high concentrations in May-June 1992 are associated with trajectories across southern Sweden from the Baltic countries, possibly implicating emission sources in the Narva-Leningrad region. We believe that the minerals are from anthropogenic emissions, combustion of solid fuels, cement production, iron and steel industry.

Sea-salt is also a main contributor to the coarse particle fraction. Chloride is depleted relative to sodium in most of the samples, particularly in the fine particle fraction. Part of the depletion is caused by reaction of nitric acid with the sea-salt particles, displacing hydrochloric acid. However, these data are not suitable for establishing a quantitative relationship.







A number of elements are ”enriched” in aerosols relative to their abundance in the earth’s crust or in seawater. These are mainly found in the fine fraction, and include elements such as lead, cadmium, zinc, arsen, antimony, selenium, bromine and iodine. Neither of these contributes significantly to the particle mass, and, since lead-free petrol has become common, none are no longer valuable as tracers of particular emission sources either.

The main constituents in the fine fraction appear to be ammonium sulphate, elementary carbon and organic compounds. Clearly, good analytical methods for the two latter components are desirable for the full quantification of the fine particle fraction, although minerals and sea-salts are also of some importance.

The measurements of the fine particle mass are quite consistent in time, with good correlation between the total mass and the identified components.

Some tentative conclusions:

- The Ghent stacked filter unit is useful for quantifying PM_{10} and $PM_{2.5}$, and can provide samples for subsequent chemical analyses. The low air volumes make the weighing somewhat demanding, and the membrane filters are also subject to electrostatic charging. On the other hand, these filters do not need the careful ”conditioning” which has to be carried out when weighing glass fibre filters.
- Secondary inorganic particulate matter is the main constituent in the $PM_{2.5}$ fraction at background sites, explaining 30-50% of the total mass.
- The second most important component in the $PM_{2.5}$ fraction is black carbon or soot, with associated organic compounds from combustion processes. Quantification of this component, preferably with more detailed characterisation of the organic fraction, is the key to understanding the composition and properties of $PM_{2.5}$, including the formation of secondary organic aerosols.
- Sea-salt components and minerals are of minor importance for the $PM_{2.5}$ fraction but account for a major part of the PM_{10}–$PM_{2.5}$. These are important in connection with deposition of sea-salt ions, and alkaline base cations.

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Application of Receptor Models for Source Apportionment of PM_{10} and $PM_{2.5}$ in Switzerland

by

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Various recent studies have shown a positive correlation between the concentration of airborne particulate matter and adverse health effects. As a consequence, air quality standards for ambient fine particles (PM_{10}) were introduced in Switzerland. Since March 1998, an annual standard of 20 $\mu g/m^3$ (arithmetic mean) and a daily standard of 50 $\mu g/m^3$ (not to be exceeded more than once a year) are in force. The new standards are regularly exceeded at urban and suburban locations. In order to develop emission control strategies and to predict the trend of future PM_{10} concentrations a quantitative understanding of source contributions to ambient PM_{10} levels is required.

The objective of this study is to identify the main emission sources of airborne particulate matter (PM_{10} and $PM_{2.5}$) and to quantify their contributions at locations which are representative for typical air pollution levels in Switzerland. Daily samples of PM_{10} and $PM_{2.5}$ from urban, suburban and rural sites were taken on quartz fibre filters (High-volume sampler). Particle samples from every 4th day between February 1998 and March 1999 were analysed for total mass, trace elements, water soluble ions, elemental carbon, and organic carbon. The generated datasets are examined by means of a multivariate statistical method (receptor model), which was developed at the Swiss Federal Institute of Technology (ETH) in Zurich.

This study is closely related to a recently published report, where a dispersion model for PM_{10} was developed and applied for estimation of annual mean concentrations and annual mean road traffic contributions to PM_{10} in Switzerland (BUWAL, 1999). The receptor modelling approach used in this study can be considered as complementary to dispersion models. Based on chemical composition data, receptor models are used to apportion sources of primary particulate matter without quantitative source information. In contrast, dispersion models require emission rates for the main sources and knowledge of the relevant physico-chemical atmospheric processes to predict concentrations of ambient particulate matter. Comparison of receptor and dispersion modelling results provides an independent way to confirm source contribution estimates.

In order to assess the source resolution capability and to validate the applied receptor model, the following investigations were performed:

- A well-documented simulated data set (Currie *et al.*, 1984) was used to test the model. The obtained source contribution estimates were found to be consistent with the known true values. However, of the nine sources present, only six were identified. It is evident from this data evaluation, that sources with low contributions (poor signal to noise ratio) cannot be resolved by the model. Moreover, sources with similar emission profiles (collinearity) cannot be resolved either, but are typically grouped into a common source category.
- The receptor model was applied to data from two nearby measuring sites in Zurich. One of the sites is located in a large courtyard surrounded by buildings (Zurich Kaserne, measuring site of the Swiss National Air Pollution Monitoring Network). The air pollution level at this site is considered to be representative for the urban background. The second site is next to a street with heavy traffic (Zurich Wiedikon, measuring site of the Department of Health and Environment of the City of Zurich). The distance between the two sites is about 900m. Therefore, the local road traffic contribution to PM_{10} at the roadside site may be assessed from the difference in PM_{10} at both sites. Consequently, the difference in modelled road traffic contribution at Zurich Wiedikon and Zurich Kaserne should correspond with the difference in PM_{10}. In fact, the difference in modelled road traffic contributions agrees well with the difference in PM_{10} at both sites.

With the receptor model applied to the dataset of primary PM_{10} characterization at Zurich Kaserne, a total of six source categories were identified. Those are:

- Resuspended mineral dust
- Resuspended road dust
- Road traffic (tail pipe and abrasion particle emissions)
- Street salt
- A thallium source (presumably cement fabrication)
- A source category including emissions from wood and agricultural waste combustion, waste incineration, and long range transport.

Evaluation of data from the other measuring sites leads to similar categories. Source attribution of particulate matter that is formed in the atmosphere (secondary particulate matter, defined here as the sum of ammonia, nitrate and sulphate) is assessed by combined evaluation of transboundary import export budgets (EMEP, 1998) and an emission inventory of the precursor gases (Corinair, 1990).

Road traffic was found to be the dominating single source of PM_{10} in Switzerland. Results of preliminary estimations of the total road traffic contribution to PM_{10} are compared with the dispersion modelling results reported in BUWAL (1999). Figure 1 shows annual averages of total road traffic contributions for different classes of PM_{10} as determined by dispersion modelling, as well as the receptor modelling results at the measuring sites Zurich Kaserne, Zurich Wiedikon, Basel (suburban site), and Bern (urban roadside site).

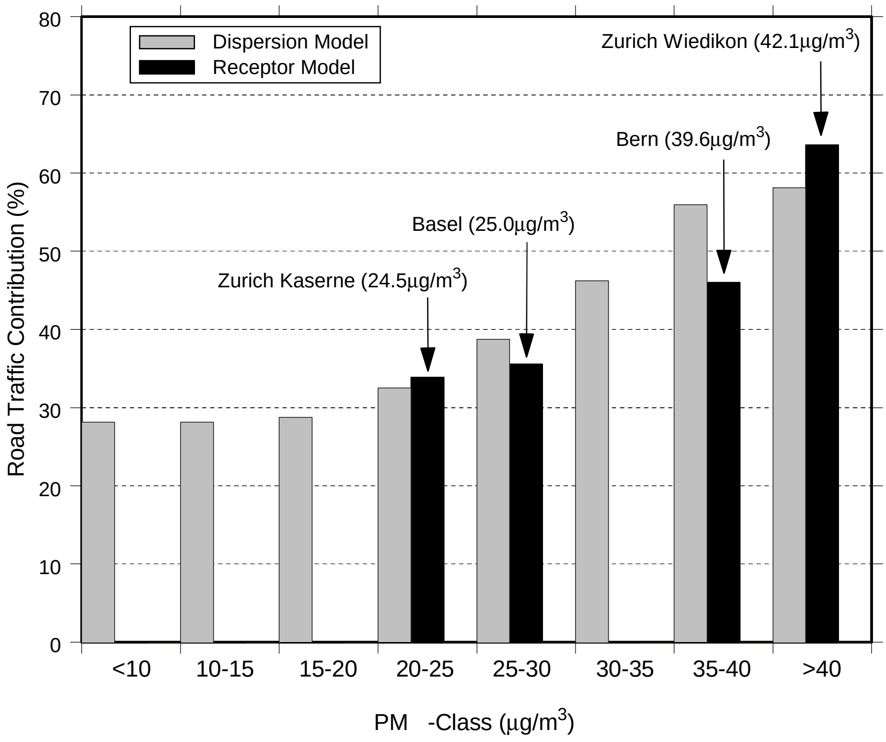

Figure 1: Comparison of total road traffic contributions to PM_{10} as determined by two independent methods: Dispersion modelling (BUWAL, 1999) and receptor modelling (this work). The indicated concentrations at the receptor sites correspond to the mean PM_{10} of the analysed samples during a period of one year. Note that the result for the Zurich Wiedikon site is not an annual average, but corresponds to the average road traffic contribution to PM_{10} during two measuring campaigns in summer 1998 and winter 1999.

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Trace element air pollution monitoring studies in Slovenia

by

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1. Introduction

Up to now, only a few investigations have been performed in Slovenia involving comprehensive studies of trace elements, toxic elements, heavy metals and radionuclides in the atmosphere. For better knowledge of the state of air pollution from industrial emissions and others polluters we participated in an International Atomic Energy Agency (IAEA) coordinated research programme of applied research on air pollution using nuclear-related analytical techniques. The program involved the sampling and analysis of ambient airborne particulate matter using the Gent Stacked Filter Unit (SFU) PM_{10} sampler. The sampler design, described by Maenhaut [1], is based on sequential filtration through two Nuclepore® filters with different pore sizes. The "Gent" SFU sampler operates at a flow rate of 15-16 l/min, is equipped with a pre-impaction stage that acts as a PM_{10} (particulate matter 10 μm) inlet, and utilizes two 47-mm diameter Nuclepore polycarbonate filters with pore sizes of 8 μm (Apiezon-coated) and 0.4 μm that are placed in series inside Norwegian Institute for Air Research (NILU) double filter cassettes. The coarse filter collects the 2-10 μm equivalent aerodynamic diameter (EAD) particle size fraction, and the fine filter the particles <2 μm EAD. One of the samplers manufactured in Belgium was compared with one built to the same design in the U.S.A. [2], and the results showed relatively good agreement. The aim of above studies was the development and application of nuclear and nuclear-related analytical techniques for air pollution studies, leading to formation of a database concerning the trace element air pollution of Slovenia. Results obtained by the k_0-standardization method of instrumental neutron activation analysis (INAA) for aerosols (coarse and fine fractions) collected at two stations in urban and in rural regions of Slovenia are presented and discussed.

Close collaboration has been established with the Hydrometeorological Institute of Slovenia for provision of meteorological data, and with the Institute for Nuclear Sciences of the State University of Gent, Belgium (quality of analytical data).

2. Methods

2.1. *Sample collection and preparation*

As stated above, aerosols were collected on two Nuclepore® polycarbonate membrane filters with different pore sizes by a Gent SFU sampler. The air enters the unit through an impactor stage designed to have a 50% collection efficiency at for particles of 10 μm equivalent aerodynamic diameter. The sample inlets are positioned 1.8 m above the ground. The initial filter is an 8 μm pore 47 mm

Nuclepore® filter and the second filter is an 0.4 μm pore Nuclepore® filter. A total of 86 samples were collected at an urban site (Hydrometeorological Institute of Slovenia (HIS) - Ljubljana city) form June 1993 to June 1994, each for a period of 24h, on a twice-a-week basis and a total of 49 samples at a rural site (Iskrba) from November 1995 to October 1996 for a period of 24h on a once a week basis.

The characteristics of the HIS stations are:

Name:	Ljubljana-Bežigrad
Co-ordinates:	46°04' N latitude 14°31' E longitude
Elevation:	298 m above mean sea-level

Start of station operation: 1968 (SO_2 + black smoke), 1971 (precipitation quality), 1981 (automatic monitoring).

The characteristics of the Iskrba station, which is completely new, are:

Name:	Iskrba
Co-ordinates:	45°33'43"N latitude 14°51'45" E longitude
Elevation:	520 m above mean sea-level

Loaded filters are weighed on a Mettler balance (AE 163) having a precision of 10 μg (Mettler Instruments AG, Switzerland), after neutralising the charge with a Nuclepore static eliminator (Nuclepore, Cambridge, USA). Filters were kept in Petri dishes prior to analysis.

The procedure for samples to be analysed by instrumental neutron activation analysis is as follows:

APM loaded filters are pelletised with a manual press (Mod. 25011, Specac, UK) in a pellet die of 5mm diameter and packed in polyethylene ampoules (Kartell, Noviglio, Italy), together with an Al-0.1% Au alloy wire (Central Bureau for Nuclear Measurements, Geel, Belgium) of 1.0 mm diameter and a 0.125 mm Zr foil (Goodfellow, Cambridge, UK), which serve as comparator and fluence rate monitors.

2.2. k_0-based instrumental neutron activation analysis (INAA)

All irradiations were performed in the channels of the TRIGA Mark II reactor of the Jožef Stefan Institute (IJS): for short irradiation (from 2 to 5 min) in the pneumatic tube at a thermal flux of $3.5\cdot10^{12}$ neutrons$\cdot$cm$^{-2}\cdot$s^{-1}, and for longer irradiations in the carousel facility at a thermal neutron flux of $1.1\cdot10^{12}$ neutrons$\cdot$cm$^{-2}\cdot$s^{-1} (irradiation time for each sample was 18-20 h). After irradiation the samples were transferred to clean 5 ml polypropylene mini scintillation vials (Atom Medical Ltd., Hove, UK) for measurement. The radionuclides used in the determination of up to 50 elements in each sample, their half-lives and gamma-energies measured were given elsewhere [3]. The samples were measured on HP

Ge detectors (Ortec, USA) with 40% relative efficiency connected to a Canberra S 100 multichannel analyser. For the k_0-standardization method we need absolutely calibrated detectors [4]. Spectra were processed by the SAMPO 90 program [5]. Elemental concentrations and effective solid angle calculations were calculated by a new software packet called KAYZERO/SOLCOI® [6].

3. Results and discussion

The primary aim was to analyse two fractions of aerosols (coarse and fine) using the k_0-based INAA method to obtain information about the levels of elements in the atmosphere and to identify significant pollution sources. Principal Component Analysis (PCA) and Factor Analysis were applied to a data set of the 30 elements Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hg, I, K, La, Mg, Mn, Mo, Na, Rb, Sb, Sc, Se, Sm, Th, Ti, V and Zn, which was selected from the elements determined as the most important ones for the identification of pollution sources. It has been found that concentration patterns in coarse and fine fractions of aerosols yielded 7 and 9 factors (source types) for the HIS and Iskrba stations, respectively. Results obtained from above statistical treatment for the HIS station are presented in Table 1. Similar results for the reference Iskrba station were obtained. In Table 1 factor 1 and factor 2 represent the coarse and fine fractions of aerosols. This is one piece of evidence that the sampler used was working well. For Br we obtained dispersion in the factors. This means that Br was present in the blank filters in high concentration and neutron activation analysis is very sensitive for the determination of Br.

Table 1: Factor loadings and estimated communalities obtained by factor analysis for the aerosols collected at HIS station.

El.	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Estimated Comm.
Al	0.95							0.94
As		0.86						0.81
Ba	0.78							0.69
Br		0.46				0.31	0.28	0.60
Ca	0.89							0.91
Cd								0.71
Ce	0.87							0.83
Cl				0.90				0.89
Co							0.57	0.52
Cr			0.76					0.66
Cs		0.67						0.53
Cu	0.31		0.58					0.60
Fe	0.83							0.92
Hg						0.71		0.57
I		0.79						0.77
K		0.93						0.91
La	0.88							0.83
Mg	0.87							0.82
Mn			0.78					0.83
Mo			0.68			0.20		0.61
Na				0.88				0.87
Rb		0.89						0.81
Sb					0.66	0.24		0.55
Sc	0.96							0.93
Se		0.79						0.79
Sm	0.53							0.63
Th	0.81							0.69
Ti	0.52					0.30		0.64
V		0.76						0.66
Zn		0.69				0.34		0.83

Detailed results for APM (coarse and fine fractions) at the two stations for the winter season are shown in Figure 1. These results show that the two stations are completely different. For the urban station (denoted by triangles and square for fine and coarse particles, respectively) we have higher variations in the data sets, whereas variations are smaller for the rural station (signs "-" and "+" for fine and coarse particles, respectively).

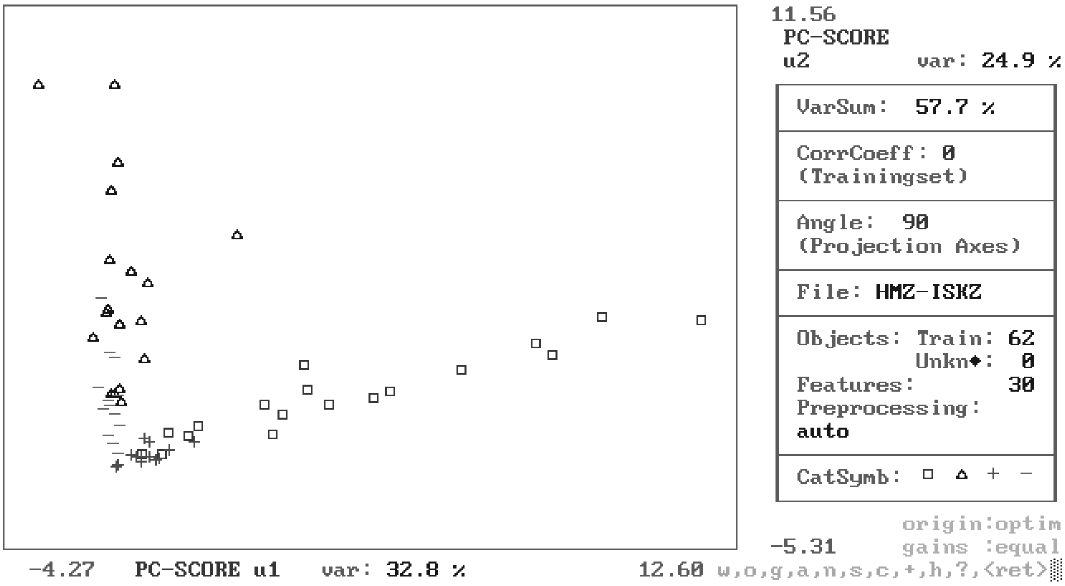

Figure 1: Comparison of the results obtained by PCA for HIS and Iskrba stations during the winter season.

4. Conclusions

By application of factor analysis for each location it was found that that first two factors, which represent the coarse and fine fraction, account around 30 and 21 % of the total variability in the original data. It was found further that the elements Al, Ba, Ca, Ce, Fe, La, Mg, Sc and Th are attached to the coarse fraction, but As, I, K, Rb, Sb, Se V and Zn to the fine fraction.

Acknowledgement

We thank the Hydrometeorological Institute of Slovenia (HIS), Environmental Protection Department, for cooperation and access to their meteorological data.

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Mathematical Modelling of Turbulent Reacting Plumes – Modelling of Particulate Matter Processes

by

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ABSTRACT

This work presents an approach for modelling photochemical gaseous and aerosol phase processes in subgrid plumes from major localized (e.g. point) sources (``plume-in-grid" modelling). This approach employs the Reactive Plume Model (RPM-AERO) which extends the regulatory model RPM-IV by incorporating aerosol processes and heterogeneous chemistry. The physics and chemistry of elemental carbon, organic carbon, sulphate, sodium, chloride and crustal material of aerosols are treated and attributed to the PM size distribution. A modified version of the Carbon Bond IV chemical mechanism is included to model the formation of organic aerosol. Aerosol dynamics modelled include mechanisms of nucleation, condensation and gas/particle partitioning of organic matter. Comparison of the model with field data from a power plant plume in Mohave (Nevada) is quite satisfactory.

1. Introduction

Photochemical Air Quality Simulation Models (PAQSM) provide a link between emissions and ambient air pollutant concentrations and so they are necessary tools for understanding the physics, chemistry and transport of pollutants and for developing environmental policies. Until recently, PAQSMs were focusing mainly on the modelling of gaseous species in the atmosphere. However, concentrations of fine particulate matter (PM) in the atmosphere are being recognized more and more as a major health concern, thus necessitating the detailed study of processes leading to the formation of PM. Relatively few modelling studies have examined the combined dynamics of gaseous and particulate matter processes in the atmosphere; some recent modelling studies of PM formation in the atmosphere include [4]-[7].

In order to evaluate control strategies for precursor emissions reductions, and in order to estimate human exposure to aerosols, it is necessary to study aerosol dynamics simultaneously at both the regional and local scales. The regional scale models are typically grid-based, with a grid resolution in the range 4-40 km. However, the grid-based models have a limit on the minimum grid cell size, reflecting the range of validity of the assumptions used in the formulation of these models (K-theory for the Atmospheric Diffusion Equation). Insight into the ``sub grid" phenomena can be obtained by coupling the grid-based models with trajectory-based plume aerosol models. This is necessary in order to evaluate the effect of industrial stack emissions on local PM concentrations, and the associated environmental consequences, while not ignoring regional scale effects.

The main objective of this work is the development of a mechanistic plume model that can be coupled directly with existing regional scale grid-based photochemical and aerosol process models, such as the Urban Airshed Model UAM-AERO [5]. Such a coupling is expected to enhance the understanding of the impact of point-source emissions on specific locales of interest, while considering regional scale and local effects in tandem. Hence, the Reactive Plume Model with Aerosol chemistry (RPM-AERO) is developed as an extension to an existing regulatory plume model, the Reactive Plume Model, version IV (RPM-IV) [1]. Modifications to the original model include the addition of modules that describe aerosol chemistry, deposition, nucleation and condensation processes, while retaining the basic structure of RPM-IV.

Numerical plume models make use of dispersion/reaction equations similar in form to the atmospheric diffusion equation, but with dispersion parameters that evolve with time. RPM-AERO considers a control volume that moves and expands downwind along the plume trajectory, and solves the dispersion/reaction equations that incorporate mechanisms for nonlinear photochemistry. It describes short term behaviour of the plume, typically ranging from 1 hour to less than 24 hours. The model in the present paper is checked against a field study data from the Mohave power plant in Nevada. Comparison of the RPM-AERO model with field data is also qualitative satisfactory.

2. RPM-AERO: Model description

The RPM-AERO is an extension of the regulatory model Reactive Plume Model (RPM), developed to simulate the atmospheric processes and dynamics of particulate matter following emissions from point source plumes. The model adopts a trajectory-based framework, where the emissions plume is divided into cells containing equal masses, according to a Gaussian plume evolution. The cells travel downwind, and expand in a way such that the amount of a (fictitious) emitted inert species remains constant within each cell.

The width and the depth of the cells are computed as functions of horizontal and vertical dispersion parameters. The chemistry term is solved using the Carbon-Bond mechanism, version IV (CB-IV) [1] as a default; however the user can input any alternative description of atmospheric photochemistry.

2.1 Modelling of the Aerosol Processes

RPM-AERO can quantify the relationships between point source emissions and primary and secondary aerosol species formation and dynamics under various meteorological conditions. The aerosol size distribution and chemical composition is modelled using 16 aerosol-size bins for the PM_{10} aerosol, where the size distribution employs a nodal point scheme [3]. In addition to the equilibrium scheme used above (CB-IV chemical mechanism) an aerosol dynamics approach is currently under development. Processes such as nucleation, condensation and deposition are incorporated in the aerosol dynamics modules of RPM-AERO.

The RPM-AERO model adopts a method which is similar to the one employed in the UAM-AERO model [5], where the condensable organic compound (COC) yields for the lumped organic compounds are used. A flexible gas-phase chemical mechanism interface that allows user modification is adopted, with the Carbon Bond IV (CB-IV) chemical mechanism [1] as the default option. Modeling of the aerosol size distribution proceeds in a manner similar to that adopted by Lazaridis and Koutrakis [3]. In the description of the background size distribution we employed a nodal point scheme [3].

2.2 Aerosol Dynamics

The RPM-AERO model has the capability to calculate the binary nucleation process for the sulphuric acid–water system. The nucleation process of additional gaseous species can be easily implemented provided that the necessary thermodynamic properties are available. The binary nucleation of the system is calculated in a manner analogous to the one provided by the revised classical theory [3].

The condensation rate onto the pre-existing aerosol particles is described by a modified Mason equation, which includes the transitional correction factors [3]. In the RPM-AERO two alternative methods are used to describe the mechanism of dry deposition for particles and gaseous species. The first method utilizes available experimental data for different species. The second method is based on quantifying the transfer of material from the atmosphere to the surface through different resistance mechanisms, i.e. the aerodynamic resistance, the surface resistance, and the transfer resistance.

3. Results and discussion

The RPM-AERO model is applied here to study dispersion and formation of sulphate aerosols from a power plant plume in Mohave (Nevada). The model is compared with field performed by Hegg et al. [2]. Emission data for SO_2, NO_x and particulate matter as well as meteorological data were obtained from Hegg et al. [2]. Comparison between model predictions and field measurements as well as the aerosol size distribution of primary aerosols at different distances from the source are performed. The field studies performed at 27 August 1979 at downwind distances of 5.5 and 27.8 kilometres. Comparisons between the model predictions and the measurements are quite satisfactory for SO_2, NO, NO_2 and O_3. For sulphate the model underestimates the mass concentration near the plume but overestimates it by a factor of two at 27.8 kilometres downwind the source. The reason is probable due to presence of aged aerosol masses that are mixed with the polluted plume. However, the results for sulphate mass are quite reasonable and in qualitative close agreement with the field studies.

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Special Aerosol Characterization Studies in Urban, Rural, and Remote Regions in Canada

by

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In recent years, the Atmospheric Environment Service (AES), Environment Canada, launched several short-term field studies on aerosol particles to probe the physical and chemical characteristics, formation, and evolution of aerosol particles in urban, rural, and remote regions in Canada. Figure 1 shows the locations of the sites and regions where the studies took place. In these studies, a large array of aerosol physical probes and sampling instruments were used, including DMAs, PCASPs, ASASP's, lidars, nephelometers, mass measurements, different cascade impactors, different bulk filterpacks with size selected inlets, and different chemical analysis methods. In most cases, the measurements were coupled to concurrent oxidant measurements involving ozone, NO_x, and VOCs. Some studies were ground based while others were airborne. We summarize here the major findings on aerosol chemical and physical characterization from these special field studies.

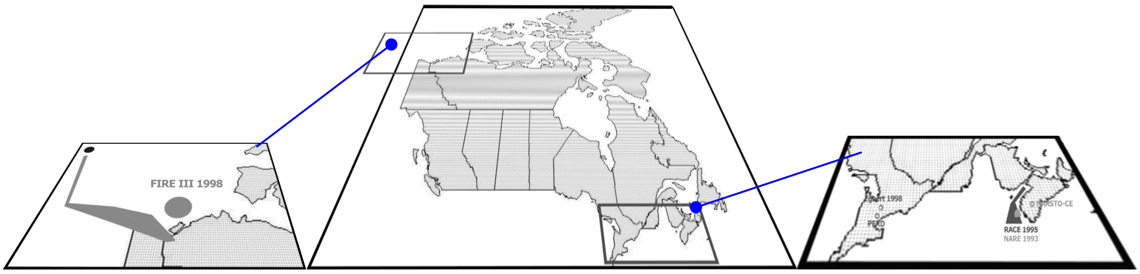

Figure 1: A map of Canada showing the sites of studies. Names of the field studies are shown. The areas indicate airborne studies.

1. Urban and Rural Studies

The primary objectives of the urban air quality studies are to determine the contributions of the transport sectors to the particle mass in the cities and in suburban surroundings, and the formation process of fine (<2.5 µm) particulate matter. The first urban study took place in the city of Toronto in the summer and winter of 1998. The results show significant formation of new particles that is heavily influenced by road traffic. Figure 2 shows the particle number size distributions, from 10 nm to 300 nm, measured using a DMA, that show a large number of new particles produced within air masses directly influenced by the near by rush hour traffic. Typically, very fine particles of about 10 nm diameter are formed starting at around 8 am and last until about 12 am. These ultrafine particles gradually grew into Aitken mode and accumulation mode particles over the day. At the same time, a large number of Aitken mode particle (30-100 nm diameter) is consistently present. Mass and chemical characterization indicates a fraction of >50% of the particle mass as organic carbon and a significant part is elemental carbon. In comparison, inorganic constituents, such as sulphate, accounted for <30% of the mass.

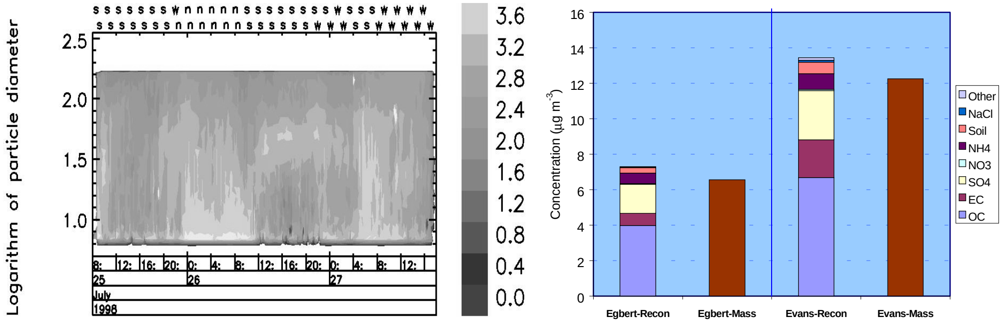

Figure 2: Particle size distribution from 10 to 300 nm, from a DMA(left), and the chemical composition (right), at an urban site in Toronto, Ontario.

At the rural site at Egbert, Ontario, 80 km north of Toronto and downwind, the same instrumentation package was setup in the summer of 1998 as a part of the city-rural comparison. Here, the particle numbers and mass are much lower than in Toronto. Figure 3 shows the particle number size distribution from 10 to 300 nm, along with the chemical composition. Generally, ultrafine particles are not present except a few distinct cases such as those found at midday July 25th and 26th, where there was clear evidence of new particle generation. These ultrafine particles were associated with biogenic sources as it was found that the carbon preference index (CPI) of long-chain alkanes in particles is well above 5 during these events. Chemical measurements of the particles indicate that a significant amount of organics were present throughout the study period, accounting for 20-65% of the particle mass at <2.5 µm diameter. Mass size distributions from concurrent MOUDI impactor sampling show that the most of the carbon mass is in the accumulation mode peaking at 0.2 µm diameter.

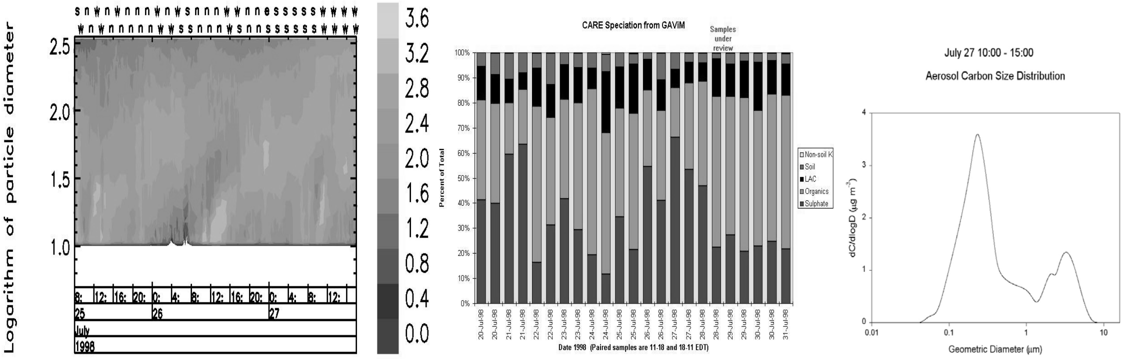

Figure 3: Particle number size distribution, chemical composition, and particle carbon size distribution at Egbert during summer of 1998.

Similar urban and rural studies are planned, including a continuation of the Toronto urban study and a new study in Lower Fraser Valley surrounding Vancouver, Canada’s third largest city. The objectives are similar, to obtain information on the emission, formation, and evolution of particles.

2. Rural and Remote Regions

On the east coast of Canada over the Gulf of Maine and Bay of Fundy, three field studies were conducted in 1993 (North Atlantic Regional Experiment, NARE), 1995 (Radiation, Aerosol, Cloud Experiment, RACE), and 1996 (North American Research Strategy of Tropospheric Ozone – Canada East, NARSTO-CE). See Figure 1 for locations of the studies. Both NARE and RACE were airborne studies over the Gulf of Maine and Bay of Fundy, at altitudes up to 5000 meters, while NARSTO-CE was ground based in a forest clearing. During these experiments, efforts were made to characterize the chemical compositions and the relationships to their physical characteristics.

During NARE, it was found that sulphate comprises of 23% of total particle mass in clear marine aerosols while accounts for over 70% in pollution aerosols from eastern North America (Figure 4). Sulphate was also found to correlate with accumulation mode particle volume, indicating that it exists in the accumulation mode. This feature was similarly found during the RACE in the same region two years later during RACE, where a further effort was made to partition particle mass as a function of size.

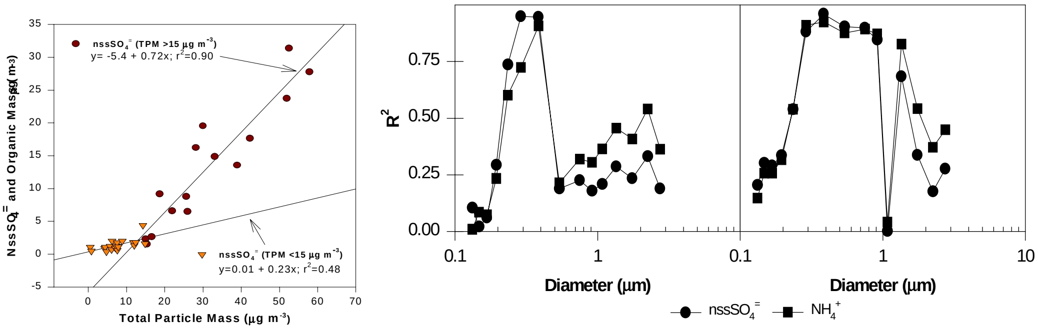

Figure 4: (left) sulfate vs. total particle mass in NARE. (right) coefficient of determination R^2 between particle volume and mass of sulfate and ammonium is shown for both low and high TPM. Particle volumes at different sizes are from PCASP probes.

Figure 5 shows the partitioning of particle mass with three chemical components, (NH_4^++$SO_4^=$), carboxylates, and sea salt in pollution and clear boundary layer air masses at different particle diameters. It shows that sulfate is a major component relative to other group of compounds. However, a large mass still cannot be explained by these components, especially in the accumulation mode. This “missing” mass is suggested to be some secondary organic matter.

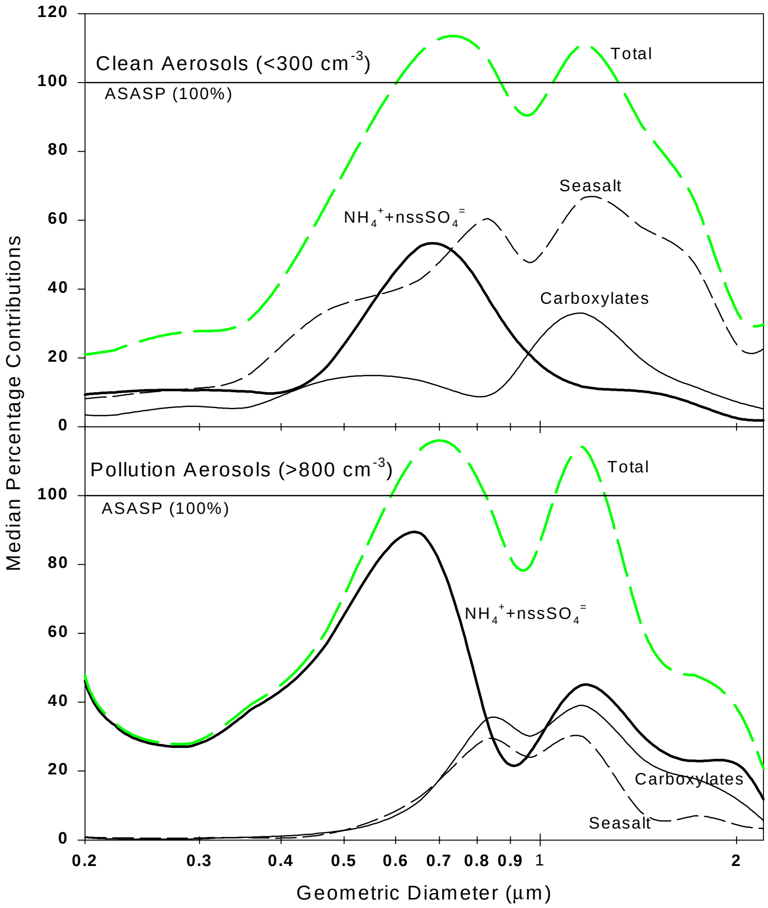

Figure 5: Partition of mass with three chemical components.

During the NARSTO-CE field study at the Kejimkujik National Park on the east coast of Canada, particle chemical and physical properties as a function of size were investigated in more details. Figure 6 shows the size distribution of sulfate and hydrogen ion in particles during this study. It can be seen that sulfate exists in the accumulation mode most of the time, but can extend to 1 µm, and is strongly influenced by episodes. The episodes are clearly accompanied by free acidity in the aerosols. However, not all free acidities were associated with sulfate, as during day of year 174-175, 181-182, and 186-187 when free acidities were found to extend to very small particles, most likely contributed by organic acids. Figure 7 shows the temporal pattern of mass size distributions of three organic acids (acetate, formate, oxalate, and propionate) in aerosol particles. These organic acids show size distribution patterns with a strong accumulation mode. These temporal patterns eliminate the doubt that they were due to sampling problems. Indeed, these organic acids occur during different periods of time from those for sulfate, and their peak particle diameters, at <0.3 µm, appear to be slightly lower than sulfate. In fact, concurrent DMA measurements indicate rapid generation of fine particles during the high periods of the organic acids, indicating that these organic acids may be linked to the new particle generation.

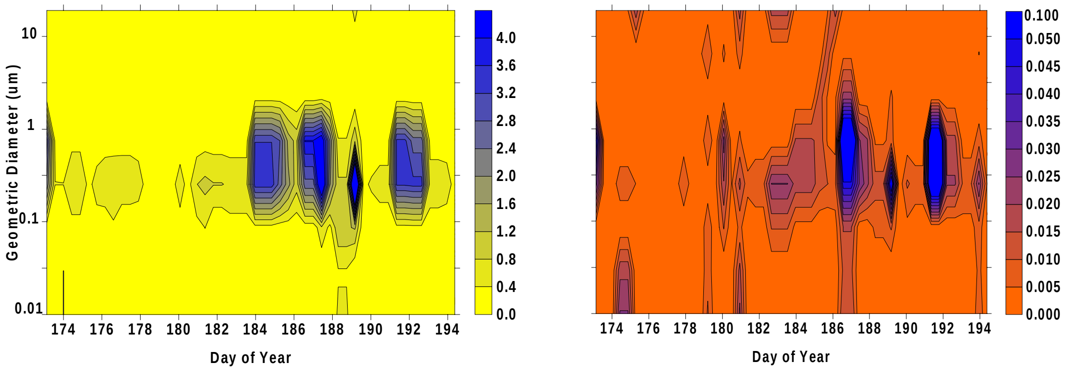

Figure 6: dM/dlogD (µg/m^3) of nssSO$_4^=$ (left) and free acidity H$^+$ (right).

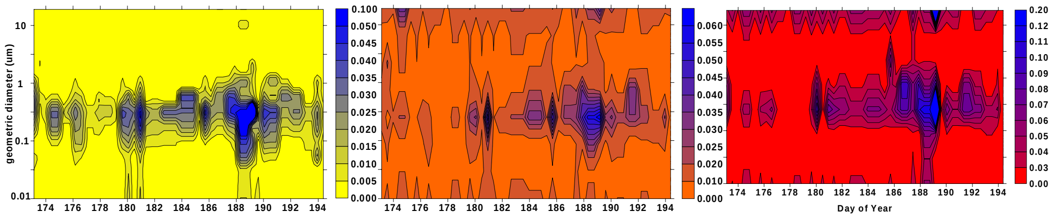

Figure 7: dM/dlogD of Organic Acids: acetate (left), formate (center), and oxalate (right) during the NARSTO-CE experiment.

3. The Arctic Troposphere: Emphasis on Carbonaceous Aerosols

In April-May 1998, the FIRE III Experiment was carried out to study the radiative balance in the Arctic troposphere. Figure 1 shows the location of the airborne study, which covers the southern part of Beaufort Sea off the coast of Alaska and Yukon Territory and over a large polynya north of the Mackenzie River delta. An instrument package of aerosol characterization, similar to those used in the other studies, was deployed that measures the particle size distribution from 10 nm to 10 µm and determines the chemical properties in aerosols.

So far, extensive chemical characterization has been done on bulk filter samples, emphasizing the carbonaceous components. Figure 8 shows the size distribution of mass and total carbon obtained from MOUDI sampling during two flights. Near the surface, carbon existed primarily in a course mode >1 µm and even close to 10 µm, but there is evidence of accumulation mode and Aitken mode carbon. At high altitude from the other flight, carbon existed in two distinct modes, an accumulation mode that extends into sizes <0.1 µm, and a course mode. The strong accumulation mode carbon was probably a result of secondary organic aerosol formation at lower altitude and transported to the Arctic. In contrast, the coarse mode carbon was more likely a result from ice crystal growth from accumulation mode aerosols in stratus clouds (often observed in the winter-spring Arctic troposphere) or in the first flight from open polynya. It should be noted that the magnitude of the carbon mass is similar to that of sulfate, as further shown in Figure 9.

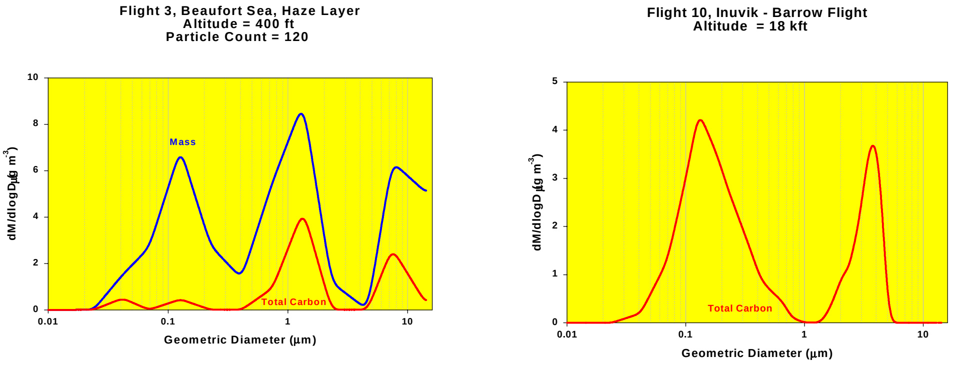

Figure 8. *Mass and carbon size distribution in the Arctic from two flights, one at close to surface and the other at 5.5 km altitude.*

Bulk filter samples collected on board the aircraft were analyzed for a number of chemical species. Inorganic ions, including sulfate, were determined. However, emphasis was given to carbonaceous components. Total carbon, water soluble organic carbon, short (<C4) and long chain (C12-C18) organic acids, long chain alkanes (C19-C33), and 10 PAHs were determined. Figure 9 shows that total carbon accounts for 40% of the total mass. This total carbon is further broken down into a portion of 45% that is water soluble, 49% that is water-insoluble, and about 6% carbonate. Of the water-insoluble carbon fraction, 25% can be accounted with the long chain organic acids from C12-C18, and 1% is in the long chain alkanes (C19-C33).

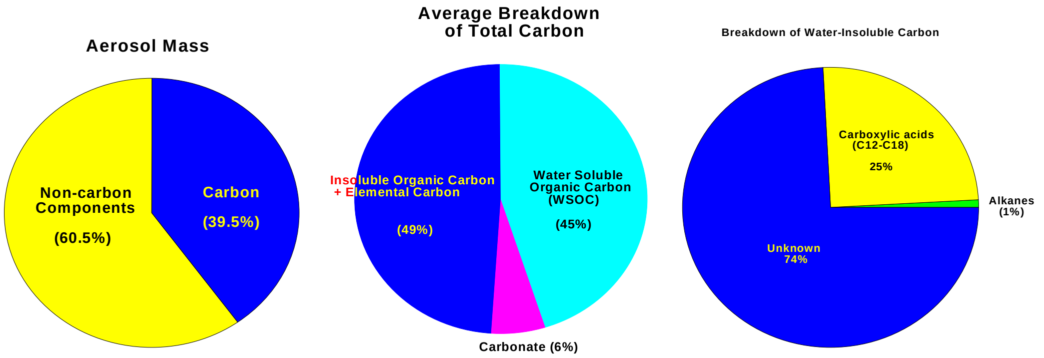

Figure 9. *The proportion of carbon in total mass (left), its breakdown into water soluble, insoluble, and carbonate (center), and the various insoluble carbon species.*

The long chain alkanes, from C19 to C33, show a CPI index of approximately 1, as shown in Figure 10, strongly suggesting that carbon in the aerosols has very little input from direct biogenic emissions. This is not surprising, given the season of the study and the distance from vegetation.

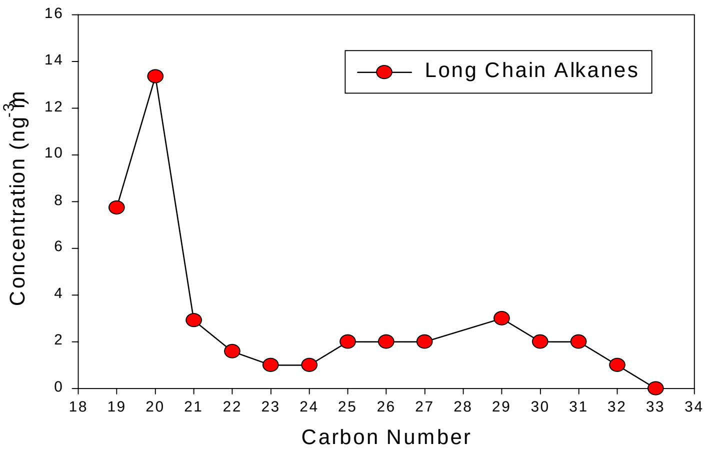

Figure 10: The alkane concentration versus carbon number.

Although small in absolute quantities compared to the total carbon observed, the PAH concentration were strong correlated with the water-insoluble organic carbon. Furthermore, they were similar to the concentrations found at Egbert. Figure 11 shows the concentration of four of the 10 PAHs measured during the study. The level of concentrations is somewhat surprising, given the remoteness of the study area. Furthermore, most of the samples were collected in mid-altitudes of 2-5 km. There are two possibilities of these high levels of PAHs in the mid troposphere in the Arctic. One is direct transport from lower latitudes. Another possibility is the emissions from jet diesel combustion from commercial jetliners which can flight at altitudes as low as 8-9 km. Trajectory analysis is underway to associate the high PAH events with potential source areas.

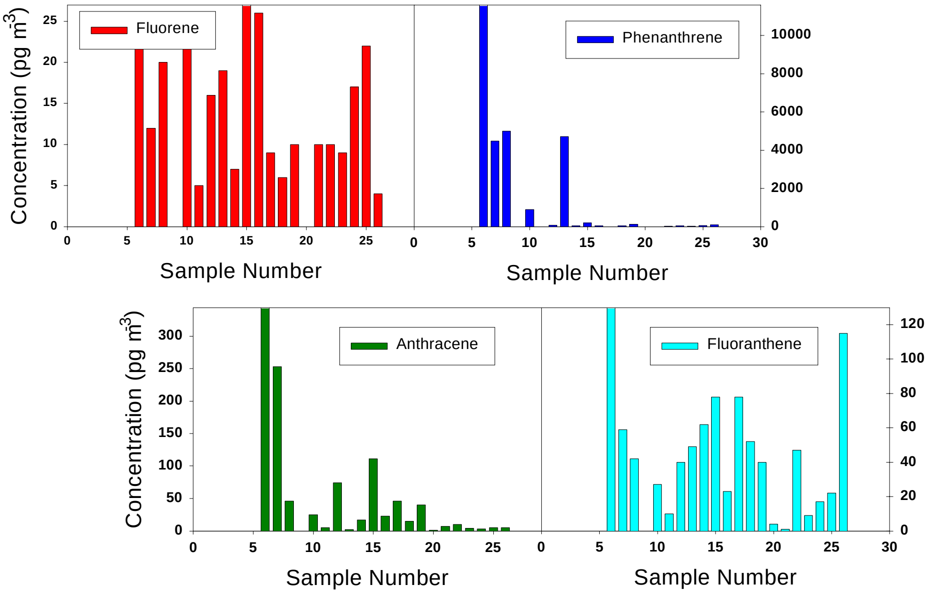

Figure 11: Four of the 10 PAHs found in aerosols in the Arctic troposphere during FIRE III.

4. Summary

The recent work on aerosol particles in different regions of Canada has produced some very interesting results in terms of physical and chemical characterization and new particle formation. It is important that these results are explored in much more depth to reveal information on the particle formation and evolution processes in these different environments, in particular those related to carbonaceous components. The results here give certain guidance to future aerosol particle research, in particular the upcoming Pacific 2001 field study, which is planned for the Lower Fraser Valley on the Pacific coast of Canada.

Acknowledgment

Data on the composition of aerosol particles are provided through the Egbert 98 study from the GAViM sampling work. Ray Hoff, George Isaac, and Jan Bottenheim provided the leadership roles in organizing the Egbert 98, FIRE III, and NARSTO-CE field studies.

Modelling Primary and Secondary Particulates using the NAME Long Range Dispersion Model

by

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Introduction

The fine fraction of airborne particulate matter (PM_{10}) is a matter of growing concern with respect to human health. The UK Met Office's Lagrangian dispersion model NAME has been used to model both primary particulates and sulphate aerosol, a major component of secondary PM_{10}. The NAME model simulates the dispersion of pollutants by releasing large numbers of particles in to the three-dimensional model atmosphere defined by the UK Met. Office's numerical weather prediction model, the Unified Model (Cullen, 1993). The three-dimensional wind field passively carries the released particles, with turbulent dispersion simulated by random walk techniques (Ryall and Maryon, 1998). Dry and wet deposition processes are parameterized, cloud and precipitation information being obtained from the Unified Model.

In order to model the transport of primary PM_{10} it is necessary to adequately represent the meteorological processes occurring in the atmosphere. That is the model must accurately link the sources to the corresponding receptors and represent any deposition processes. In order to model the sulphate aerosol component of secondary PM_{10} the model must also parameterize the key chemical processes involved. The NAME sulphur chemistry scheme models both gaseous and aqueous phase oxidation of sulphur dioxide. Gas phase oxidation is dominated by the reaction with the hydroxyl radical (OH). The aqueous phase chemistry is based on the mechanism used in STOCHEM the Met Office's global chemistry model (Collins *et al* 1997) and includes both oxidation by hydrogen peroxide (H_2O_2) and ozone (O_3). Cloud pH is calculated to drive the ozone oxidation and this requires the ammonia life cycle to be modelled.

The aim of this study was to investigate the feasibility of modelling total PM_{10} at London. The model is validated by comparison with the average of PM_{10} measured at 6 London monitoring sites.

Model Setup

The work reported here is a study of August 1997. Three model runs have been undertaken, the results of which can be added together to estimate the total PM_{10} at any location. The model domain was longitude 15.0°W to 50.0°E and latitude 43.0°N to 65.0°N. The first model run used emissions of UK primary PM_{10} only, taken from the 1 km area National Atmospheric Emissions Inventory for 1996 (http://www.aeat.co.uk/netcen/airqual/index.html). The data was split into traffic and industrial sources, the traffic particulates being released from 0-20 m and the industrial from 20–40 m. Large emitters were kept at 1 km resolution, whilst lower emitting grid squares were combined to give 10 km area sources. The second NAME run was to model primary PM_{10} emissions from Europe (excluding the UK). The emissions data were derived using EMEP 1996 50 km area NO_X emissions (http://www.emep.int/emis_tables/tab1.html), scaled by the country totals for primary PM_{10} obtained from the TNO database (APEG, 1999). The third model run was to generate sulphate aerosol (a combination of sulphuric acid and ammonium sulphate) by releasing sulphur dioxide and ammonia (EMEP 1996, 50 km area) over the model domain. The resulting time series are then added together to estimate the total PM_{10} and then plotted against an averaged London measurement. This estimate is lacking the contribution to secondary PM_{10} from sources other than sulphate aerosol.

The measurement data was obtained from the National Air Quality Information Archive provided by NETCEN (National Environmental Technology Centre) on behalf of the Department of the Environment Transport and the Regions (DETR) (http://www.aeat.co.uk/netcen/airqual/index.html). The UK automatic urban network of measurement sites use direct reading TEOM (Tampered Element Oscillating Microbalance) instruments. These have the advantage of real time mass concentration measurements (obtained at hourly intervals), however the filter has to be kept at 50°C, which has lead to differences between mass concentrations measured by co-located (unheated) gravimetric filter samplers. Generally the TEOM sampler's read lower, due to evaporation of semi-volatile species such as ammonium nitrate and some organic compounds. Care must therefore be taken with estimation of the secondary component of PM_{10} based on this measurement data. The secondary sulphate aerosol modelled in this study will be detected by the TEOM, however, the magnitude of secondary aerosol detected from other sources is not clear.

Results and Discussion

The current UK air quality standard for PM_{10} is 50 μgm^{-3} as a 24 hour running average (based on TEOM monitoring data). Figure 1 is the result of applying a 24 hour running average to the data. The three modelled components (red = sulphate aerosol, blue = primary UK PM_{10}, green = primary European PM_{10}) are plotted against a 24 hour running average of the London measurement data (averaged over 6 sites) for August 1997.

The model is clearly picking up the pattern of the PM_{10} episode over this period, although it is not achieving the actual magnitude observed. Further detailed study at a shorter time resolution is required to resolve this model under prediction.

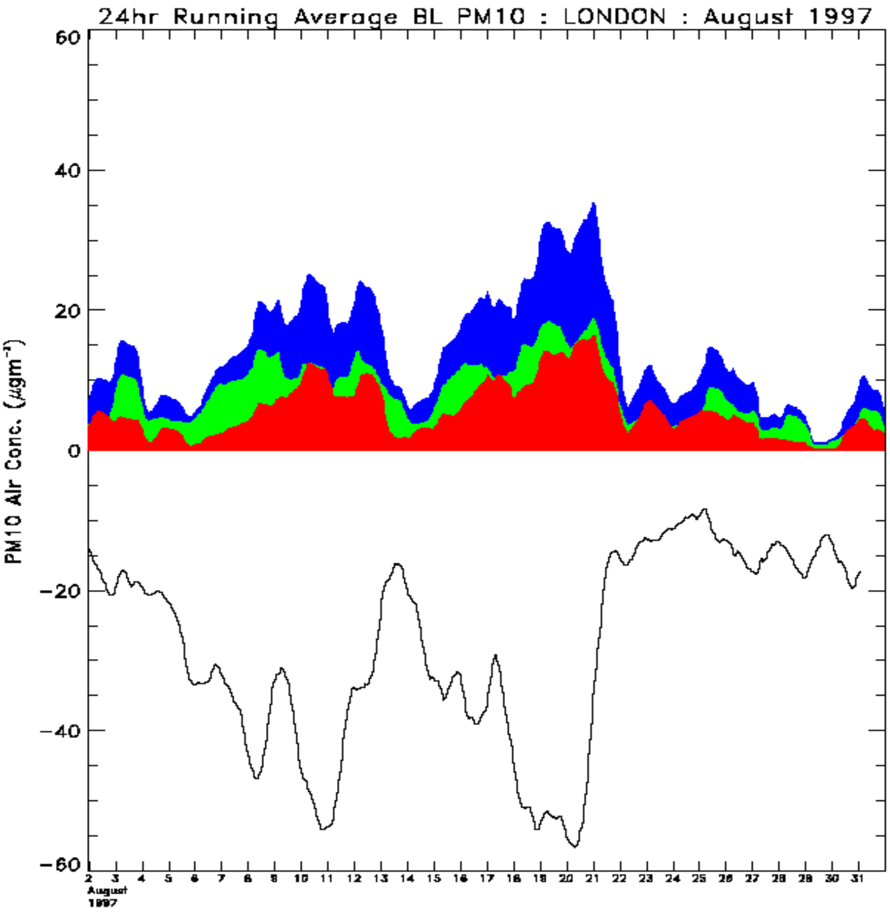

Figure 1: *NAME model output (red = sulphate aerosol, blue = primary UK PM$_{10}$, green = primary European PM$_{10}$) plotted against observed PM$_{10}$ at London in •g/m^3. A running 24 hour average has been applied to both sets of data.*

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Mass Median Diameters (MMD's) of Aerosol Substances

by

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ABSTRACT

Particulate matter of ambient air consists of many substances. Empirically it was found that the Mass Median Diameter (MMD) of every aerosol compound can be related to its melting point and boiling point. A formula is given in which the MMD is described as a function of the melting and boiling point and ambient air temperature. Thus it can be predicted which compounds are bound in fine particles and which ones are in coarse particles. The calculated MMD's of many inorganic and organic compounds are listed.

Relevance of MMD

The MMD of an aerosol substance mainly influences its tropospheric residence time, the deposition velocity, the bioavailability in soil and water and the depth of inhalability for human beings. A substance which accumulates in fine particles has significantly different properties than substances which are found in coarse particles. Toxic substances in fine particles become more harmful to fauna, flora and human beings due to enhanced bioavailability and deeper inhalability. Accumulation mode particles (fine particles of diameter between 0.1 and 2.5 µm) which can be transported more than 1000 km predominantly consist of salts and acids which to a large extent are captured by clouds and rain and therefore may cause acidification and eutrophication.

Calculated MMD's

Empirically it was found that the MMD can be related to the boiling point (T_B) and melting point (T_F) as well as ambient air temperature (T in °C):

$$MMD = d_o \left(\frac{2\,Tm}{273.15^\circ C + T} - 1 \right) \qquad (1)$$

$$T_m \left(^\circ C\right) = \frac{T_F + T_B}{2} \quad d_o = 0.5\ \mu m$$

For many substances the melting and boiling points are known. In the case of inorganic compounds on an average T_B and T_F are related by:

$$T_B = \frac{7}{4} T_F \tag{2}$$

In Table 1 the calculated MMD’s of many inorganic compounds and several PAH-compounds are listed.

Discussions and Conclusions

By use of formula (1) it can be considered that aerosol compounds of T_m between 150°C and 900°C are incorporated in the fine particle mode. Compounds of T_m beyond 900°C (particle diameter bigger than 2.5 µm) belong to coarse particles.
Compounds of T_m below the vicinity of 150°C have sufficiently high specific vapour pressures to induce them to be totally in gas-phase under ambient air conditions.

Compounds roughly in the T_m-range between 150°C and 300°C under ambient air conditions partly exist in gas-phase and partly in particulate-phase as often has been measured within the last two decades.

Compounds of T_m roughly above 300°C were observed to be totally in particulate-phase. Up to date heavy volatile species in particulate matter of ambient air only insufficiently can be analyzed. Elements but no species can be measured by AAS, ICP-MS or several nuclear analytical methods (NA or PIXE).

However, by use of measured elemental mass size distributions of particulate matter also inorganic species can be determined. To each mode of the elemental mass size distribution due to different specific vapour pressures different species can be assigned (Müller, 1998). A measured mass size distribution also is a finger-print of the existing species. Thus the MMD of many species also can be measured.

In Table 1 can be seen that the fine particle mode mainly consists of electrolytis. The calculated MMD’s of the PAH-compounds also belong to this size range. This is consistent with the measurement of the MMD’s of PAH-compounds in particulate matter of ambient air.

In the coarse mode mostly heavy volatile metaloxides are found. However, the catalytic species Fe_2O_3 and V_2O_5 accumulate at the relatively small MMD of 3 µm. Thus they contribute also to gas-particle-reactions and enhance the formation of secondary aerosols.

Reference

[1] Müller, J. (1998) Measurement of Inorganic Species in Aerosols by Aid of Impactor Sampling. *J. Aerosol Sci.*, **29**, Suppl. 1, pp. 219-220.

Table 1: Calculated Mass Median Diameters (MMD's) of substances (inorganic compounds and PAH-compounds) in airborne particulate matter.

MMD (µm)	
0.1 – 0.2	H_2SO_4, $SbBr_2$
0.2 – 0.4	NH_4NO_3
0.4 – 0.6	$AlCl_3$, $Cr(VI)O_3$, $FeCl_3$, $KHSO_4$, $TlNO_3$, BbF
0.6 – 0.8	CHR, BkF, BaP, BeP
0.8 – 1.0	$NaNO_3$, U_3O_8, PER, BghiP, DahA
1.0 – 1.2	As_2O_3, COR
1.2 – 1.4	As_2S_3, Cd(met.), PtO_2, $ZnCl_2$
1.4 – 1.6	KNO_3, TlCl
1.6 – 1.8	PbO
1.8 – 2.0	NH_4Cl, $(NH_4)_2SO_4$, $PbCl_2$, $PbBr_2$
2.0 – 2.2	$CdCl_2$
2.2 – 2.4	AlF_3, $CuCl_2$, Sb_2S_3, $ThCl_4$
2.4 – 2.6	$CoCl_2$, KOH, $Sr(NO_3)_2$
2.6 – 3.0	CuCl, Fe_2O_3, $MnCl_2$, $MnSO_4$, Pb(met.), $PdCl_2$, Tl_2O_3
3.0 – 3.5	$Al_2(SO_4)_3$, KCl, $MgCl_2$, Na_2CO_3, NaCl, NiS, Sb_4O_6, $TiCl_2$, UCL_2
3.5 – 4.0	$CaCO_3$, $CaSO_4$, K_2CO_3, Na_2O, Na_2SO_4, PdS, RuO_2, V_2O_5
4.0 – 4.5	$CaCl_2$, $CdSO_4$, CdS, $CoSO_4$, K_2SO_4, $LaCl_2$, $NiCl_2$, $PbSO_4$, $SrCl_2$
4.5 – 5.0	$CrCl_3$, $MgSO_4$, PbS, RhO
5.0 – 5.5	CoO, Cu_2O, Fe_2SiO_4
5.5 – 6.0	CuO, Cu(met.)
6.0 – 6.5	
6.5 – 7.0	Fe_3O_4, La(met.), Mn_3O_4, Ni(met.), $SrSO_4$
7.0 – 7.5	Fe(met.), SiO_2, TiO_2
7.5 – 8.0	Al_2O_3, $3SiO_2$, CoO, MnO_3, Ti(met.)
8.0 – 8.5	NiO, Pd(met.), Ti_2O_3
8.5 – 9.0	Al_2O_3, Cr_2O_3, SrO, VO, ZnO
9.0 – 9.5	Rh(met.)
9.5 – 10.0	CaO, Pt(met.)
10.0 – 10.5	La_3O_3
10.5 – 11.0	Ir(met.), Ru(met.)
11.0 – 11.5	
11.5 – 12.0	ThO_2
12.0 – 12.5	MgO, UO_2

A new beta gauge monitor for the measurement of PM^{10} air concentration

by

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Introduction

Figure 1: The Atmospheric Dust Automatic Monitor.

As a consequence of the growing interest in the measurement of fine particles, an advanced system for sampling and measuring the air concentration of suspended particulate matter has been devised. The new instrument (ADAM: Atmospheric Dust Automatic Monitor) collects atmospheric particles on standard 47-mm membrane filters and performs the determination of the collected amount of particles by using the beta rays attenuation method. Sampled filters are then available for any subsequent chemical analysis of the particulate matter and for possible gravimetric determination of the collected mass amount.

One of the most important features of the instrument is its ability to perform both the sampling and the beta measurements on two different filters at the same time: this allows to increase the beta measurement time to 2 hours and to get a very high accuracy of the results. The accuracy is also assured by the many automatic Quality Control procedures implemented in the ADAM. The features of this instrument make it a very valuable tool in monitoring networks.

Instrument description

The Atmospheric Dust Automatic Monitor is made of the following sections: – a sampling head; – a sampling module that includes a flow rate control module; – a mass measurement module; – a separate pneumatic circuit able to generate a known and constant flow rate, used to automatically check the calibration of the flow rate reading. A schematic drawing of the instrument is reported in Figure 2.

The sampling head may be chosen according to the aerodynamic size of the particles to be collected. Care is taken in order to keep the temperature of the air flow as close as possible to the ambient air temperature, so as to minimise the sampling artefacts due to the loss of volatile compounds.

The sampling module consists of two filter holders, one containing clean filters, the other one containing sampled filters. Up to 40 membrane filters, each one inserted in a plastic ring, can be placed in each filter holder. Membrane filters can be added to the first holder or removed from the second one without any interruption of the sampling and measurement procedures. These features can be of great utility when the instrument is used in monitoring networks and unattended operations are required.

At the end of the sampling phase, each filter is moved to the mass measurement unit.

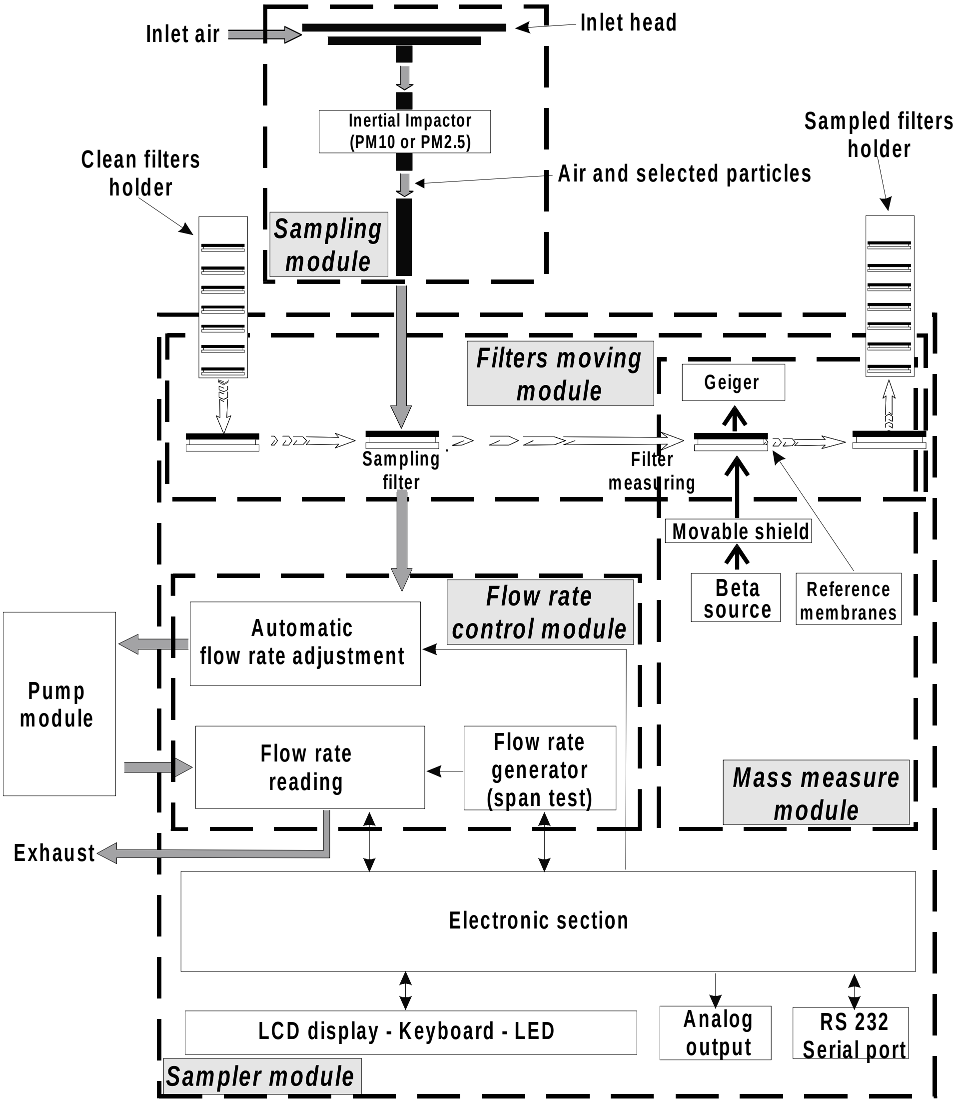


Figure 2: Schematic drawing of the Atmospheric Dust Automatic Monitor.

The sampling flow rate is controlled by means of motorised valves, so as to assure an independence of the flow rate from both the thermodynamic conditions and the pressure drop across the filter membrane (that is, from the filter loading). The ADAM automatically carries out a series of checks on the sampling flow rate, in order to assure a high accuracy in the determination of the sampled volume. These checks include: leak test, pressure drop monitoring, check of the stability and of the calibration of the pressure transducers, span test. The detection of serious failures in the tests causes the interruption of the sampling, while minor problems are reported to the operator. The results of the span test over a one-month period (1 test per day) are reported in Figure 3.

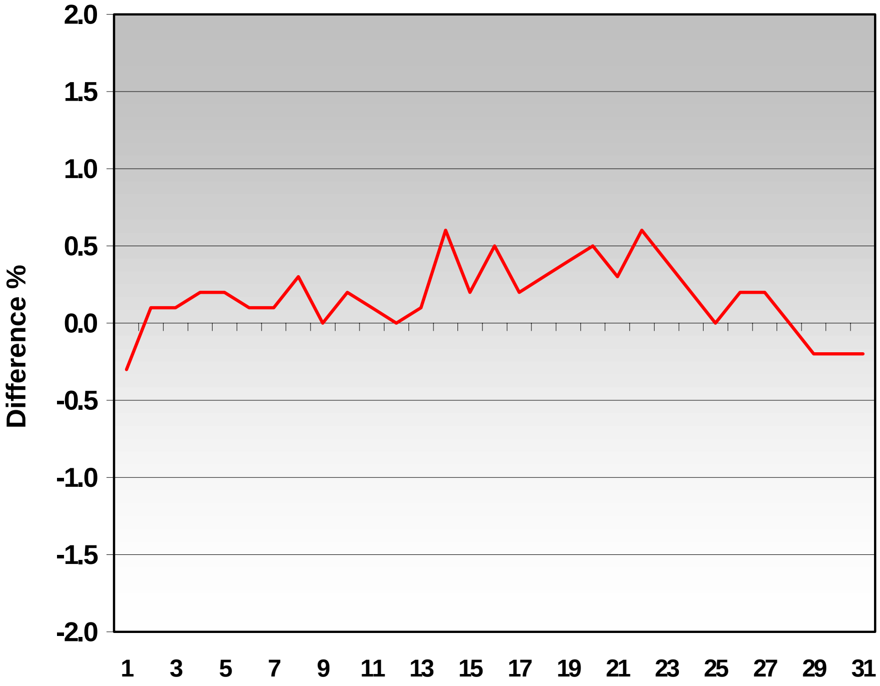
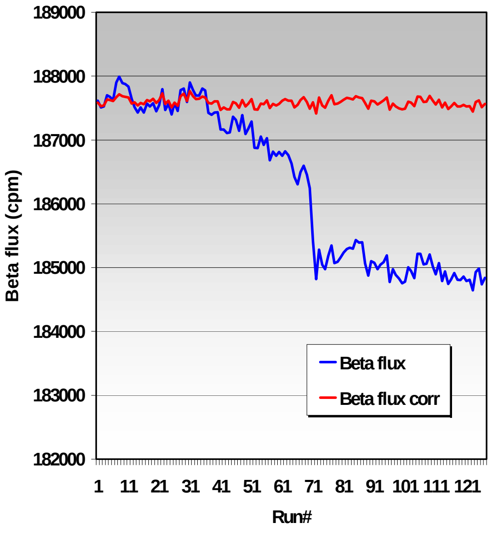


Figure 3: Span test: trend of the % difference with respect to the original calibration of the flow rate.

The mass measurement module consists of a C^{14} sealed beta source and a Geiger detector that provides the beta counts measurement allowing the determination of the dust mass. The principle of operation is the physical law governing the attenuation of beta rays when passing through a thin layer of matter. The attenuation of the beta rays emitted from the C^{14} source is measured by the Geiger detector before (blank filter) and after (loaded filter) the sampling step. The geometry of the ADAM allows that a new filter undergoes the sampling step while the previous one is subjected to the measurement phase, avoiding any lost of time and increasing the time duration of beta measurement phase.

The accuracy and the precision in the measurement of the particles mass amount depend on the following parameters: - density of the air layer between the beta source and the Geiger; - filter positioning during the blank and the measurement phases; - stability of the high voltage to the Geiger detector; - natural radioactivity of the collected particles.

In order to take into account the small variations in the density of the air layer between the source and the Geiger, the pressure and temperature in the measurement chamber is measured and a correction is calculated and applied. The temporal trend of the beta flux before and after the air density correction is reported in Figure 4.



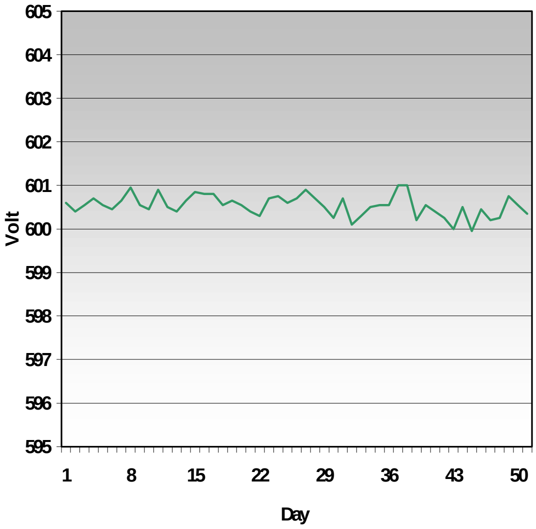


Figure 4: Temporal trend of the beta flux before and after the correction for the air density.

Figure 5: Stability of the high voltage to the Geiger.

An accurate control of the positioning of the filters in the measurement unit is carried out, so as to assure that the possible difference in the position of the blank and the loaded filter is minimised.

A good performance of the Geiger detector is closely linked to the stability of the high voltage. For this reason, the ADAM continuously monitors this parameter and normalises the flux value to a reference high voltage value. The stability of the high voltage to the Geiger over a 52 days period is reported in Figure 5; the standard deviation is 0.2 volt, that is 0.03 %.

The presence of short-life Radon daughters on the particulate matter causes a positive artefact in the beta flux measurement aimed to determine the particulate mass collected on the filter. In order to avoid this artefact, immediately before carrying out the measurement of the loaded filter the ADAM measures the residual beta activity on the particles and carries out a quantitative correction of the beta flux.

The determination of the natural radioactivity of the collected particles provides an additional piece of information that has proven to be extremely useful for the characterisation of the atmosphere under study. The temporal variations in the Radon daughter air concentration are in fact closely linked to the variations in the height of the mixed layer; this parameter, therefore, offers precious information about the ability of the atmosphere to dilute pollutants.

The overall precision of the ADAM on 24-hour samplings is 0.7 µg/m^3 (standard deviation). The detection limit is 2 µg/m^3 and the quantitation limit is 7 µg/m^3. The accuracy is 2% of the read value.

Comparison with gravimetric analysis

The ability of the Atmospheric Dust Automatic Monitor to perform any kind of physico-chemical measurements on the collected filter offers the possibility to compare the results obtained by the automatic beta gauge instrument with the results obtained by applying the traditional gravimetric procedure to the same filters. The result of this comparison is reported in Figure 6. The temporal trend of the measurements (Figure 6a) and the scatter plot (Figure 6b) show that there is a very good agreement between the two sets of measurements, with a very high correlation coefficient between the data ($R^2 = 0.99$).

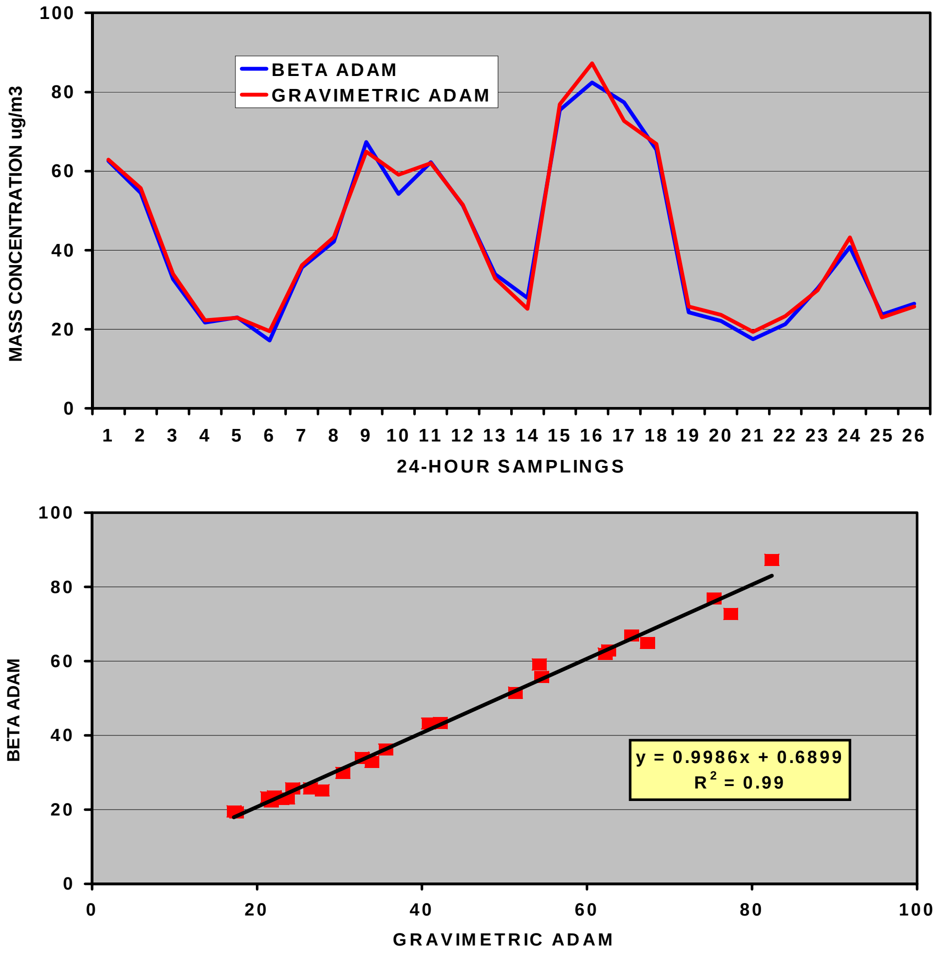


Figure 6: Comparison of the beta and the gravimetric 24-hour measurement of particle concentration: temporal trend (a) and scatter plot (b).

Conclusions

The Atmospheric Dust Automatic Monitor proves to be a very reliable tool for the determination of the atmospheric concentration of particulate matter. Its features (40 days of unattended operation on 24-hour samplings, possibility of an overall remote control, automatic QC/QA procedures) make it very suitable for being used in atmospheric networks.

Ionic content of atmospheric PM$^{2.5}$ sampled by the diffusion denuder/filter pack technique

by

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Introduction

The ionic content of atmospheric particles having aerodynamic diameter lower than 2.5 µm can be determined by using diffusion lines made of a series of annular diffusion denuders and a filter-pack. A typical diffusion line used in the EMEP station of Montelibretti is shown in Figure 1. The line is made of five denuders set in series: two NaCl-coated, two Na_2CO_3 plus glycerol-coated and one phosphorous acid-coated device. The denuders allow the determination of the following pollutants in the gaseous phase: nitric acid, sulphur dioxide, ammonia, hydrochloric acid, nitrous acid. The use of diffusion denuder upstream of the cyclone and filters allows avoiding any interference of the gaseous compounds on the collected particles.

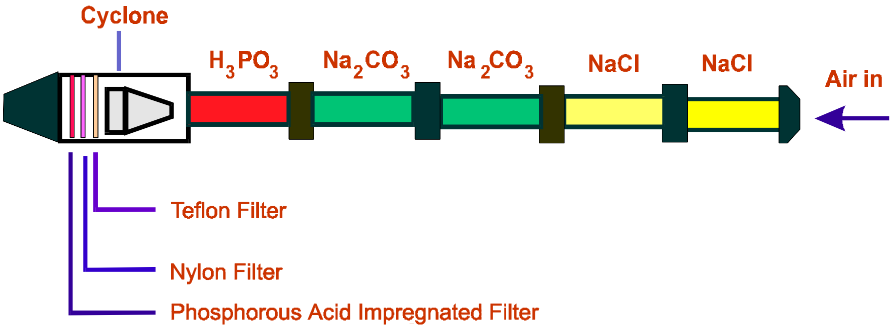

Figure 1: Diffusion line used in the EMEP sampling station of Montelibretti.

Downstream to the denuders, a cyclone allows the collection of the coarse fraction of the particulate matter. Downstream to the cyclone, particles having aerodynamic diameter lower than 2.5 µm (at the operative flow rate of 15 l/min) are collected on a Teflon membrane filter; the gaseous species evolved from the Teflon filter are recovered on the two back-up filters (acid gases on the Nylon filter, alkaline gases on the acid-coated filter). The analysis of the collected species is carried out by ion chromatography.

The possibility to take into account the gaseous species that are released from the first filter of the line in the course and after of the sampling constitutes an improvement with respect to the other methods for determining PM$^{2.5}$ that can be, in some conditions, important. An evaluation of the extent of this phenomenon in the measurements carried out in two stations located in the vicinity of Rome is reported in this paper.

Measurements

The data set discussed in this paper has been obtained from the measurements carried out in the EMEP station of Montelibretti, 20 km NE of Rome, and in the Monitoring Station of Gallese, 50 km from Rome in the same direction.

In the Monitoring Station of Gallese the gravimetric determination of PM^{10} was performed side-by-side to the diffusion line measurements. The comparison of the data gathered by means of the two techniques is reported in Figure 2. The scatter plot shows that most of the data are distributed around a value of the $PM^{2.5}/PM^{10}$ ratio higher than 0.6. A noticeable fraction of the PM^{10} mass amount is thus constituted by $PM^{2.5}$; this indicates that in the Gallese area the particulate matter is mainly of secondary origin.

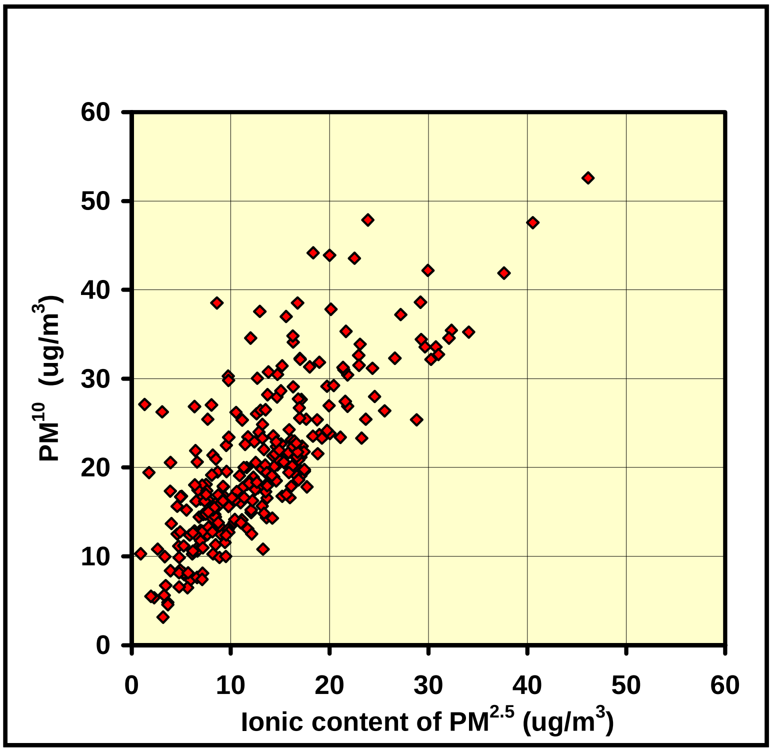

Figure 2: Scatter plot of the PM^{10} and the ionic content of the $PM^{2.5}$. Data refers to 24-hours measurements carried out in the Monitoring Station of Gallese by means of the gravimetric and the diffusion line technique, respectively.

According to the thermodynamic conditions during the sampling, volatile salts, such as ammonium nitrate and ammonium chloride, evaporate from the Teflon filter and are recovered on the back-up filters. The interconversion between the solid and the gaseous phase in the diffusion lines reproduces the situation that occurs in the atmosphere, where the volatile salts are in equilibrium with their gaseous precursors. The temporal trends of atmospheric nitric acid, ammonia and particulate nitrate in the course of the year, in fact, show an increase of the gases during the warmer months and an increase of particulate nitrate during the winter; the same situation can be observed for ammonium chloride.

The temporal trend of the species evolved by the Teflon filter and recovered on the back-up filters is shown in Figure 3. The data show that during the winter months the ammonia amount recovered on the acid-impregnated back-up filter and the sum of hydrochloric and nitric acids recovered on the Nylon filter were generally in equimolecular amounts.

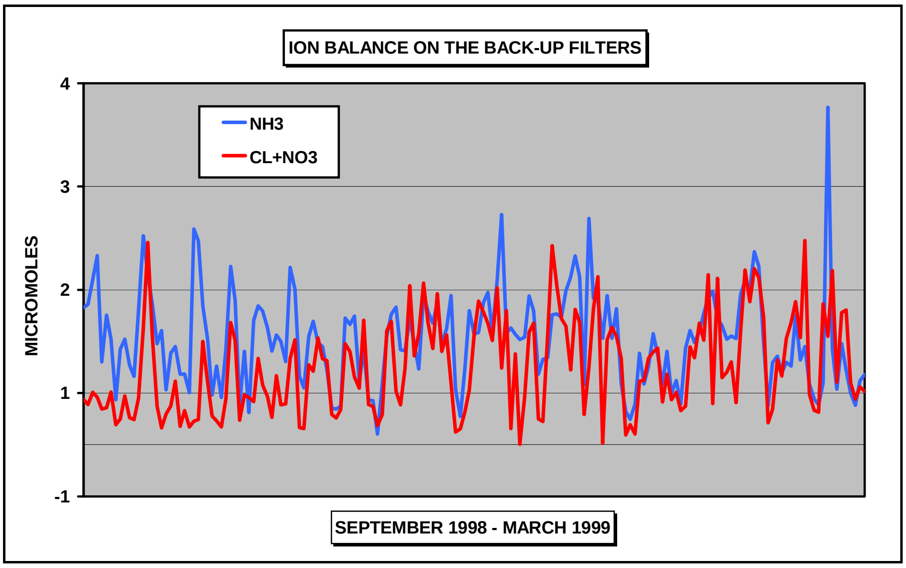

Figure 3: Ion balance on the back-up filters of the diffusion line. Measurements had 24-hour duration and were carried out in the Monitoring Station of Gallese.

During the warmer months, instead, ammonia exceeded the sum of the anions; this observation can be explained on the basis of the presence of gaseous ammonia adsorbed on both the coarse and the fine fraction of collected particles, which undergoes desorption during the sampling phase.

In the Monitoring Station of Gallese, during the period from 15 July 1998 to 15 June 1999 the per cent amount of the ammonia recovered on the back-up filter with respect to the total collected ammonia varied from 8 to 97%, with an annual average value of 49.4 %; similar values were obtained in the EMEP station of Montelibretti.

During the same period, the total amount of gases recovered on the back-up filters (sum of hydrochloric acid, nitric acid and ammonia amounts) varied between 10 and 82 % of the total ionic content of the particles collected in the filter pack (sum of chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium and calcium), that is of the ionic content of $PM^{2.5}$. The average value was 37%.

Conclusions

The determination of the soluble fraction of $PM^{2.5}$ by means of the diffusion lines allowed to highlight that a significant fraction of the collected particles may undergo desorption and evaporation phenomena; the extent of the release depends on the thermodynamic condition of the atmosphere under study.

In the examined location, the soluble fraction of $PM^{2.5}$ constituted more than 50% of PM^{10}, indicating that release of volatile compounds can be of importance also in the determination of the PM^{10} fraction.

The described phenomena constitute a bias in the determination of particulate matter concentration by means of methods that do not take into account evolved gases.

Natural and anthropogenic sources of PM_{10} and $PM_{2.5}$ in Spain. Incidence on the new PM_{10} limit values exceedances

by

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Introduction

The implementation of the recent European air quality Directive (99/30/CE) will require an assessment of the ambient levels of several pollutants in the Member States. With respect to particulate matter, source apportionment studies will be needed to discriminate its natural/anthropogenic origin. This would imply size distribution and chemical characterisation, in order to evaluate the different contributions mainly in the Mediterranean and south European areas, where the proposed PM10 levels could be exceeded by natural particulate inputs, like Saharan air mass intrusions, resuspension of natural soils particles, wild fires, etc

In Spain, a project has been launched aimed at characterising the natural contribution of the particulate matter levels recorded in regional air quality networks. The main objectives of this study are:

- To establish a methodology to discriminate anthropogenic/natural and local/ remote PM_{10} sources in the regional air quality networks in Spain.
- To determine when the future PM_{10} limits are exceeded by natural causes. According to this issue, the suitability of measuring $PM_{10}/PM_{2.5}$ as a local indicator of the anthropogenic contribution.
- To reach and apply a methodology to establish equivalent measurement methods to the PM_{10} reference method in the networks monitoring stations.

1. Methodology

For a better achievement of these purposes, six main study areas have been selected (Figure 1) taking into account meteorological, geographical and emission sources criteria. The study will be developed in four main stages, which will consist of:

STAGE 1. Interpretation of recent PM_{10} and TSP time series through the following steps:

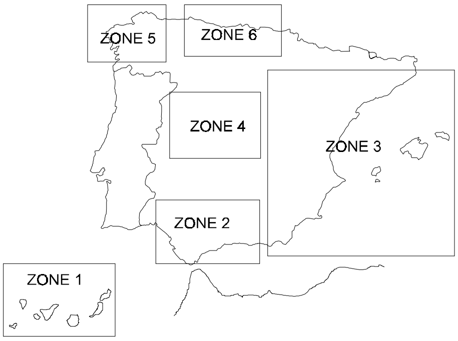


Figure 1. Location of the six study areas.

a) Selection of 30 monitoring stations.

b) Inventory of PM_{10} emission sources around the monitoring stations.

c) Study and interpretation of time series for:
   - Identification of PM_{10} peaks exceeding the standard limits.
   - Interpretation of the meteorological series for PM_{10} peak.
   - Correlation with gaseous pollutant levels.
   - Correlation with time series of background areas to identify long range transport events.

High PM_{10} "peaks" or events will be characterised for each area and a preliminary discrimination of their potential origin will be extracted a the end of this stage.

STAGE 2. Interpretation new time $PM_{10}/PM_{2.5}$ series obtained from selected monitoring stations and physicochemical characterisation of the high $PM_{10}/PM_{2.5}$ events. This will be based on the following steps:

b) Study of PM_{10} and $PM_{2.5}$ simultaneous series obtained by means of automatic analysers in 12 monitoring stations (two per area).

c) Periodic sampling of PM_{10}, by gravimetric reference method (EN12341) and $PM_{2.5}$ by continuous on-line samplers, in 6 monitoring stations and in a blank/ background area.

d) Particle size sampling with cascade impactors.

e) Chemical characterisation of filters and particle size fractions.

e) Meteorological interpretation for the high $PM_{10}/PM_{2.5}$ events.

The last step will be complemented with the interpretation of the back-trajectories provided by modelling tools. These will contribute to establish the potential origin of the air masses reaching the monitoring stations during or the previous days to the event.

STAGE 3. Intensive measurements in identified situations when PM_{10} levels could exceed the new PM_{10} standards by natural inputs. These will be carried out under those meteorological scenarios in which high PM_{10} events usually occur. The selection of the scenarios could be done after the results of the previous stages, and will be performed for each selected area. The field campaigns will include:

a) Simultaneous sampling of PM_{10} and $PM_{2.5}$ by means of Hi-Vol samplers.

b) Particle size sampling by means of cascade impactors.

c) Meteorological characterisation during single events.

d) Physicochemical characterisation of particles.

STAGE 4. A final phase of integration of the results obtained in the previous stages is foreseen in order to achieve the defined objectives.

2. Preliminary results

Previous experimental results obtained by the working group in some areas of Spain have contributed to define the work hypotheses.

Figure 2 shows an example of what could be expected from the time series analysis to be performed in STAGE 1. Seasonal patterns of the PM_{10} exceedances of the daily limit values depend on the contribution of the different sources in each region. In this way, it can be observed the higher number of daily exceedances at a rural environment in the South of Spain (CARBONERAS) during spring and summer (Figure 2 a). This could be related to the greater influence of natural processes during these seasons, i.e. higher levels of soil-related particles produced by strong convective conditions, lower aerosol scavenging potential (scarce rainfall periods), and higher influence of Sahara air masses intrusions. Figure 2 b) depicts the typical winter maximum at an urban site (Madrid) where the PM_{10} number of exceedances in this season is related to the major man-made emissions (mainly the road traffic exhausts and heating devices) and the strong atmospheric stability conditions. Finally, at the bottom (Figure 2 c)), corresponding to Sagrera, near Barcelona, the typical distribution of PM_{10} maxima at urban sites is not so clearly observed as in addition to the winter maximum PM_{10} exceedances are also achieved in spring, probably due to external or remote influences.

External influences have frequently been documented at this site, like the episode of March, the 9th-10th in 1999 shown in Figure 3. An increase of the PM_{10} levels was clearly observed in Barcelona at this occasion (Figure 3 a). The 850 hPa wind field forecasting of the previous day (Figure 3 b) confirmed a long range transport event from the Sahara desert, related to the presence of a high pressure system over the central Mediterranean and an air mass trajectory passing through the north African coast.

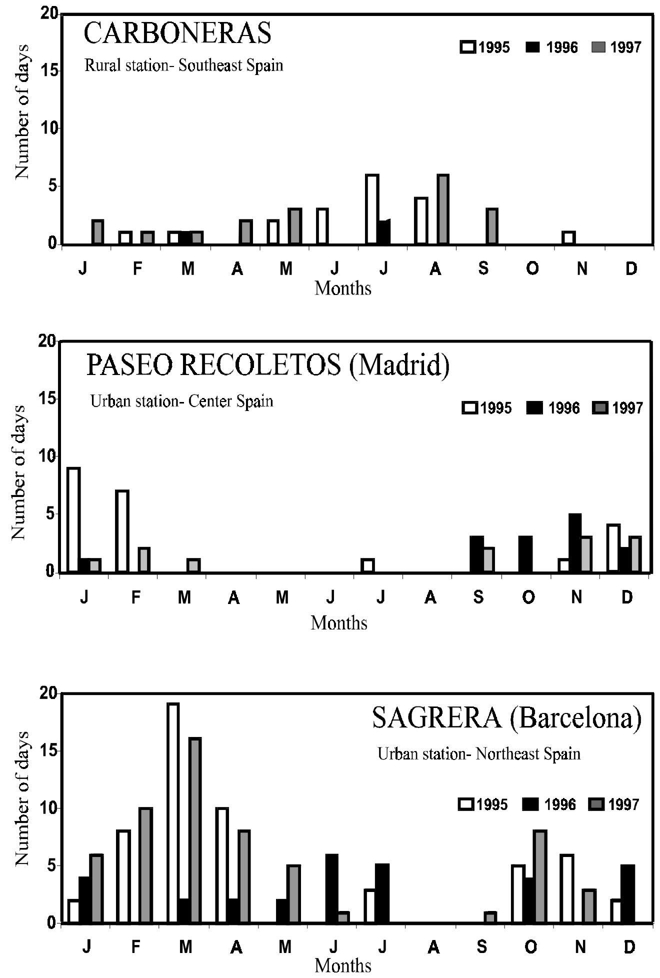
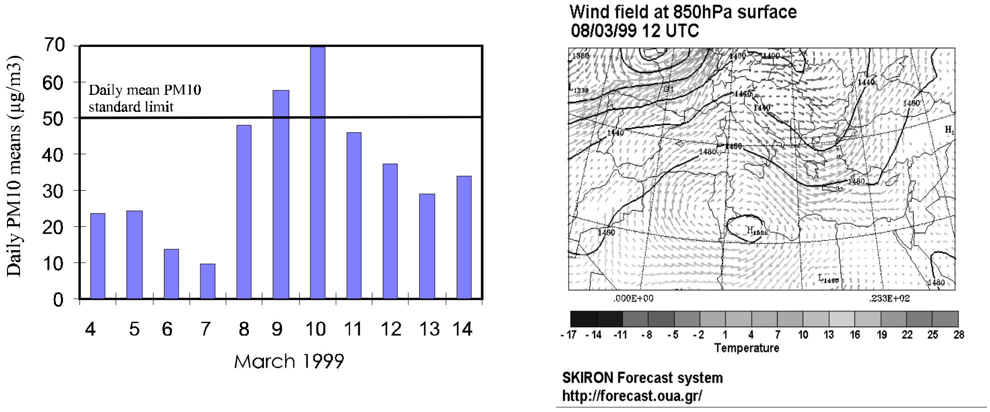


Figure 2 a), b) and c):

Number of daily exceedances of the new PM_{10} *daily average limit value (50 µg/*m^3*) at a rural site a), an urban site b) and an externally influenced urban site c).*



SKIRON Forecast system
http://forecast.oua.gr/

a)

b)

Figure 3 a) and b):

PM_{10} daily average values at and 850 hPa wind field forecasted by the SKIRON system on March, the 8th.

The PM_{10} and $PM_{2.5}$ chemical analysis revealed that the PM_{10} fraction was affected by the intrusion, but not the $PM_{2.5}$, as can be extracted from Table I. The large difference between the PM_{10} concentration calculated by gravimetric measurements and by the sum of major ions was due to the high levels of SiO_2 and CO_3^{2-} in the Saharan dust (not measured).

Table I: Chemical analyses of the PM_{10} and $PM_{2.5}$ fractions during the 09-10/03/99 episode.

Date		PM2.5 09-10/03/99	PM10 09-10/03/99
	Particles concentration		
GRAVIMETRIC	µg/m^3	31.00	70.41
SUM OF IONS	µg/m^3	23.83	39.52
Al	µg/m^3	0.23	1.37
Ca	µg/m^3	0.77	6.08
Fe	µg/m^3	0.21	1.47
K	µg/m^3	1.41	1.43
Mg	µg/m^3	0.12	0.45
Na	µg/m^3	0.59	1.97
P	µg/m^3	0.20	0.39
NH_4^+	µg/m^3	2.59	1.79
SO_4^{2-}	µg/m^3	3.24	3.99
Cl^-	µg/m^3	0.53	1.22
NO_3^-	µg/m^3	6.28	9.87
C	µg/m^3	7.40	8.94
Ba	ng/m^3	50.1	105.6
Cr	ng/m^3	7.0	15.7
Cu	ng/m^3	42.8	93.8
Mn	ng/m^3	12.6	30.6
Ni	ng/m^3	<dl	11.8
Sr	ng/m^3	2.1	9.7
Ti	ng/m^3	22.0	89.6
V	ng/m^3	6.6	13.7
Zn	ng/m^3	101.3	165.8

Other long-range transport event of particulate matter from North Africa occurred ending April 1999 in the area of Barcelona. In this case it was due to the simultaneous presence of an anticyclone in the Central Mediterranean and a low-pressure system at the Southwest of the Iberian Peninsula. The TSP and PM_{10} levels were affected by the western extreme of the dust plume passing over Barcelona (northeast coast). In contrast, the $PM_{2.5}$ and PM_1 levels only showed a slightly perturbed evolution, (Figure 4).

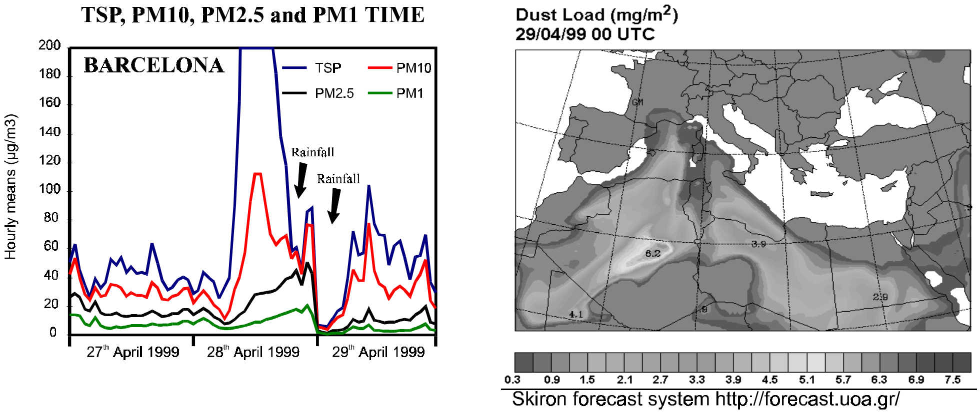


Figure 4: Impact of a Sahara intrusion episode on the TSP, PM_{10}, $PM_{2.5}$ and PM_1 time series.

A basic objective of the project is to define a good indicator of the anthropogenic or natural contribution based on $PM_{10}/PM_{2.5}$ measurements. Under a very stable atmospheric situation in Barcelona, associated to a high pressure system placed over the Iberian peninsula, the highest pollution levels are usually registered. In these conditions the $PM_{2.5}$ and PM_1 levels experience a large increase, as occurred during December, the 18th and 19th 1998 (Figure 5). On 20th and 21st, when the anticyclone moved, the $PM_{2.5}$ and PM_1 levels decreased, while the TSP and PM_{10} ones did not show a significant variation. So, it could be concluded that PM_{10} could be a good indicator of the natural sources influence on the particulate matter levels, whilst the finer fractions, namely $PM_{2.5}$ and PM_1, are better related to the anthropogenic sources. Nevertheless further experiments are required to verify this behaviour at other sites with different sources contributions.

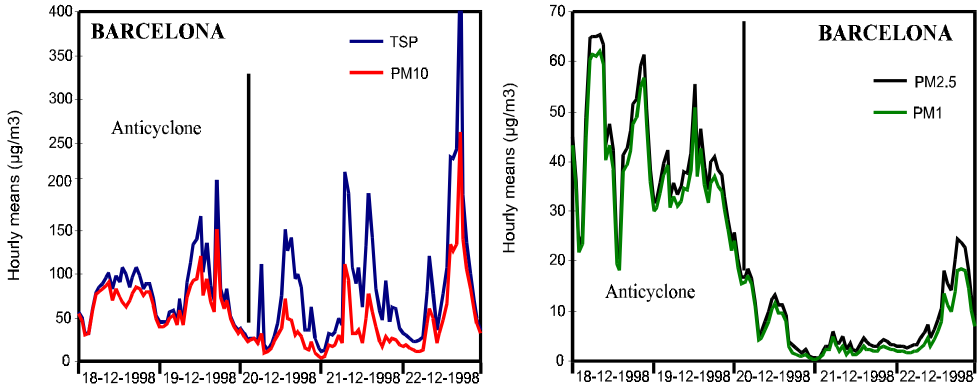


Figure 5: TSP, PM_{10}, $PM_{2.5}$ and PM_1 time series during a high pressure situation in winter in Barcelona.

Finally, intercomparison exercises are being performed to achieve the last objective of the project. At present, experimental results show a good correlation between the reference gravimetric method for PM_{10} with the Graseby Andersen device and other gravimetric devices (MCV, DIGITEL) as well as with a continuous method (GRIMM). Although no reference method is yet established for $PM_{2.5}$, a good correlation has been also obtained between the gravimetric and the continuous device (Figure 6) for this fraction.

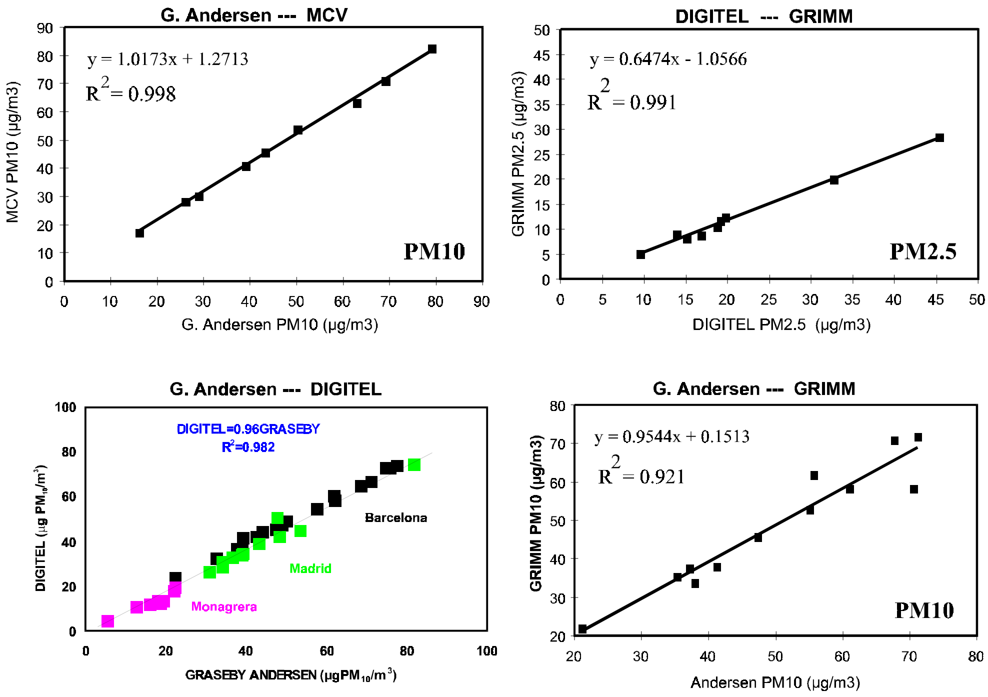


Figure 6: Comparison between PM_{10} *and* $PM_{2.5}$ *samplers used during intensive measurements.*

Acknowledgements: This study has been supported by the Spanish Ministry of Environment, the Plan Nacional de I+D under project AMB98-1044, and the Plan Regional de I+D de la Comunidad de Madrid CAM (Ref: 07M/0014/1998). We would like to express our gratitude to ENDESA, the Direcció General de Qualitat Ambiental from the Generalitat Valenciana, and the Township of Madrid for their help in supplying the air quality data.

Influence of the anthropogenic sources on the air quality in Ljubljana region

by

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Introduction

The understanding of the fine particulate (PM_{10} and $PM_{2.5}$) transport is important on the local, regional as well global level. The information about the elemental composition of the particulates serves for identification of the sources and contributes to the estimation of the anthropogenic pollution influences. The quantitative data on emissions from combustion of solid fuels, road and city transport, and industrial processes are necessary for evaluation of these influences. The receptor modeling needs to be done properly taking into account the air mass transport and meteorological parameters. The prerequisite for the mentioned activities are the quality assured sampling and measuring procedures developed for the specific tasks related to the air quality issues.

Ljubljana, a capitol of the Republic of Slovenia, has been taken in the study as a potential pollution source, and the regional influences from industry and traffic has been studied. The city with around 400.000 inhabitants and area of 75 km^2 has several factories which are the pollution sources, uses combustion of coal for heating, and is crossed with highways, some of them connecting the EU south-west with east countries. A burden with heavy traffic transport to some of the Mediterranean harbors through Ljubljana is increasing. Besides, the meteorological and topological conditions in Ljubljana are not in favor of this increasing burden. The location of the town in between the mountains generates the conditions for temperature inversions, especially in the winter time. Also the wind directions, predominantly blowing in the SW-NE direction, coincide with the most inhabitated areas of the town. All that mentioned was strong enough a warning signal to start the study of the fine particulate emissions and their transport in the region.

The sampling and analytical approach is described, and the preliminary results are presented, definitely showing the anthropogenic source emissions influences.

Sampling and analysis

For the sampling the “Gent” type of the sampler has been applied. The sampler which selects between the $PM_{2.5}$ and PM_{10} fine particles is located at the accelerator centre of J. Stefan Institute, approximately 10 km from the Ljubljana downtown in the NE direction. The sampler is equipped with the simple meteorological station which enables the measurement of the wind speed, wind direction, air temperature, and humidity on the sampling spot. The meteorological data at the sampler are permanently checked with the representative data from the nearby meteorological station. The samples are colleted twice per week, Wednesday and Saturday, giving the 24 hour averages over these two days. The particulate material collected on the filters is used then for the elemental concentrations determination.

The Proton Induced X-ray Emission (PIXE) method is applied for the samples analysis. The standard PIXE in-vacuum arrangement is used, having the protons with energies of 2 MeV, and the currents of up to 50 nA. The current doses are normally equal to 100 µC. The X-rays produced by the proton bombardment are measured with semiconductor detector, and the concentrations of the chemical elements above Al are determined simultaneously. The PIXE method is sensitive enough to trace the presence of the elements bound to aerosols at levels far bellow ng/m^3. The measurement of the X-ray spectra and their computer analysis are made automatically to overcome the cumbersome manipulation of the big amount of samples.

The computer codes were written for sorting the measured data in a time scale, and to correlate the information with the most important meteorological data, the wind speed and direction.

Results

Time variation of mass concentrations

Fourteen elements above Al are being detected in the particulate samples. Ca, Ti and Fe, which are known as mostly of natural origin, show very similar time variation patterns. Their $PM_{2.5}$ mass concentrations are generally lower than PM_{10} mass concentrations. Behavior of K and Mn is similar in coarse fraction but they have higher fine fractions with somehow different patterns.

On the other hand each of anthropogenic elements (Pb, Cu, S) shows unique time variation pattern with some common characteristics. They are mainly present in fine fraction and perform very strong and sudden peaks in mass concentration of both fractions. The peaks of different elements do not necessarily coincide. It is not yet known whether the peaks are of very local origin (such as near chemical factory or agricultural activity) or are they to stem from the activities in Ljubljana region.

An increase of K and S fine fractions is found in late July and August. This can be understood as seasonal variation due to very stable and dry weather. There is also no Cl observed in late spring.

Correlations of concentrations with the wind direction and speed

As our samples are 24 hour averages we calculated wind averages for the sampling days. For each chemical element we plotted a 3D histogram having average wind direction and speed on x- and y-axis respectively and corresponding concentrations on vertical axis (Figure 2). We eliminated the effect of uneven distribution of wind by dividing each bin by the number of its hits. This made the second histogram.

For most elements there is evidence of higher concentrations coming from the direction of Ljubljana (SW). For some elements we are observing high concentration coming from NE, possibly from more distant industrial towns.

Objectives

Another sampling station is being planed to be installed on the opposite side of Ljubljana in order to distinguish its contributions from the background and to eliminate local contributions. The concentration-wind correlation will be determined with greater certainty when more data is gathered.

We expect to detect an influence of a major highway which is being built near our first sampling site (approx. 500 m). It will come into operation in late 2000 or 2001.

Conclusions

The sampling and analytical procedures were installed to follow the emissions from the activities in the Ljubljana region. The measured data show the sources which can be related to the anthropogenic activities. The meteorological data determination at the sampling spot has been proven as a reliable auxiliary tool for the source emitter identification.

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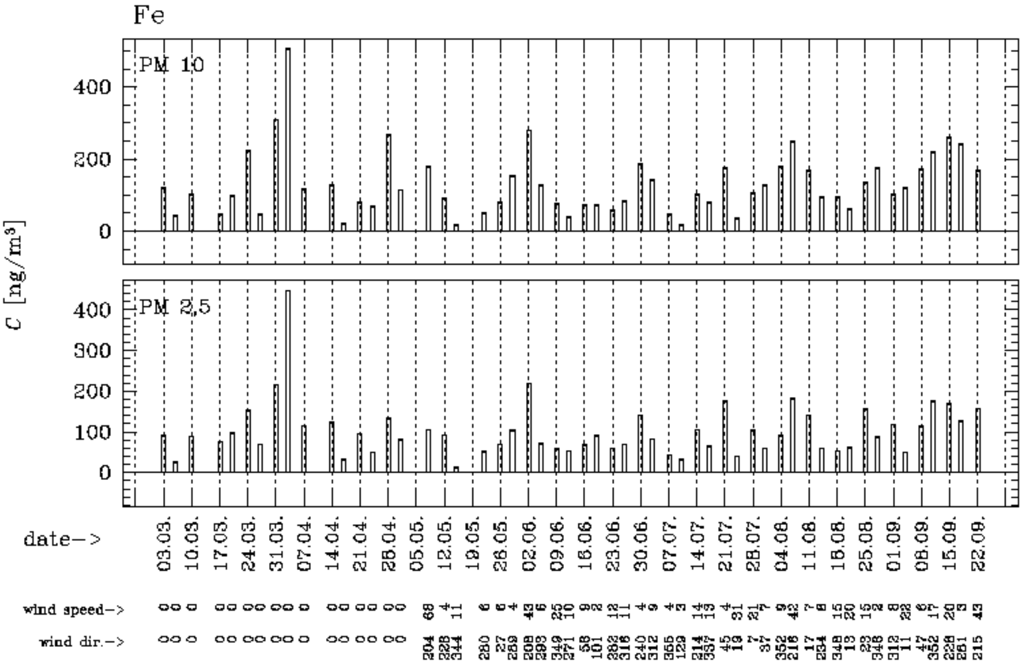
[3] Applied Research on Air Pollution Using Nuclear-Rrelated Analytical Techniques, NAHRES-26, IAEA, 1995.



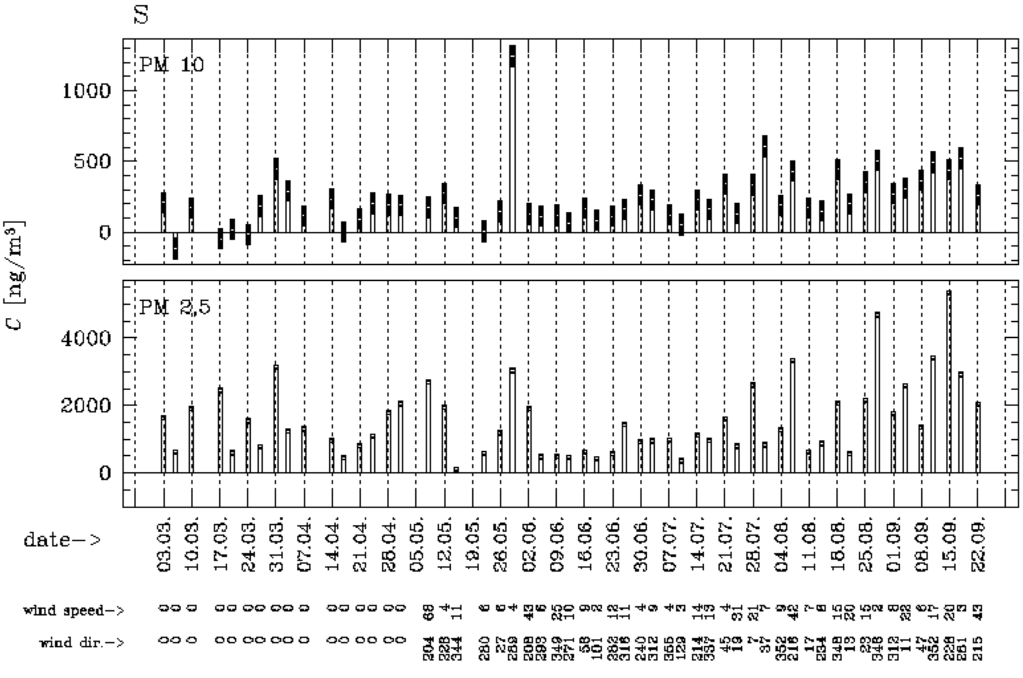


Figure 1: *Dependence of absolute concentrations of Fe and S in coarse and fine fractions.*

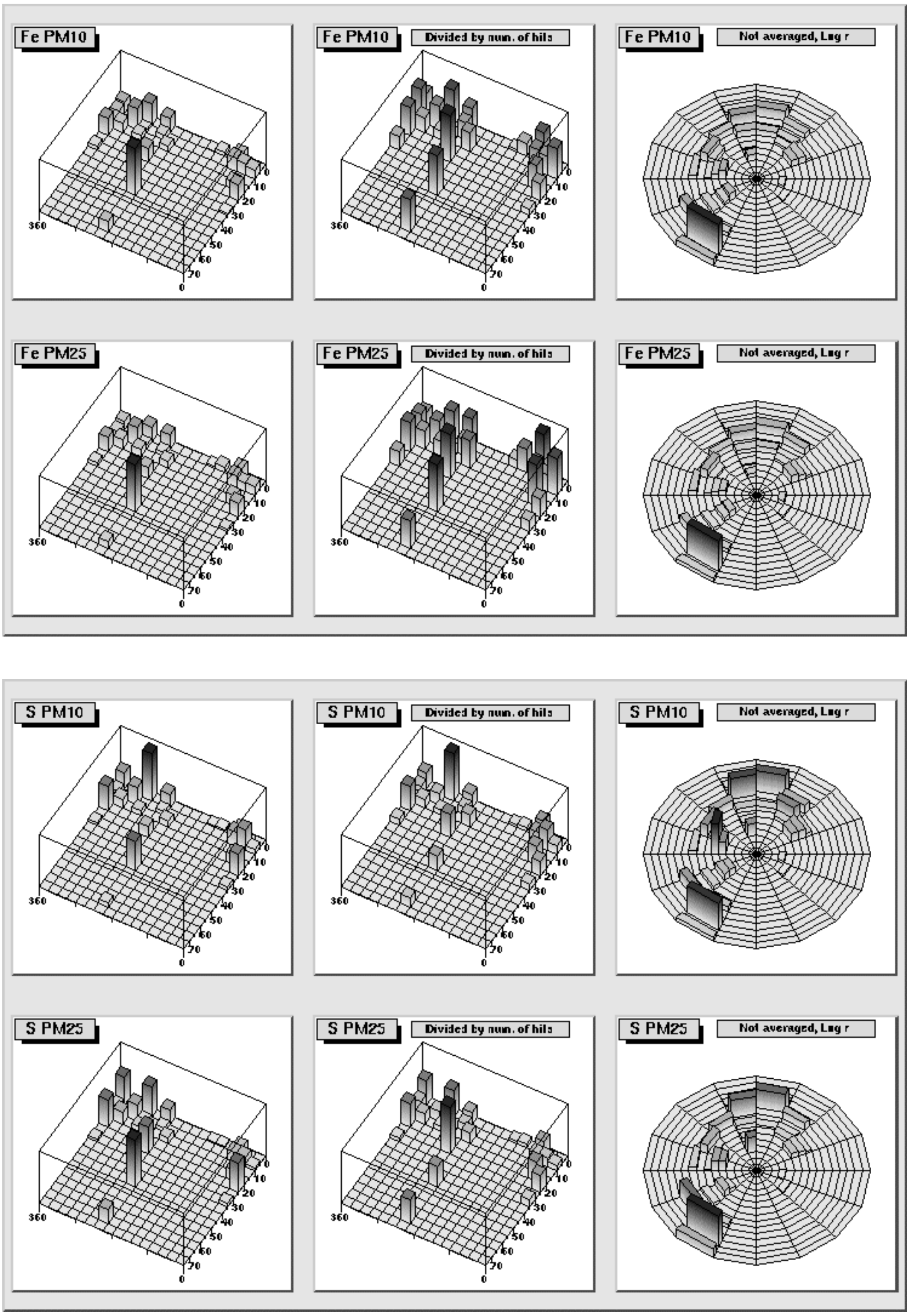


Figure 2: *Correlation between wind parameters and concentrations of Fe and S.*

Measurement of particles at the monitoring station of the Joint Research Centre, Ispra, 1988 - 1998

by

Diana Rembges, Laure Dutaur, Claude Brun and
Wilfried Leyendecker

Joint Research Centre Ispra, Environment Institute, Air Quality, IT–21020 Ispra (VA)

Since the end of 1985, when the station has been set up, the station is managed by the Joint Research Centre Ispra, Environment Institute, Air Quality Unit and is operating on a regular basis in the EMEP measurement programme. The station is situated in a semi-rural region close to the Lago Maggiore, between the Alps to the north and the Po-Valley to the south and far away from Milano, about 60 km to the southeast.

The measurement of the **t**otal **s**uspended **p**articles (TSP) as part of the basic EMEP measurement programme, was set up at the Ispra EMEP Station in 1985. The data of these long time measurements show significant annual changes in the TSP air concentration with maximum values from the end of September to February / March. These annual changes can be observed during all years. Until 1994 there is a significant decrease in the air concentration of the TSP (average as well as maximum values), while in the following years the TSP air concentrations as well as the annual variations remain at the same level, with a slightly decreasing trend. The composition of the basic ions NO_3, NH_4 and SO_4 on the collected aerosol filters remain the same during the measurement period.

The comparison of the periods with the highest air concentrations for the TSP with the air monitoring data show increasing NO_2 and NH_4 air concentration with increasing particulate air concentration while the trend for O_3 is vice versa.

Some pilot studies of parallel sampling of TSP, $PM_{2.5}$ and PM_{10} were carried out in 1998 at the Ispra EMEP Station with further analysis of the aerosol filters on heavy metals by the means of X-ray fluorescence. Some preliminary results will be presented in this poster.

COMPARISON OF CONTINUOUS PARTICULATE MONITORS

Prague, November 1998 – March 1999

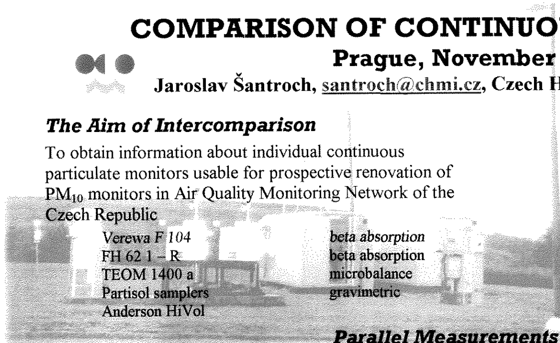
Jaroslav Šantroch, santroch@chmi.cz, Czech Hydrometeorological Institute, Czech Republic

The Aim of Intercomparison

To obtain information about individual continuous particulate monitors usable for prospective renovation of PM_{10} monitors in Air Quality Monitoring Network of the Czech Republic

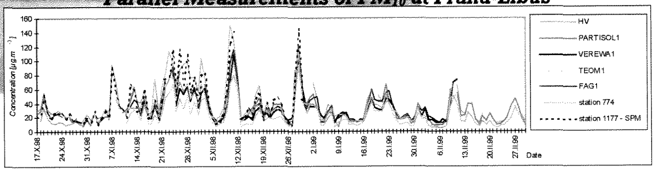
Compared Instruments

- two instruments of each manufacturer
- all instruments equipped with PM_{10} heads



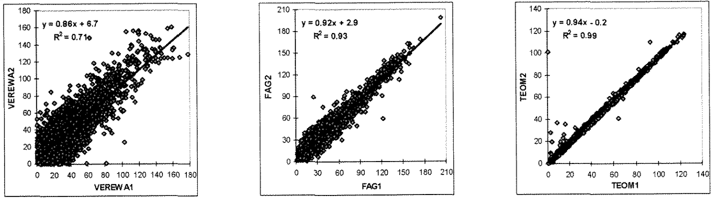
Verewa F 104	*beta absorption*	by Verewa Umwelt und Processmesstechnik
FH 62 1 – R	beta absorption	by ESM Eberline
TEOM 1400 a	microbalance	by Ruprecht & Patashnik
Partisol samplers	gravimetric	by MLU
Anderson HiVol		EN 12341 Reference method (only one instrument)

Parallel Measurements of PM_{10} at Praha-Libuš

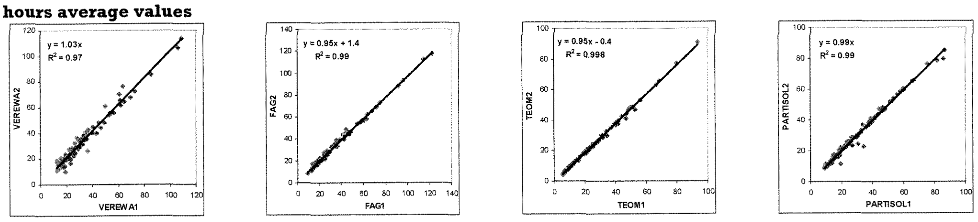


Data Evaluation of Individual Monitors of each manufacturer

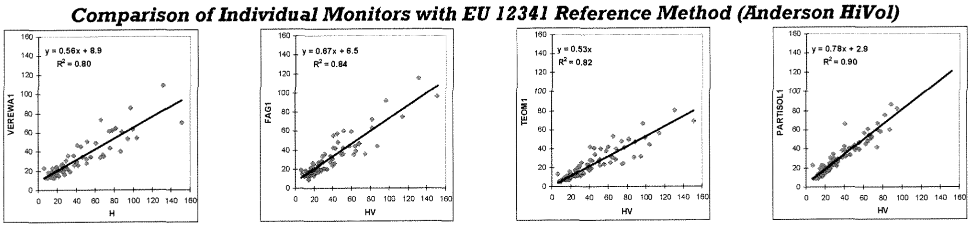
30 minutes average values



24 hours average values



Comparison of Individual Monitors with EU 12341 Reference Method (Anderson HiVol)



Conclusions

- good correlation between the pairs of the same monitors for 24 hours average values for all monitors (r > 0.98)
- good correlation for 30 minutes average values for TEOM and FAG (r > 0.96)
- lower correlation for 30 minutes average values for Verewa (r = 0.84)
- the lowest measured values of TEOM against Andersen HiVol reference method or Partisol Sampler (coef. 1.88 or 1.47 respectively)
- losses of volatile components seem to be the biggest for TEOM in comparison to the beta absorption method. The reason could be explained by the loss of volatile components (organic compounds, ammonium nitrates) caused by the heating system of the TEOM instrument
- losses of all instruments and especially TEOM instruments against the reference method could be caused by the high relative humidity in the winter season in Prague

Acknowledgement

This work was supported by the Czech Hydrometeorological Institute, Prague. Instruments were kindly lent by manufacturers (Verewa Umwelt und Processmesstechnik, ESM Ebrline, Ruprecht & Pataschnik and MLU). I would like to thank to the engineers and technicians from Central Air Quality Laboratory of CHMI (Mr. J. Novak, Chief) for organisation and service of intercalibration measurement and Mr. J. Horalek from CHMI for the statistical evaluation.

Analyses of results obtained with High volume aerosol sampler and Andersen low volume sampler in capital city of Macedonia

by

Radmila Simeva

Section Air Quality/Republic Hydrometeorological Institute, Skopje, Republic of Macedonia (not presented)

Introduction

The monitoring of SPM in capital city of Macedonia, Skopje is established from 1997 on four automatic stations. A Study Team from Japan International Cooperation Agency (JICA) and Ministry of Environment carried out “The Study on Air Pollution Monitoring System in the Republic of Macedonia” together with the cooperation of other relevant institutions.

Among the target substances stipulated by EU directive, the following pollutants have been measured continuously in Macedonia

- The compound -Specific Directive (CSD): SO_2 (24 hr), Black smoke (BS) (24hr), NO_2, O_3
- The Exchange of information decision (EoI): SO_2 (24hr), BS (24hr)

In addition to this instrument, the following substances were monitored by JICA’s monitoring instruments

CSD: SO_2, PM_{10}, NO_2, O_3
EoI: SO_2 (1hr), CO (1hr), NO_2 (1hr), O_3(1hr)

Continuous monitoring of SPM was also possible using PM_{10} instead of traditional BS monitoring. Furthermore, 24-hour monitoring of heavy metals from SPM of ambient air was made after installing a High volume air sampler. During the project the study team has carried out sampling and ingredient analysis of $PM_{2,5}$, PM_5 and PM_{10} for research besides the survey program of its visit. These data are very important to analyze ambient air pollution because the results of statistical analysis on health damage by respiratory disease in Skopje are very serious.

Data of SPM in Ambient Air

1. Survey by High Volume Sampler

Sampling and components analysis of SPM including heavy metals by a high volume sampler was performed. The method of survey and the results of survey are as follows:

a) The Method of Survey

- Measurement points:
  Automatic continuous measurement points in four different locations.
- Measurement method:
  24 hours sampling per mouth. Samplings were for heavy metals and carbon analysis, and suction flow rate was 455 l/min respectively. Diameters of particle of SPM were three stages including $PM_{2.0}$, $PM_{2.0-10}$, > PM_{10}. $PM_{2.5}$ was utilized for components analysis as large amount of extracted SPM
- Components analysis:
  Pb, Cd, Cr, Ni, Fe, Cu, Zn, Mn, Na, K, Ca, Mg, C-ele, C-arg, etc.
- Analysis method:
  Republic Hydrometeorological Institute analyzed components by using an atomic absorption spectrophotometer which is provided by JICA.

b) Results of survey

In heavy metal components, Pb (less than 0,4 $\mu g/m^3$) was not exceeded the environmental standard level (0,7 $\mu g/m^3$). In Carbon components, C-ele and C-arg levels are the same. C-total dominated about 30% of SPM.

2. Particle Size Distribution by Andersen-type low-volume Sampler

The purpose of the sampling of particulate matter by size ($PM_{2.5}$, PM_5, PM_{10}) is the evaluation of emission source contribution by SPM size.

a) Survey Method

- Survey Period: December 24,1997 to February 21,1998
- Survey Point : No.1: Kinder Galten, No.2 RHMI, No.3 Railway Station
- Sampling time: 24 hours
- Sampling method: The filters for heavy metal analysis carbon are made of Teflon and Quartz respectively. Sampling was avoided rainy weather.
- Measurement Method:

- SPM concentration
  The direct reading type balance weighed SPM volume. Such balance measured less than 0.1mg weight. SPM concentration was approximated by SPM weight divided by flow volume aspirated.
- Heavy metal analysis
  Analytical instruments in use were XRF analyzers and ICP analyzer Metal components measured were same as SPM sampling by high volume sampler.
- Carbon analysis was done by NDIR about elemental as well as organic carbon.

a) Monitoring Method
The distribution of particle sizes of aerosols suspended in the air by an impact method equipped with multistage, multi-hole jet nozzle was measured by the Andersen Samples.

b) Result of Analysis
The result of carbon analysis is show in Table 1.

XRF analysis is non-distractive and allow the simultaneous multi component analysis but deviation by type is found large in terms of sensitivity as well as accuracy. Also analytical method like AAS result applied after acid dissolution often shows wide variance, which necessitates the use of analytical result info careful consideration. Table 2 shows effort of XRF analytical data evaluation by grouping the sampling filters (due to small SPM available) and subjecting to acid dissolution and AAS. The analysis data are show in term of component dissolved in SPM, µg/mg.

The result of AAS analysis clearly showed the high content of Pb and as compared the sample taken near RHMI (Sample 1, 2, 3) the sample 4, 5 showed the higher Pb concentration. As for carbon RWS point showed higher value of carbon content in SPM size between < 2,5µm and that of < 10 µm showed the higher value of carbon in < 2,5 µm SPM.

Table 1: The Results of Carbon Analysis in SPM (Andersen Low Volume Samples).

Sampling Point	**Sampling Date**			**PM**	**SPM**	**Carbon**					
	Date	**Month**	**Year**		**Conc. ($\mu g/m^3$)**	**C-org**		**C-ele**		**C-total**	
						Conc. ($\mu g/m^3$)	**Content (%)**	**Conc. ($\mu g/m^3$)**	**Content (%)**	**Conc. ($\mu g/m^3$)**	**Content (%)**
RHI	24-25	12	1997	PM10	221	9.2	4.2	24.3	11.0	33.5	15.1
	25-26*	12	1997	PM10	126	7.6	6.1	17.6	14.0	25.3	20.1
	26-27	12	1997	PM10	371	10.5	2.8	29.3	7.9	39.8	10.7
	8-9	1	1998	PM2.5	163	12.8	7.9	30.8	18.9	43.6	26.8
	9-10	1	1998	PM2.5	166	14.1	8.5	38.3	23.1	52.3	31.6
	10-11	1	1998	PM2.5	13	1.5	11.3	2.6	19.5	4.1	30.8
RWS	17-18	2	1998	PM10	325	38.8	11.9	83.1	25.6	121.9	37.5
	18-19	2	1998	PM10	153	16.5	10.8	47.7	31.0	64.2	41.8
	19-20	2	1998	PM10	130	17.4	13.4	47.3	36	64.7	49.8
	20-21	2	1998	PM10	245	29.7	12.1	78.7	32.1	108.4	44.2
	21-22	2	1998	PM10	261	35.4	13.6	86.9	33.3	122.3	46.9

Note RHI: Republic Hydrometeorological Institute
RWS: Rail Way station
Content (%): Ratio of component for SPM
25-26*: It is not 24 hours flow (problem with pomp)

Table 2: Results from Metal Analysis from Mixed Filter Samples of SPM taken by Andersen-type Low-Volume Sampler.

Month/ station	Total mass mg	**Element, µg/mg**										
		Na	K	Zn	Mg	Fe	Pb	Mn	Cr	Cu	Ni	Cd
Sample 1	13.3	1.128	5.732	0.226	1.977	6.240	1.278	0.748	0.145	0.154	0.172	0.0375
Sample 2	8.25	2.624	8.564	0.1576	3.164	7.758	1.273	1.067	0.0958	0.091	0.201	0.071
Sample 3	9.44	0.567	5.713	0.1695	1.086	3.072	1.006	0.577	0.0095	0.159	0.147	0.0106
Sample 4	3.96	2.487	15.05	0.581	4.90	13.89	7.071	0.795	0.0417	0.53	0.303	0.0353
Sample 5	9.79	1.798	8.655	0.398	7.666	21.55	3.473	1.236	0.136	0.408	0.202	0.0215

Sample 1 (RHMZ, PM 10 µm): T1; T2; T8; T10 and T12
Sample 2 (RHMZ, PM 10 µm): T23; T45; T49; T51 and T53
Sample 3 (RHMZ, 2 samples 2,5 µm; 3 samples 5.0 µm): T4; T5; T7; T9 and T11
Sample 4 (Majcin Dom, PM 10 µm): T44; T50; T52; T54 and T60
Sample 5 (Railway Station, PM 10µm): T61; T63; T64; T65 and T66

Preliminary model investigations of the fine particles distribution in the Northern Hemisphere

by

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Introduction

There is a growing concern about various negative effects caused by the anthropogenic aerosols. This issue is included in the work programme of the Convention on Long Range Transboundary Air Pollution, which has established a joint Task Force with the World Health Organization to investigate it. World Meteorological Organization is addressing the problem of fine particles monitoring at a global scale.

Current study is aimed at preliminary numerical simulation of the production and distribution of acid chemical aerosol, which is primarily formed from the oxidised sulphur, nitrogen and ammonia during the atmospheric transport and transformations of those pollutants. The 3-D Dispersion Model of Atmospheric Transport DMAT-acid used for the calculations was developed in the scientific team of M. Galperin. Its current version is described in Sofiev (1999) with the multi-layer vertical structure outlined in Sofiev & Grigoryan (1996).

The calculations cover the whole year 1995 and were made for the Northern Hemisphere to the north of 10°N with spatial resolution of 150 x 150 km^2 in polar stereographic projection. The emission data were taken from Global Emission Inventory Activity GEIA DB (Benkovitz *et al.,* 1996) for oxidised sulphur and nitrogen. Ammonia emission was the same as in Galperin & Sofiev (1998).

The model outline

The DMAT model v.2.0 is based on 3-D Eulerian advection scheme, which can be classified as “pseudo-Lagrangian” one. Its advantages are zero numerical viscosity and high computational efficiency. The disadvantage is considerable non-monotonicity of the instantaneous concentration fields. These fluctuations do not break the scheme stability and can be reduced by averaging over certain time period. According to the experience of the model exploitation, a weekly averaging is enough to reduce the non-monotonicity down to ~10% of the mean values.

Current model version can work with two vertical structures – semi-analytical continuous profile and “classical” multi-layer construction with up to 10 layers of variable thickness. For current calculations the 10-layer scheme was employed, providing the model top at 7650 m above the relief.

The model chemical scheme considers 11 species and 17 reactions including 5 ones of second order for SO_2, H_2SO_4, $SO_4^=$, NO, NO_2, HNO_3, NO_3^-, NH_3, NH_4^+, PAN, O_3 and extends the scheme described in (Pressman *et al.*, 1991). The main addition is connected with ammonia part based on (Finlayson-Pitts & Pitts, 1988). Dry deposition parameterization distinguishes the water and land surfaces. For terrestrial systems the effects of soil moistening and water freezing at low temperatures are taken into account. For oceans and seas the deposition velocity increases proportionally to the second power of wind velocity, which takes into account the process of wave creation. Wet deposition of SO_2 is considered to be non-linear with regard to atmospheric concentrations (Galperin, 1989). The saturation effect introduced in the model decreases the washout efficiency in the regions with very high air concentrations, which well corresponds to the observed phenomena. For oxidised nitrogen this effect is smaller, and for cationproducing substances like ammonia it is not considered.

Discussion of calculation results and model accuracy

The results of calculations include maps of concentrations and depositions for all considered pollutants. The most important for current study are near-surface concentrations of sulphates and nitrates, as well as their total column burden (Figure 1). In general they confirm that in the Northern Hemisphere there are three mainly self-polluted regions – Europe, South-East Asia and North America. Their inter-action is quite small and episodic. At monthly or annual levels of averaging the absolute values of cross-depositions are within the model precision limits.

It is important that concentrations of nitrogen aerosol (if taken in moles) are comparable and often higher than those of sulphates. It means that the amount of particles produced from nitrates is larger than sulphate ones. Nitrogen species are generally transported over longer distances than sulphur compounds, so the negative effects can be observed over much broader areas.

The model validation in Europe for 1995 was split to two parts. First, the daily and monthly values were compared with EMEP air quality observations (Hjellbrekke *et al.*, 1997) – see Table 1. Second, the spatial distribution of the pollutants with annual averaging was compared – see scatter plots in Figure 2. Not all the stations measuring in 1995 were included into the analysis. The selected sites have met the following criteria: the completeness of time series should be more than 50% for each substance separately; the station should belong to the quality group 1 or 2 in EMEP quality list (see e.g. Barret & Berge (1996) for details); station height above the sea level should not differ from the mean grid cell value for more than 150 m, which assures the station location inside 1st or 2nd levels of the model.

Considering the agreement of daily values it is necessary to take into account that representativeness of daily measurements for 150 km grid cell is very low. According to EMEFS inter-calibration experiments (Seilkop, 1994) the 95% confidence limit for daily point measurement of SO_2 in air for 80 km grid cell is between -76% and +172%. For $SO_4^=$ the corresponding range is from -40% up to +56%. This means that daily averaging is insufficient and one monitoring site cannot reproduce the meteorological and pollution patterns in the area of 80 x 80 km^2 and, consequently, in 150 x 150 km^2 grid. In this light the correlation between daily modelled and observed concentrations and depositions becomes surprisingly good. Monthly concentrations, correlate considerably better for almost all substances. Station representativeness at this averaging level is better (relative standard deviation is 20–30% depending on the substance – see (Galperin & Sofiev, 1994)), and also the non-monotonicity of the advection scheme is smoothed.

Mean annual values correspond well for all substances – the deviation is not more than 20–25%, which is within the fluctuations of the values themselves (represented by the standard deviations in the last two columns of Table 1).

For other parts of the model domain (North America and South-East Asia) additional work is needed for correct assessment of the model accuracy. The difficulties are caused by the different principles of the site locating in United States, where the bulk of the stations are very close or inside cities, which raises certain doubts in their representativeness for the regional pollution (EPA, 1997). In Asia the data are scarce and not well inter-calibrated with the others.

Table 1: Daily and monthly time series comparison for 1995. Results are averaged over EMEP network.

Substance, unit	*Nbr of stations*	*Mean observed*	*Mean calculated*	*Correlation coefficient daily*	*Correlation coefficient monthly*	*Standard deviation observed*	*Standard deviation modelled*
Precip., mm	59	*2.59*	2.49	0.42	0.72	5.76	4.76
SO2	*55*	1.49	2.37	0.36	0.52	1.82	2.84
NO2	53	2.02	2.58	0.22	0.35	1.28	1.74
SO4=	70	0.90	0.75	0.31	0.39	0.74	1.26
NO3-	13	0.56	0.71	0.20	0.33	0.49	1.02
NH4+	19	0.99	0.82	0.26	0.23	0.81	1.21
HNO3+NO3-	36	0.44	0.53	0.22	0.29	0.40	0.79
NH3+NH4+	31	1.41	1.39	0.20	0.19	1.21	1.16
NO3-wet dep.	57	0.96	0.88	0.16	0.25	2.25	1.70
NH4+ wet dep.	58	1.30	1.05	0.19	0.38	3.60	1.66
SO4= wet dep.	60	1.68	2.16	0.23	0.33	4.25	3.33

Conclusions

The numerical simulations performed for the Northern Hemisphere for the complete year 1995 for sulphur and nitrogen oxides and ammonia have shown the comparable amount of sulphate and nitrate aerosol over the whole domain. Fraction of nitrogen particles becomes larger in remote areas, which is caused by the larger transport distance of those species.

The model demonstrated good accuracy of annual values – the differences have not exceeded 25%. Correlation coefficients are quite diversed for different substances and averaging intervals. Still even for daily values the deviations between the model and observations are comparable with the uncertainties of the measurements themselves. For monthly averaging better representativeness of the monitoring data enables to highlight the groups of substances reproduced better (mainly primary pollutants) and the others, whose accuracy needs further improvement.

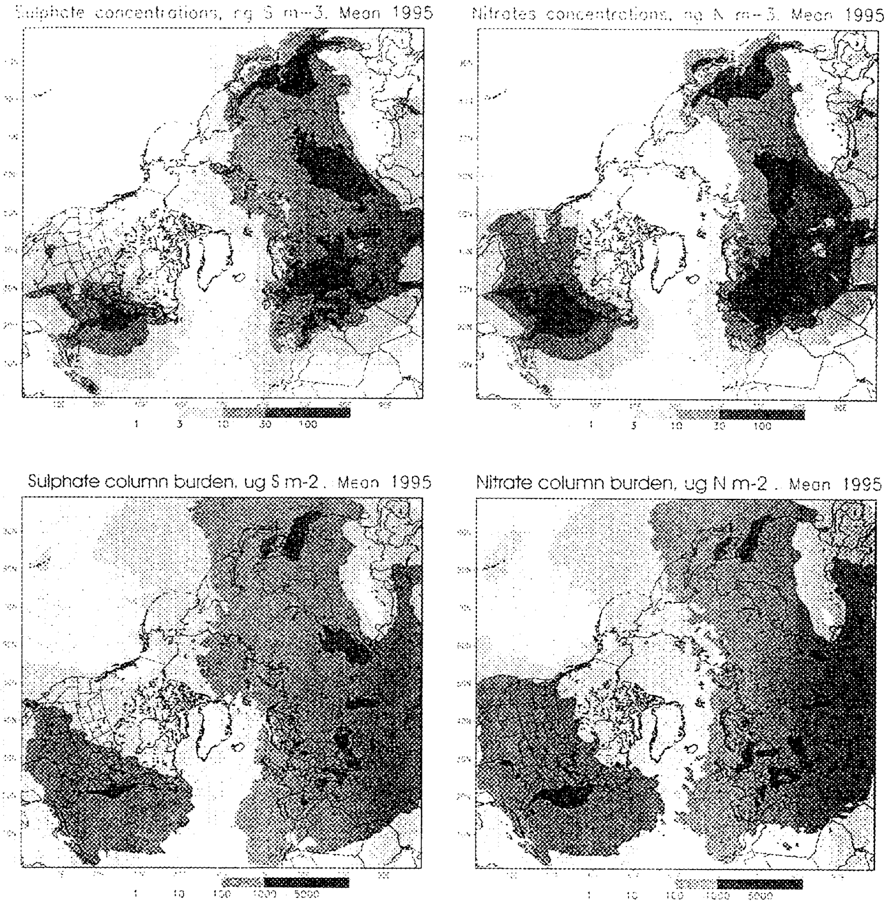

Figure 1: Maps of mean annual concentrations (above, unit µg S/N m^{-3}) and column burdens (below, unit mg S/N m^{-2}) for sulphates (left) and nitrates (right).

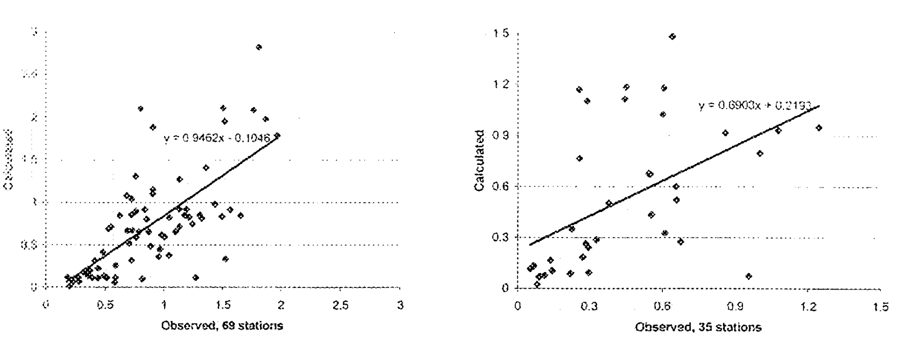

Figure 2: Annual model-measurement comparison for 1995 for EMEP stations.

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Receptor modelling of PM_{10} concentrations at a site in Central London

by

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Introduction

The European Union ‘Daughter Directive’ proposes ‘Stage 1’ limit values for PM_{10} to be achieved by 1 January 2005: annual mean value of 40 μgm^{-3} and 24-hour limit value of 50 μgm^{-3}, not to be exceeded more than 35 times a year (approximately equivalent to a 90th percentile of 50 μgm^{-3}). Additional indicative ‘Stage 2’ limit values have been proposed for achievement by 1 January 2010.

The UK National Air Quality Strategy (NAQS, DoE, *et al.*, 1997) includes a provisional objective for PM_{10} of the daily maximum of the 24-hour running mean of 50 μgm^{-3}, measured as the 99th percentile, to be achieved by the end of 2005. The recently reviewed NAQS (DETR, *et al.*, 1999) concluded that the provisional objective is unlikely to be achievable across a large part of the country. It was therefore proposed that action should be concentrated in the short term on achieving the EU Stage 1 limit values, replacing the existing objective.

The conclusions of the review were based, in part, on projections of future PM_{10} concentrations derived from a receptor model method developed within the framework of the UK Airborne Particles Expert Group (APEG, 1999; Stedman *et al.*, 1998). These projections were derived from a receptor modelling analysis of daily PM_{10} measurement data from 1995, 1996 and 1997. Projections derived from receptor modelling of 1998 monitoring data have now been completed and the results highlight the large year to year variability in PM_{10} concentrations in the UK.

PM_{10} receptor modelling was undertaken for the London Bloomsbury site in Central London and projected concentrations have been compared with the original NAQS objective and proposed limit values. The monitoring site at London Bloomsbury is an urban background site, approximately 35 metres from a major road. PM_{10} and $PM_{2.5}$ are measured hourly using a Tapered Element Oscillating Microbalance (TEOM) instrument and NO_x measurements are made using a chemiluminescent monitor. Daily mean particulate sulphate concentrations have been measured at two rural sites in south-east England. Annual mean concentrations of PM_{10}, NO_x and particulate sulphate are shown in Table 1.

Table 1: Annual mean concentrations of PM_{10}, NO_x and particulate sulphate at London Bloomsbury 1996-98.*

	PM_{10} (μgm^{-3})	NO_x (μgm^{-3})	SO_4 ($\mu g\ SO_4 m^{-3}$)
1996	30.3	151.3	4.8
1997	26.6	160.6	3.4
1998	22.7	128.2	2.8

* Particulate sulphate concentration is the average of the measurements at two rural monitoring sites in south east England

Annual mean PM_{10} concentrations in the UK fell rapidly over the three year period. Annual mean particulate sulphate also declined rapidly during these three years. Annual mean NO_x was highest in 1997 and lowest in 1998.

Source apportionment of monitoring data

The receptor modelling technique enables the measured daily mean PM_{10} concentration at a monitoring site to be divided into three components (APEG, 1999; Stedman, 1997; Stedman, 1998):

- primary combustion particles
- secondary particles
- ‘other’ particles, are assumed to be coarse particles (diameters of 2.5 to 10 µm), which are primarily made up of resuspended dust and sea salt

Oxides of nitrogen (NO_x) measurements are used as an indicator for primary combustion particles and rural sulphate measurements are used as an indicator for secondary particles. A multiple regression analysis is carried out to determine the coefficients *A* and *B* for primary combustion and secondary particle concentrations:

$$[\text{measured } PM_{10}] = A\,[\text{measured } NO_x] + B\,[\text{measured sulphate}] + C$$

The daily mean concentration of ‘other’ particles is determined by difference. The value of the regression coefficients is reasonably consistent through 1996, 1997 and 1998.

Figure 1 shows the annual mean PM_{10} concentrations at London Bloomsbury in 1996, 1997 and 1998, apportioned into primary, secondary and ‘other’ contributions. Measured PM_{10} concentrations decreased from 30.3 μgm^{-3} to 22.7 μgm^{-3} during the period. The measured fall in particulate sulphate is reflected in the fall in the modelled secondary contribution. The primary contribution is highest in 1997.

It could be suggested that particulate sulphate is becoming a poorer indicator of secondary PM_{10} during this period due to the decline in primary combustion emissions and concentrations of secondary particles. As these concentrations decline the proportion of variance in daily mean PM_{10} concentrations that is unexplained by the model is increasing. It is important to note that sulphates do not necessarily make a dominant contribution to secondary PM_{10} in comparison to nitrates. The relative proportions of sulphate and nitrate will depend on the emissions and atmospheric chemistry that takes place in air mass. We are forced to focus on using sulphate as an indicator because of the scarcity of nitrate monitoring sites. The effectiveness of this indicator is dependent on the degree to which sulphate and nitrate concentrations vary in the same manner.

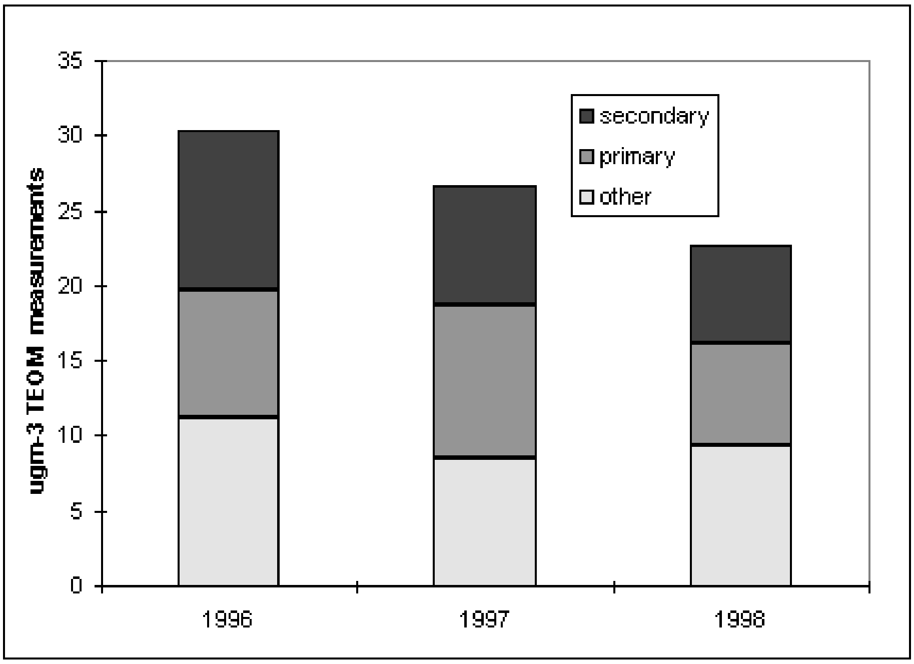

Figure 1: Estimated contributions to annual mean PM_{10} at London Bloomsbury in 1996-98.

Figure 2 shows the daily mean PM_{10} concentrations at London Bloomsbury in 1998, apportioned into primary, secondary and 'other' contributions, and the measured coarse particle concentration (PM_{10} concentration - $PM_{2.5}$ concentration).

One of the key uncertainties within the receptor modelling method is the assignment of the residual PM_{10}, remaining after the assignment of primary combustion and secondary particle contributions, to the 'other' particle fraction. An examination of the difference between measured PM_{10} and $PM_{2.5}$ concentrations enabled us to confirm our assignment of the bulk of this residual to coarse particles of diameter in the range from 2.5 to 10 µm. The modelled coarse particle concentration varies in the same way as the measured concentrations. There is reasonable correlation between the measured and modelled coarse concentrations, although the modelled value consistently overestimates. This is to be expected since any particles whose concentration does not vary in the same way as either NO_x or particulate sulphate is included in the 'other' contribution. For 1998 data, the measured annual mean coarse concentration was 7.1 μgm^{-3} and the modelled annual mean 'other' concentration was 9.3 μgm^{-3}. The correlation coefficient r^2 was 0.41.

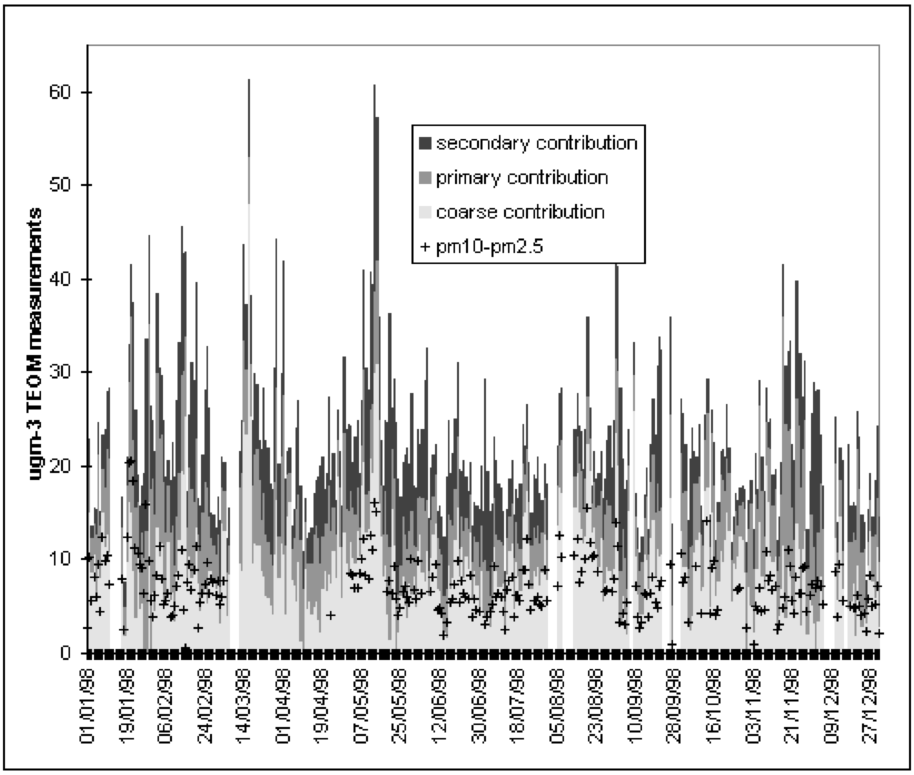

Figure 2: Estimated contributions to daily PM_{10} and the daily measured coarse concentrations at London Bloomsbury in 1998.

Projecting PM_{10} concentrations in future years

By separating measured PM_{10} concentrations into their component parts in this way, we can make relatively sophisticated estimates of both annual mean and high percentile PM_{10} concentrations for future years. We apply appropriate reductions to concentrations based on an understanding of the likely impact of current policies on future levels.

Projections of the 90th percentile of the 24-hour mean are shown in Figure 3. The Stage 1 limit value can be approximated to be 50 μgm^{-3} as the 90th percentile of 24-hour means. The European Union ‘Daughter Directive’ specifies that the standard instruments for measuring PM_{10} are the gravimetric instruments. An appropriate scaling factor (1.3) has been applied to the measured and projected concentrations to adjust for the fact that TEOM instruments were used in this study.

This statistic displays a large amount of year to year variability. The highest predictions result from 1996 data and the lowest are based on 1998 data. Predictions based on 1997 and 1998 data suggest that the EU Daughter Directive target will be reached, but 1996 based projections predict it will be exceeded by around 3μgm^{-3}. Unusual meteorological conditions lead to significant episodes of secondary particles throughout the UK during the early part of 1996 (Stedman, 1997).

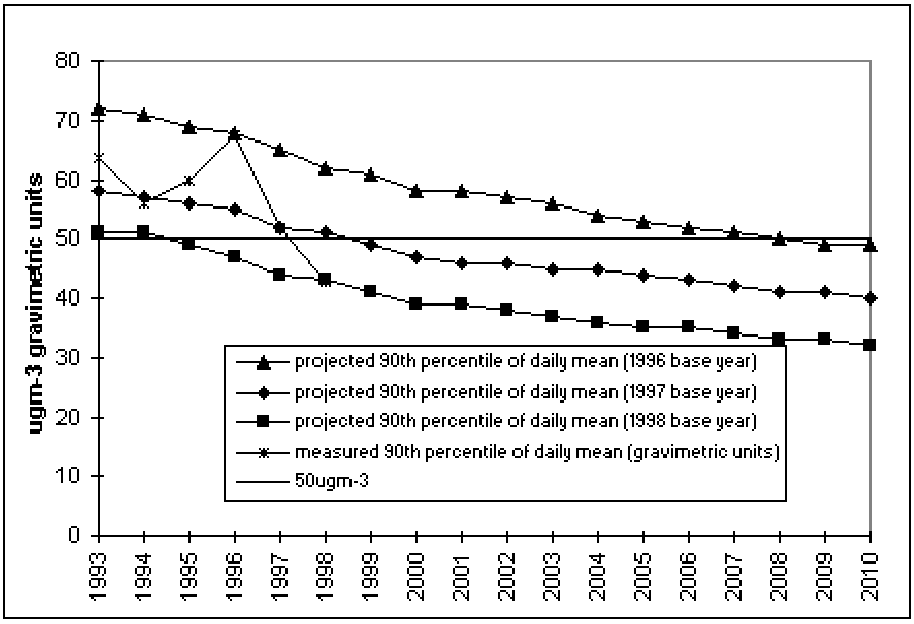

Figure 3: Projected and actual 90th percentile concentrations of PM_{10} at London Bloomsbury.

The model also projects backwards to previous years. The measured values lie within the range of projected concentrations in all years, but this range of projected concentrations is very large, spanning 18 μgm^{-3} in 2005.

Acknowledgements

This work was funded by the UK Department of the Environment, Transport and the Regions in partnership with the Scottish Executive, The National Assembly for Wales and Department of the Environment for Northern Ireland as part of their Air Quality Research Programme.

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Number concentration and chemical composition of fine particles measured at EMEP station Preila

by

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The recently revised interest can be observed in the health effect of particulate air pollution in the urban and non-urban areas during last decade. General studies have shown that short-term variation in levels of particulate air pollution are associated with adverse respiratory health effects even on the low levels of pollution observed currently in Western Europe. It may by that the adverse effect of pollution on public health is number, not mass concentration dependant. It has been hypothesized that the high number of fine particles in air may be the explanation of the observed health effects. Therefore, it is important to study relationship between number concentration and chemical composition of aerosol particles.

The goal of this presentation is to study relationship between aerosol number concentration and mass concentration of major inorganic ions in fine particles in a rural coastal station located in Preila.

A newly developed virtual impactor with the cutoff size of 2.5 μm has been employed for the collection of aerosol particles classified into two size fractions. Air sampling was performed at the research station Preila situated on the Curonian Spit, which separates the Curonian Bay and the Baltic Sea. Two field measurement campaigns were carried out within the European BASYS project in summer 1997 and in winter 1998. Aerosol samples collected onto the Whatman 40 cellulose filters were extracted with 30 ml of deionized water. Concentrations of anions (SO_4^{2-}, NO_3^-, and Cl^-) in aerosol water extracts were measured by means of ionic chromatography with the conductivity detector. Meanwhile, spectrophotometric method was used for measurements of NH_4^+ and flame photometry - for Na^+. Commercial optical aerosol counter AZ-5 have been used for continuous aerosol ($d > 0.4$ μm) number concentration measurements.

Mass concentrations of major constituents found in fine particles and number concentration presented in Figures 1-2. The highest mass concentration of major inorganic ions (14.8 $\mu g/m^3$) and number concentration (39 cm^{-3}) were measured in winter season. Similar situation occurred with constituents of major ions. Lowest number concentration in both seasons was related with air mass back trajectories from northwest and highest - from south.

The correlation coefficient is highest between ammonium mass concentration and number concentration in winter season ($R = 0.604$). The lowest correlation coefficient is calculated between nitrate mass concentration and number concentration in summer ($R = 0.257$). As can be seen from Figures 1-2 that sometimes course of mass concentration of major ions follows number concentration curve in a very similar way. However, on the other hand, sometimes seems that other constituents in fine particles are more important than major ions. The measured mass concentration of major ions and number concentration varied from 1.8 to 6.3 $\mu g/m^3$, from 7 to 22 cm^{-3} in summer season and from 4.2 to 14.8 $\mu g/m^3$, from 7 to 39 cm^{-3} in winter season, respectively. The calculated correlation coefficients are generally enough low (< 0.7). Nevertheless in some episodes relationship between number and major inorganic ions concentrations can be high and indirectly represent variation of mass concentration of fine particles.

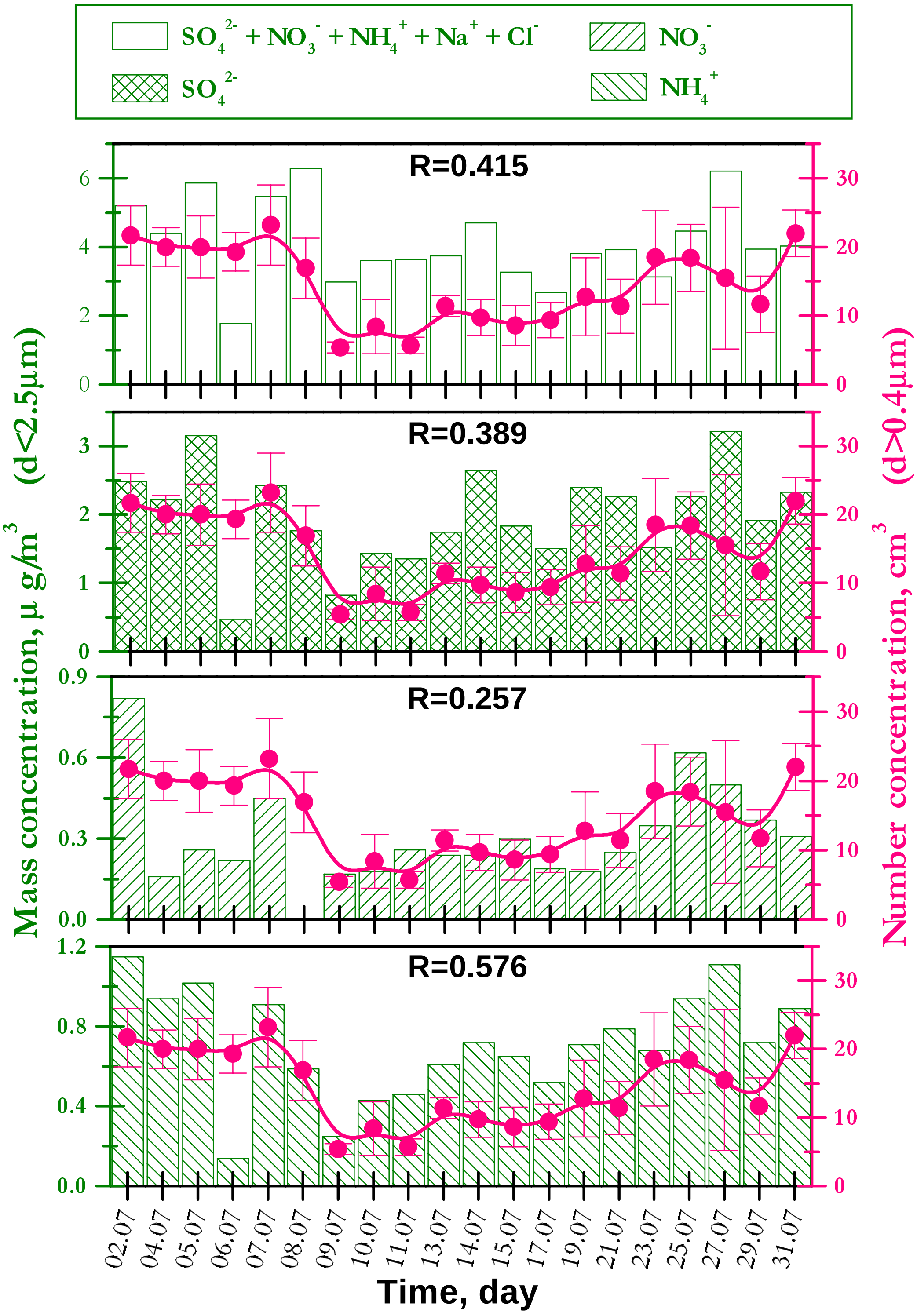

Figure 1: Mass concentration of major inorganic ions in fine particles and number concentration measured in Preila at July 1997.

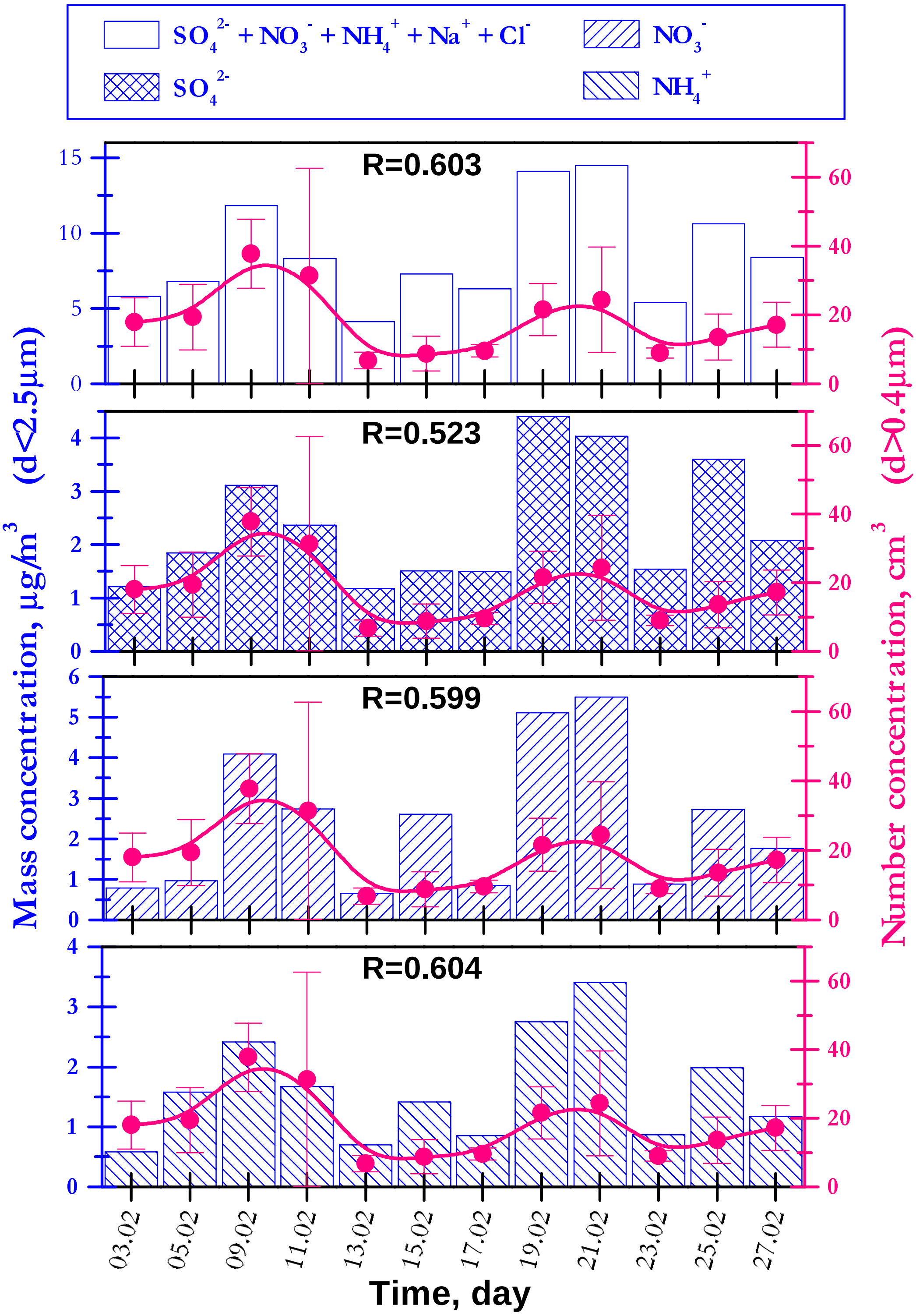

Figure 2: Mass concentration of major inorganic ions in fine particles and number concentration measured in Preila at February 1998.

Seasonal and diurnal variation of aerosol size distributions (10 < D <750 nm) at a high-alpine site (Jungfraujoch 3580 m asi)

by

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Introduction

Because of the importance of monitoring long-term trends of gaseous and aerosol parameters in the free troposphere, the high-alpine research station Jungfraujoch (JFJ, 3580 m asl), Switzerland, has been conducting measurements under the Global Atmosphere Watch (GAW) program. The following climatically important aerosol parameters have been measured since July 1995 (Baltensperger *et al.*, 1997; Nyeki *et al.*, 1998; Weingartner et *al.*, 1999): Total and backwards hemispheric scattering coefficients (σ_{SP}, σ_{BSP}; TSI 3563 IN), absorption coefficient (σ_{AP}; Magee AE-10), surface area concentration (S; PSI Instrument), condensation nuclei concentration (CN; TSI CNC 3010), and the cloud liquid-water content (LWC). In this work, results are presented from a 14-month campaign during the period March 1997 to May 1998 to measure the submicrometer number size distribution at the Sphinx Observatory at the JFJ.

Inlet Design

Owing to its exposed location on a mountain col, the JFJ experiences a high frequency of clouds (annual average ~37%). Therefore, the main aerosol inlet was designed to sample the interstitial aerosol as well as the activated droplets. It consists of a heated and insulated vertical stainless-steel tube (length: 200 cm; diameter: 6 cm) and a heated snow-hood. The temperature of the sampled air was measured and electronically regulated to +20°C. Heating was necessary (1) to essentially dry all activated droplets as early as possible to reduce transmission losses and (2) to prevent riming of the inlet system during harsh conditions, especially in winter. The inlet was designed such that cloud droplets with $D < 40$ µm were sampled up to a wind speed of 20 m s^{-1}. The relative humidity of sampled air at the instrumental inlet was < 20% (laboratory temperature 22-23°C) throughout the campaign. Calculations for the above typical wind speeds and droplet sizes showed that virtually all activated droplets were sampled.

Seasonal Variations

The SMPS data set is illustrated in Figure 1 in the form of a two-dimensional contour plot of d*N*/dln*D* as a function of *D* and time for the whole measuring period. In addition, Figure 2 shows seasonal averages of the number distributions during the campaign and their bimodal parameterizations.

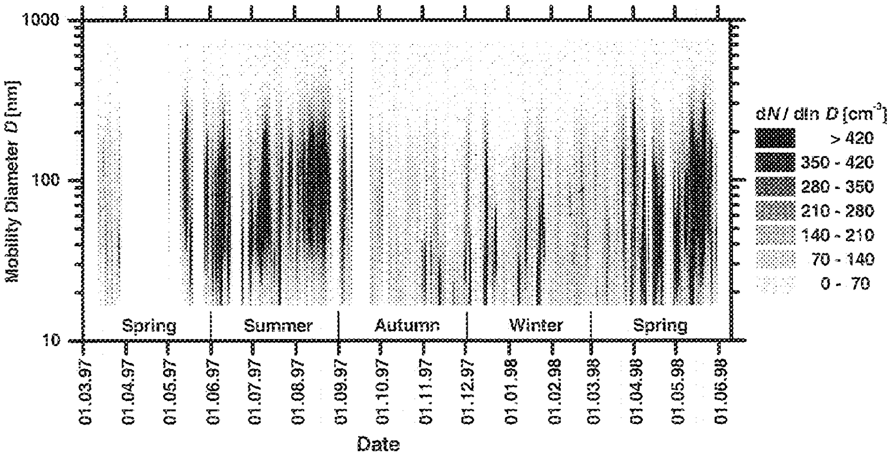

Figure 1: Time history of dN/dlnD size spectra (24 -hour average) at the Jungfraujoch in form of a contour plot. Data are not edited for cloudless conditions.

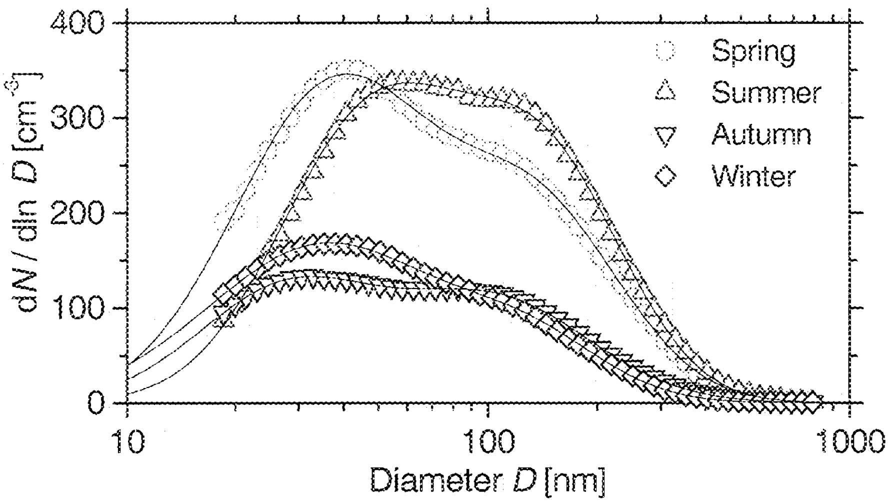

Figure 2: Measured size distributions averaged for the four seasons (points) and bimodal fits (lines).

Monthly averaged spectra were fitted with a bimodal size distribution and the fitparameters are shown in Table 1. The number concentration is observed to be governed by the Aitken mode concentration, and is shifted toward smaller particle sizes during the colder months.

It is interesting that fitted modal diameters (D_{Ait}, D_{Acc}) and standard deviations (σ_{Ait}, σ_{Acc}) exhibit a low seasonality. The shape of the measured number size distribution is mainly determined by the number concentrations N_{Ait} and N_{Acc}. These values experience a strong seasonal variation which is more distinct for the accumulation mode. This variation of N_{Acc} is mainly due to transport of planetary boundary layer air to the station and has an important influence on the seasonality of the surface area (as well as the volume) concentration in the submicrometer size range. In contrast, particles with $D < 20$ nm exhibit an inverse seasonality (higher concentration during winter). This feature is observed to result from a higher fraction of small particles that are produced by homogeneous nucleation during the colder seasons.

Table 1: Results of fitting monthly average dN/dlnD spectra for FT and "All" conditions, as the sum of two lognormal size distributions. Number concentrations in different size bins, average values (AVE), standard deviations (ST ERR), and the seasonality (SEA) are also presented. SEA is the ratio of summer to winter values. A SEA < 1 denotes higher values in winter than in summer.

			Aitken mode			Accumulation mode			Number concentrations				
Date	n [days]	χ^2 [cm^{-6}]	σ_{Ait}	D_{Ait} [nm]	N_{Ait} [cm^{-3}]	σ_{Acc}	D_{Acc} [nm]	N_{Acc} [cm^{-3}]	$N_{Ait}+N_{Acc}$ [cm^{-3}]	N_{10} [cm^{-3}]	N_{10}-N_{18} [cm^{-3}]	N_{18}-N_{25} [cm^{-3}]	$N_{Ait}/(N_{Ait}+N_{Acc})$
Mar-97	17	9	1.86	42	221	1.62	152	113	333	498	184	33	0.66
Apr-97	-	-	-	-	-	-	-	-	-	-	-	-	-
May-97	14	18	2.20	59	467	1.63	158	233	700	1008	343	46	0.67
Jun-97	22	11	1.68	41	480	1.66	126	313	793	975	217	76	0.61
Jul-97	31	12	1.95	57	538	1.50	169	132	670	767	123	49	0.80
Aug-97	28	21	1.92	64	471	1.66	164	310	782	822	55	33	0.60
Sep-97	17	1	2.36	51	346	1.72	131	141	487	676	231	40	0.71
Oct-97	29	1	2.46	39	206	1.50	120	32	238	403	208	30	0.87
Nov-97	29	1	1.64	26	218	1.80	99	86	303	575	327	67	0.72
Dec-97	31	1	1.84	35	300	1.61	130	90	389	557	214	60	0.77
Jan-98	30	7	2.38	41	400	1.39	162	18	418	561	215	58	0.96
Feb-98	28	2	2.68	33	315	1.50	116	47	362	531	258	47	0.87
Mar-98	31	4	2.76	33	351	1.66	147	80	430	617	286	52	0.82
Apr-98	22	122	1.79	38	756	1.58	136	241	997	1285	339	137	0.76
May-98	30	22	2.03	47	642	1.70	156	302	944	1012	130	82	0.68
AVE			2.13	43	422	1.61	140	156	578	753	227	60	0.76
ST ERR			0.11	3	46	0.03	6	32	72	73	25	8	0.03
SEA			0.83	1.74	1.68	1.06	1.17	7.10	2.26	1.64	0.54	0.97	0.77

Diurnal Variations

The diurnal variation of the SMPS spectra is illustrated in Figure 3 for four days in summer and winter. During summer, planetary air masses arrive at the JFJ at about noon, and the aerosol concentration reaches its highest value at about 1900 hours. In winter, the JFJ is decoupled from the PBL which results in a smaller diurnal variability. In winter a shift toward increased number concentrations for $D < 40$ nm is apparent and results from the increased formation of particles by homogeneous nucleation.

During all seasons, nucleation mode particles (10 nm $< D <$ 18 nm) are probably formed by homogenous nucleation. This hypothesis is corroborated by the fact that the number concentration of particles in the size range D = 10–18 nm exhibits a diurnal variation (see Figure 4), which is most probably due to photochemical processes. During values of N_{10}–N_{18} exhibit two distinct maxima that may be explained as follows: The onset of solar radiation in the morning triggers the photochemical production of new particles, for example, $SO_2 + OH \rightarrow H_2SO_4$. If the pre-existing aerosol surface area concentration is low enough, homogeneous nucleation is favoured, and new particles are formed. These nucleation mode particles are not detected until they grow into the "visible" size range of the instruments. At noon, the precursor vapour gas reservoir is exhausted which results in lower production rates. Concentrations of N_{10}–N_{18} then increase again due to thermal convection which provides new precursor gases from the PBL. The decrease in new particle formation from 1500-1800 hours is most probably due to the increase in surface area and the decrease in solar radiation. In winter higher nucleation mode concentrations are found. This may be due to the lower surface area concentration. In addition, the lower temperatures during winter may also favour the formation and growth of new particles.

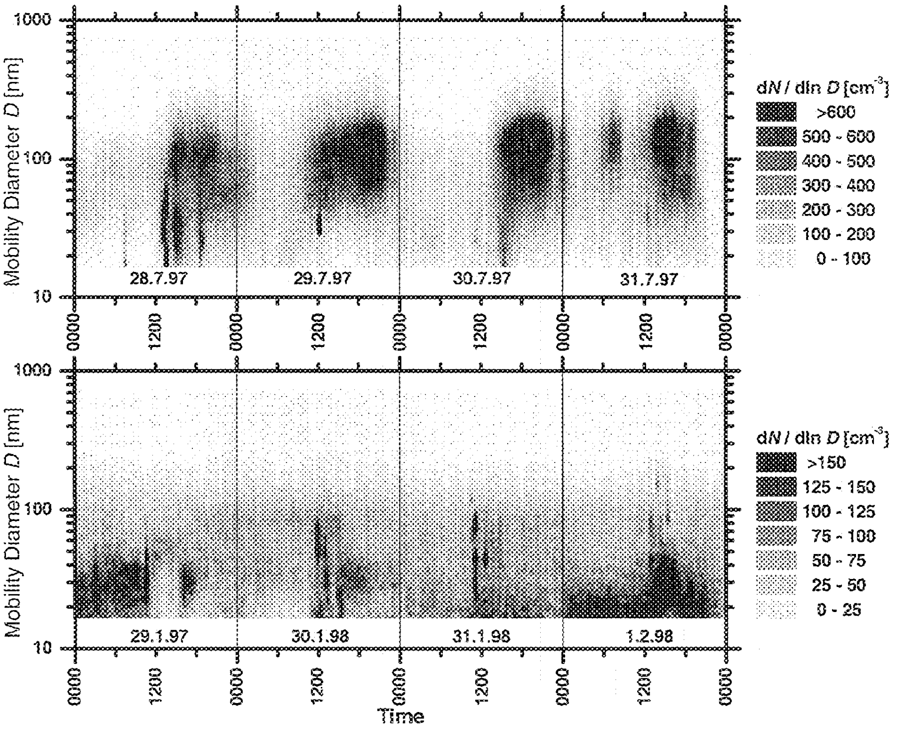

Figure 3: Examples of the diurnal variation (30 min resolution) during 4 days in summer (top) and winter (bottom). Note that the colour concentration scales are different in both graphs.

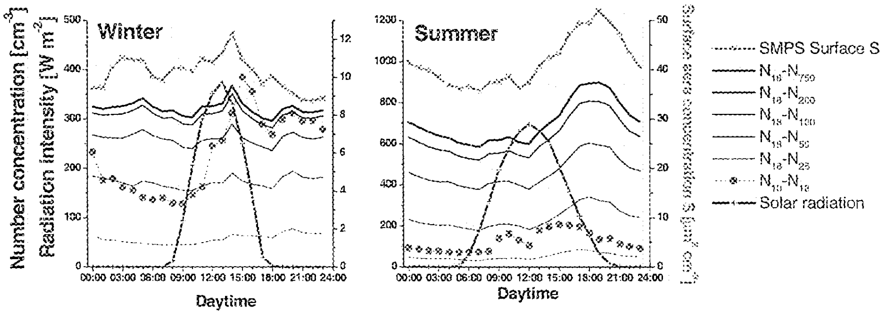

Figure 4: Average diurnal variations of the surface area concentration measured by the SMPS (bold line with stars, right-hand scale) and number concentrations in different size bins (see legend, left-hand scale). Average solar radiation intensity measurements are also shown.

The Influence of Clouds on the Size Distributions

SMPS data with a time resolution of 1 hour were classified into five different LWC ranges and average measured number size distributions for different LWC are shown in Figures 5 for “All” conditions and the ET period 0300-0900 hours. The spectra exhibit a bimodal shape and were parameterized by the sum of two lognormal size distributions.

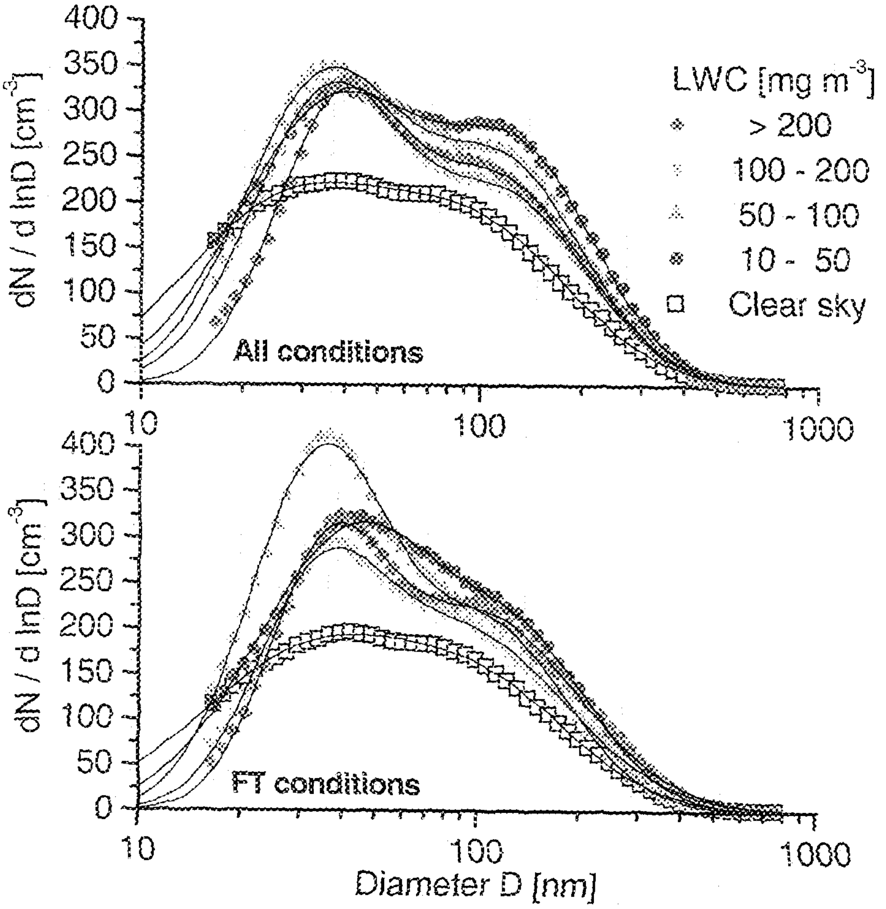

Figure 5: *Average number size distributions for clear-sky and different liquid water contents (LWC) during in-cloud conditions. Symbols and solid lines represent measurements and lognormal distribution fits, respectively. Measurements are presented for the period February to May 1998 inclusive.*

It is found that the bimodality is more distinct during cloudy events which are most probably due to preferential scavenging of the smallest particles by cloud droplets. Accumulation mode particles grow from D_{Acc} = 120 nm under clear-sky conditions to D_{Acc} ~137 nm under cloudy conditions which can be explained by the absorption of trace gases onto cloud droplets. Aqueous phase reactions then produce additional aerosol material. Upon evaporation of the droplet, the residue is larger than the original CON on which the droplet was formed. The increase in D_{Acc} is responsible for the separation in the size spectrum at the critical particle diameter that depends on the cloud supersaturation and the particle chemical composition *(*Hoppel *et al.,* 1990). This process is an important factor in shaping the background aerosol size distribution, as more than 90% of clouds re-evaporate without the formation of precipitation.

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Measurements of Airborne Particle Mass, Number and Size Distribution at Urban Sites in the United Kingdom

by

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Introduction

- Continuous measurements of airborne particulate mass, numbers and size distributions are being made at two sites in London, UK. Marylebone Road (LM), a kerbside site, is heavily polluted by frequently congested traffic whereas London Bloomsbury (LB) is an urban background site situated within a central London garden, which is about 1.8 km away from Marylebone Road.

- Particle mass was measured as PM_{10} and $PM_{2.5}$ (aerodynamic diameter equal or smaller than 10 and 2.5 μm respectively) using TEOMs (Tapered Element Oscillating Microbalance). Particle number and number based size distribution data were obtained from an SMPS system (a scanning mobility particle classifier plus a condensation nucleus counter)

Aims

- Assessment of both particle mass and number concentrations at the two different sites over different periods

- Investigation of the relationship between particle mass and number concentrations

- Determination of the size distribution of airborne particles measured at these sites

- Comparison between an urban background and a roadside site

Results (presented in the following figures)

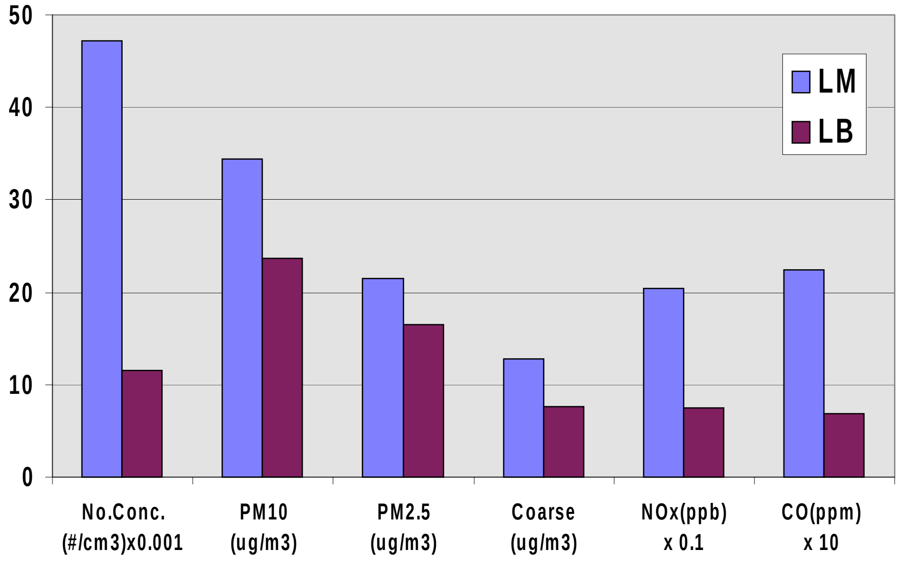

Figure 1: *Clear differences in the average concentrations of airborne particle mass and numbers as well as the gaseous pollutants have been observed between the Roadside (LM) and Urban Background (LB) site over the period from 06/97 to 02/99 indicating that air pollution is heavily affected by road traffic. Particle numbers show a greater difference at the two sites.*

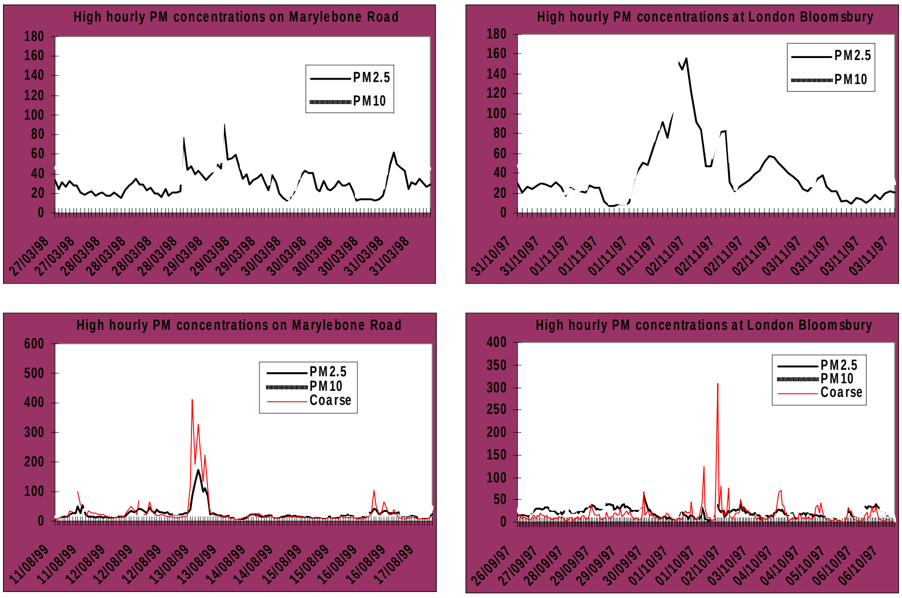

Figure 2: *Very high hourly concentrations of airborne particles were observed at both sites. PM*$_{10}$ *concentrations (µg m*$^{-3}$*) were dominated mostly by fine particles except on a few occasions when coarse particles contributed substantially to PM*$_{10}$ *levels.*

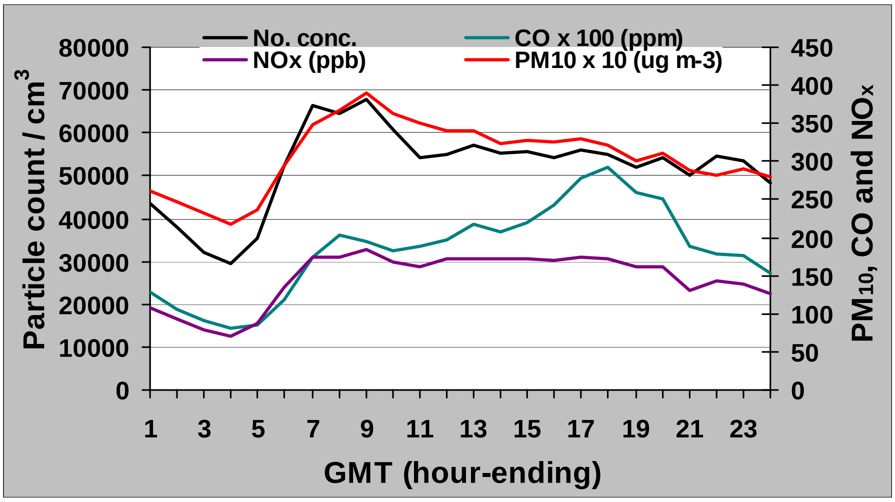

Figure 3: High consistency of diurnal variation between particle mass and number concentrations and traffic related gaseous pollutants (NO_x and CO) was found on Marylebone Road over the whole sampling period. The following figure shows the period of April and May in 1998, in which CO appeared to have an additional peak in early evening when the others did not.

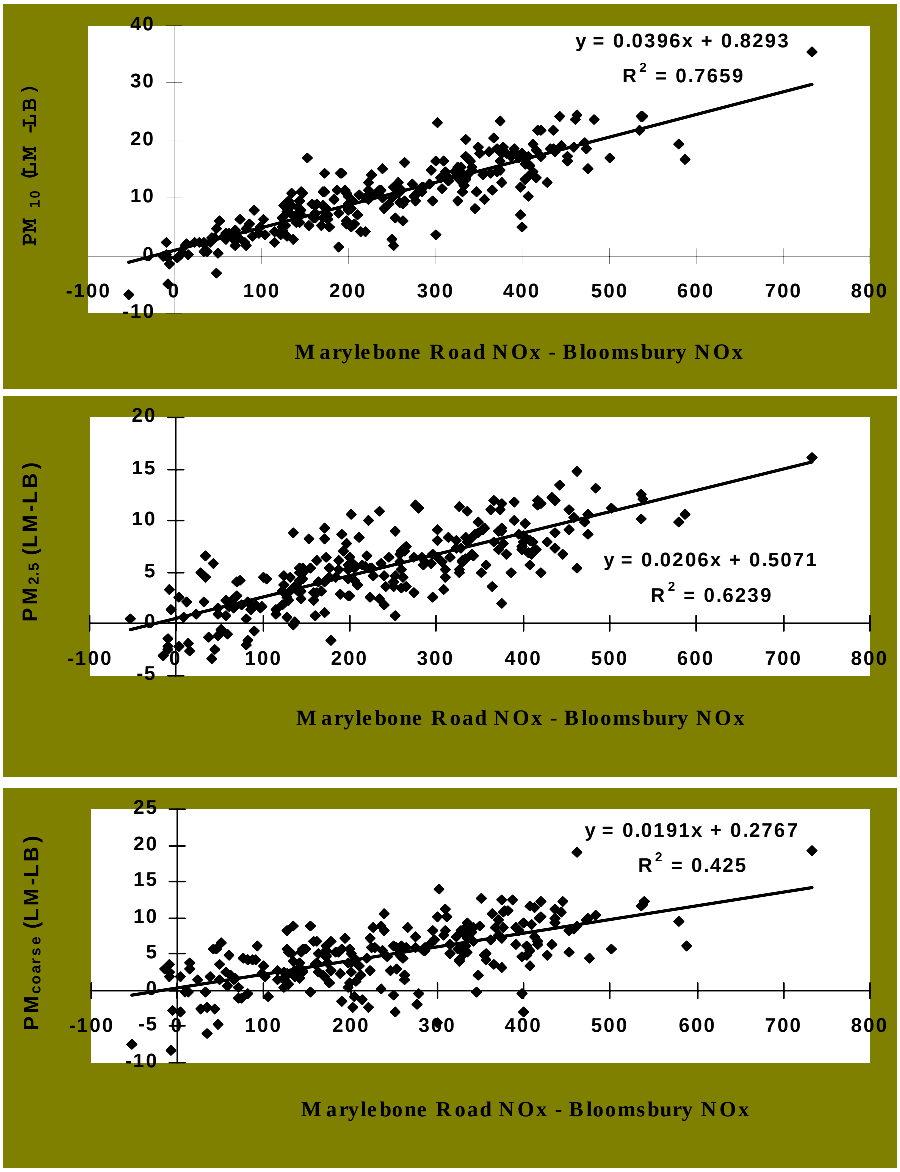

Figure 4: Comparison between Marylebone Road and London Bloomsbury was made using daily average concentrations of PM and NO_x for the period from June 97 to September 98. High correlation was found between the roadside concentration increment (LM-LB) of PM and NO_x with small intercepts showing that London Bloomsbury can be treated as an appropriate background site.

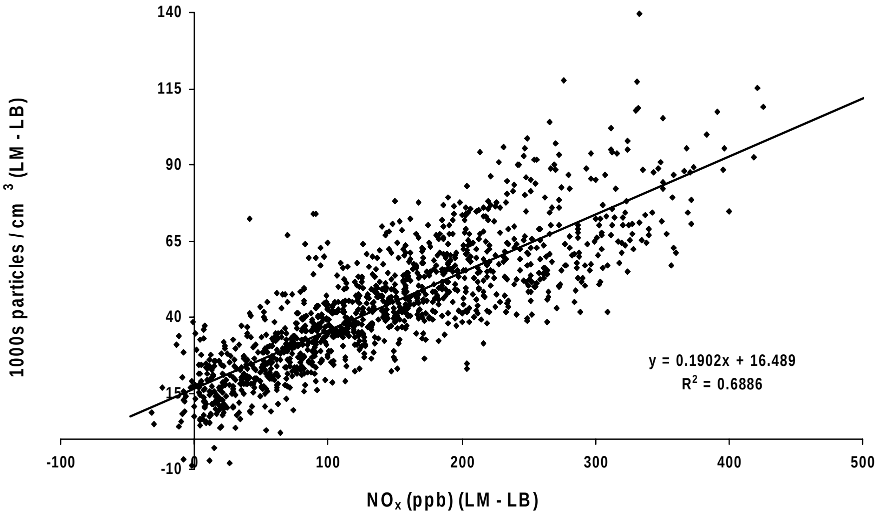

Figure 5: *Strong correlation was also found between the incremental concentration of particle numbers and NO_x over a summer period in 1998 demonstrating the impact of vehicle exhaust emissions on particle number concentrations.*

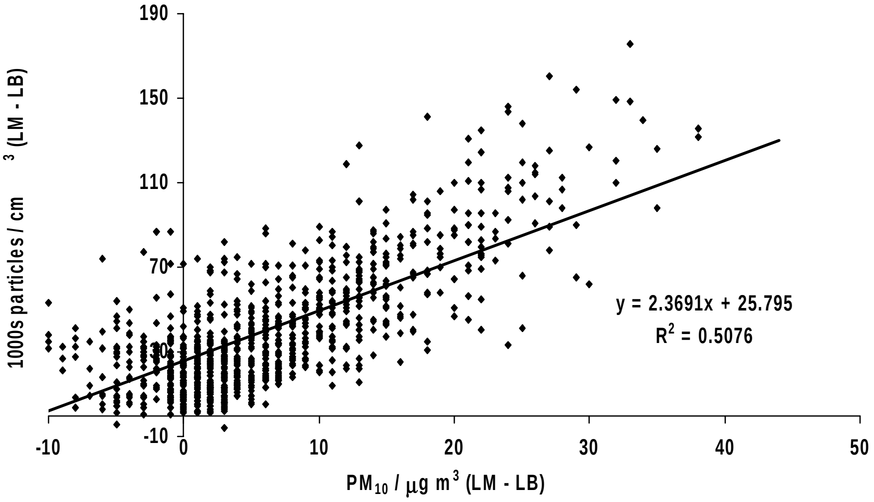

Figure 6: *Comparison was made between the roadside enhancement of particle numbers and PM_{10} mass for spring 1998.*

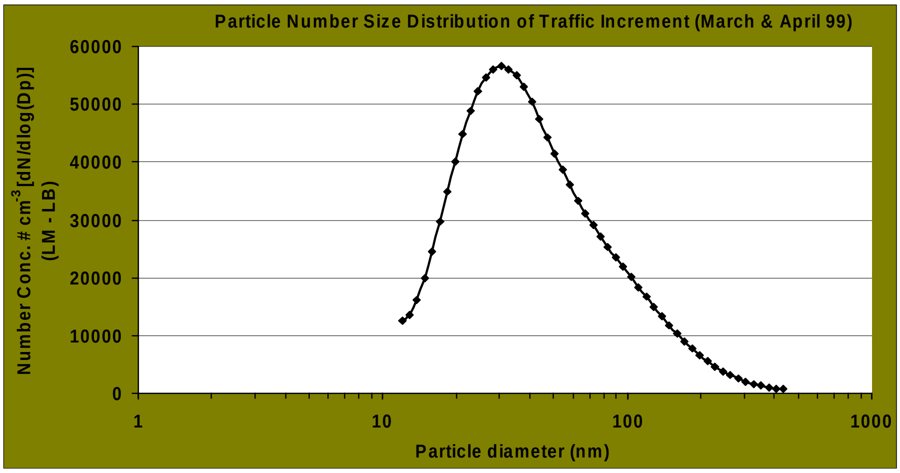

Figure 7: *The number size distribution of particles generated from road traffic has been investigated and the average size mode is within the range from 20 to 30 nm. The figure here shows a peak at about 30 nm, which is significantly smaller than the typical particle size distribution mode around 100 nm reported from the engine test bed measurements.*

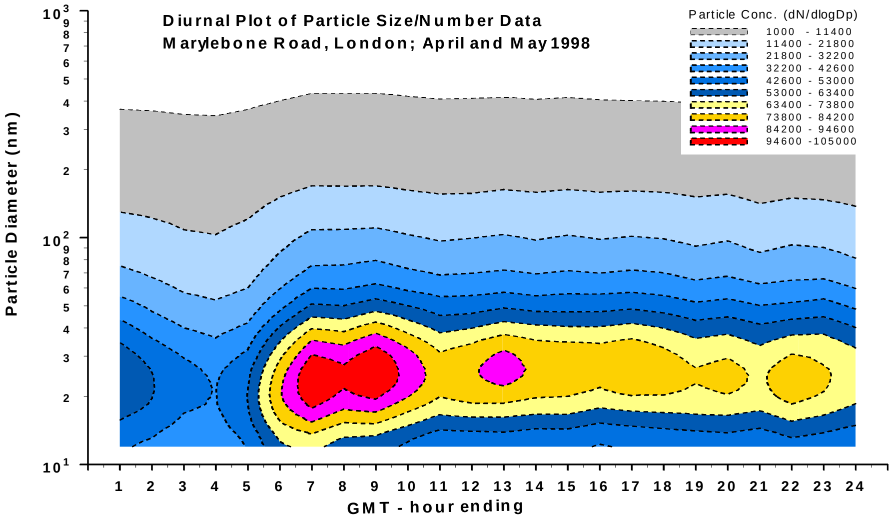

Figure 8: *The plot below illustrates the diurnal behaviour of particle size and numbers on Marylebone Road. A morning peak appeared from 7 to 9 hours when the particle numbers reached up to* 10^5 *cm*$^{-3}$ *with a size mode around 25 nm. As in figure 3, an evening peak is not discernible.*

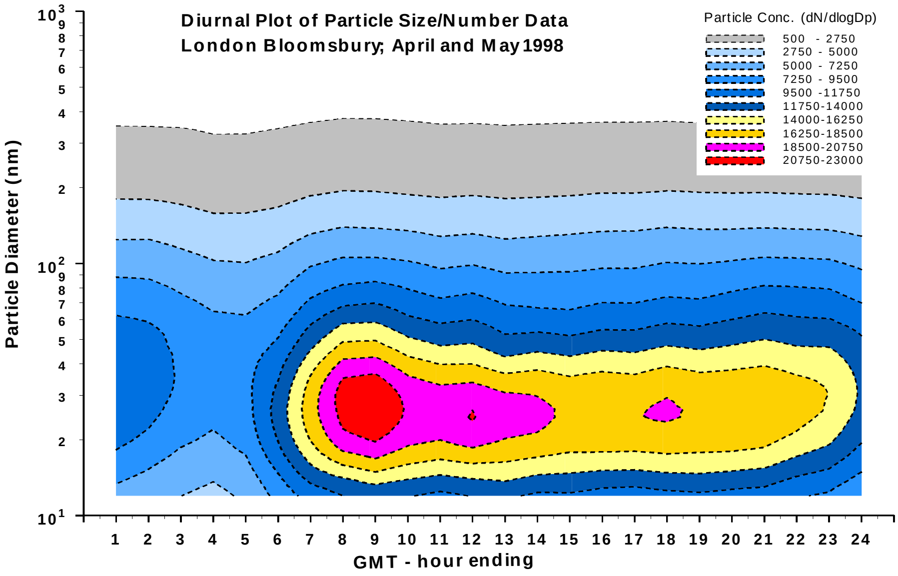

Figure 9: Similar diurnal variation was observed in London Bloomsbury except a later and shorter morning rush-hour peak with lower particle numbers and bigger size mode around about 30 nm.

Conclusions

- Substantial differences in average concentrations of particles expressed as mass and numbers were found between a roadside and a background site in central London.

- PM_{10} episodes were dominated mainly by fine particles. On a few occasions coarse particles were the major contributor.

- Good correlation was found between particle mass and numbers at both sites, but particle numbers appear to give a better indication of vehicle exhaust emissions.

- High correlation of the roadside enhancement of particle mass and numbers with NO_x was observed confirming the impact of road traffic on airborne particles.

- Particles generated from vehicle exhaust are very small showing a number size distribution mode smaller than 30 nm, which is considerably smaller than the mode of about 100 nm reported from some engine test bed studies.